Characterization of Polymer Composites for Cryogenic and Allied Applications

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By

SHRABANI GHOSH, M. Sc.

Under the supervision of

Prof (Dr.) Swapan C. Sarkar
Director

Centre for Rural and Cryogenic Technologies
Jadavpur University
Kolkata -700032

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I
Dedicated the work
To
My parents and My supervisor
For their overwhelming support throughout the study

CERTIFICATE FROM THE SUPERVISOR

This is to certify that the thesis entitled **"Characterization of Polymer Composites for Cryogenic and Allied Applications"** submitted by Smt. Shrabani Ghosh who got her name registered on 12th March 2018 for the award of Ph.D. (Science) degree of Jadavpur University, is absolutely based upon her own work under the supervision of **Prof. (Dr.) Swapan Chandra Sarkar** and that neither this thesis nor any part of it has been submitted for either any degree /diploma or any other academic award anywhere before.

27.12.2023

Signature of the supervisor and date with official seal

Prof. (Dr.) Swapan C. Sarkar
Director
Centre for Rural & Cryogenic Technologies
Jadavpur University
Kolkata-700032

DECLARATION BY THE CANDIDATE

I do hereby declare that the thesis entitled, **"Characterization of Polymer Composites for Cryogenic and Allied Applications",** is an innovative research work carried out by me, under the supervision of Prof (Dr.) Swapan C. Sarkar, Director, Center for Rural & Cryogenics Technologies (CRCT), Jadavpur University. This work has neither been published nor has been presented anywhere for the award of any degree.

Shrabani Ghosh
27.12.2023
Shrabani Ghosh

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PREFACE

The progress in the cryogenic application is strongly dependent on advances in the development of materials. It is revealed from the available literature that most often the suitability of a large number of metals and alloys for their use at low temperatures has been studied but much less work has been reported in the field of characterization of non-metallic materials at low temperatures particularly that of different polymer resin impregnated fiberglass composites. These polymer composites may have a reasonable edge over many metallic components for cryogenic and allied applications e.g. in a cryogenic container, LNG tank, high vacuum application, expansion turbine rotors, expansion engine parts, space rocket shells, etc. Moreover, such composites are also used as non-conducting structural components in combination with metallic cryogenic storage vessels. The potential for these polymer composite materials in the low-temperature range still remains unexplored, particularly for the lack of adequate data and characterization and there lies tremendous scope to have in-depth studies of the behavior of such composites down to the boiling point of Liquid Nitrogen. The present work is from the consideration of the utilization of polymer composites in the fabrication of cryogenic storage containers,plant components, cryostat, and other equipment being used at cryogenic temperature.

The materials studies have been done both from theoretical and experimental points of view on the basis of the determination of some of the mechanical and physical properties of the composites for cryogenic and allied applications.

The objective of the present investigation is to first review the present status of polymer composites along with their characterization and then to establish the feasibility of indigenous development of Glass Fibre Reinforced Plastic-based tube and its subsequent use as a neck of an indigenously built liquid nitrogen vessel as well as performance study of aluminized mylar as a Multi-Layer Insulation system of a cryogenic vessel. The thesis emphasizes material characterization, design, analysis, fabrication, and experimental run of the prototype component and protype cryogenic dewar developed. The thesis chapters highlighted the following areas:

1. Properties of materials at low temperatures
2. Characterisation of polymer composites for cryogenic applications - a state-of-art report (literature survey)
3. Preparation of Glass-Fiber Impregnated Epoxy Resin Tube and Investigation of its Physical and Mechanical Properties .Compatibility study of the tube by immersing it in liquid nitrogen (-196^{0}C) for its Use as a Structural Component at Cryogenic Temperature.
4. Study of 12 micron Aluminized Mylar as Radiation Shield in the Quest of an Effective Multi-Layer Insulation Development for a Laboratory Scale Cryogenic Dewar Vessel.

5. Successful Design and Prototype Development of 3 Liter Cryogenic Container followed by its performance study in storing liquid nitrogen.

Hope, this work will open up avenues in the diversified use of polymer composite materials either alone or in conjunction with metallic parts in the cryogenic temperature range. Since component /equipment/storage vessels are practically developed with innovative design, the thesis will have immense reference value.

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CHAPTER -9:

NOMENCLATURE

T- Temperature

RT- Room Temperature

CT- Cryogenic Temperature

CT-C- Cryogenic Temperature Conditioning

K- Kelvin

^{0}C- Degree Celsius

θ- Theta

π- Pi

λ- Wavelength

V- Volume

D- Diameter

D_0- Outside Diameter

h- Hight

S- Second

P- Pressure

P_c- Critical Pressure

P_a- External Pressure

E- Young modulus

γ- Poisson’s ratio

L- Length

T_1- Temperature of inner vessel

T_2- Temperature of outer vessel

T_s- Temperature of radiation shields

T_b- Boiling temperature

A_1- Surface area of the inner vessel

A_2- Surface area of the outer vessel

A_s- Surface area of shields

ε- Efficiency

ε_w- Weld efficiency

t_{iw}- Inner vessel thickness

t_{ow}- Outer vessel thickness

m- Meter

m^3- Meter (volume)

kN - Kilo Newton

N- Newton

mm- Millimeter

mbar- Millibar

kg- Kilo-gram

mA- Milli Ampere

Pa- Pascal

kPa- Kilo Pascal

MPa- Mega Pascal

GPa- Giga Pascal

kV- Kilo Volt

e_s- Emissivity of shield

e_1- The emissivity of the inner vessel

e_2- The emissivity of the outer vessel

N_s- Number of shields

S- Stress

S_a- Maximum allowable Stress

σ- Stephan-Boltzmann constant

Q_r- Heat transfer by radiation

F_{1-2}- View factor

F_e- Emissivity Factor

K_a- Thermal conductivity of shields

h_s- Thermal conductivity of spacers

LN_2- Liquid Nitrogen

LO_2- Liquid Oxygen

LCH_4- Liquid Methane

SWG- Standard Wire Gauge

SS- Stainless Steel

CFRP-Carbon Fiber Reinforced Polymer

MWCNT-Multi Wall Carbon Nano Tube

SEM-Scanning Electron Microscope

XRD-X-Ray Diffraction

TGA- Thermogravimetric Analysis

UTM-Universal Tensile Machine

Cu-Kα- Copper K alpha

EP3-Special type epoxy resin

ASTM- American Society for Testing and Materials

ASME- American Society of Mechanical Engineers

FRP-Fiber Reinforced Plastic

GFRP- Glass Fiber Reinforced Plastic

E-glass- Electrical glass

S-glass- Strength glass

C-glass- Chemical resistance glass

AR-glass- Alkali Resistance glass

SiO_2- Silicon dioxide

Al_2O_3- Aluminum Oxide

TiO_2- Titanium Oxide

B_2O_3- Boron trioxide

CaO- Calcium Oxide

MgO- Magnesium Oxide

Na_2O_3- Sodium carbonate

K_2O- Potassium Oxide

MLI-Multilayer insulation

CMS- Charcoal trap

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SYNOPSIS

Advances in the development of materials play a crucial role in the progress of cryogenic technologies. Polymers composites are excellent engineering materials and can be a substitute either fully or partially combined with metallic parts for the development of various types of equipment/components to be operated at cryogenic temperatures (below -150^{0}C).

The potential for these polymer composite materials in the low-temperature range still remains unexplored, particularly for the lack of adequate data on characterization.

Therefore, the characterization of polymer composites from the consideration of their utilization in the fabrication of cryogenic storage containers, plant components, cryostat, and other equipment being used at cryogenic temperature becomes the need of the hour.

In this regard, a rigorous study from the theoretical and experimental points of view on the basis of the determination of some of the mechanical and physical properties of the glass fiber-reinforced plastic composites for cryogenic applications has been conducted which finally establishes the feasibility of the indigenous development of Glass Fibre fiber-reinforced plastic tube and its subsequent use as a neck of an indigenously built stainless steel cryogenic Dewar vessel of 3 litre capacity for storing cryogenic fuel, liquid nitrogen, liquid oxygen etc as well as a performance study of aluminized mylar as a Multi-Layer Insulation system of a cryogenic vessel. The work stresses material characterization, design, analysis, fabrication, and successful experimental run of the prototype cryogenic Dewar developed.

CHAPTER - 1

Introduction

CHAPTER-1

INTRODUCTION

1.1 Cryogenics

Cryogenics is defined as the science of producing ultra-low temperatures. The word originally derived from the Greek word **Kryos** for frost and **genos** for origin or creation. However, Cryogenics covers low-temperature production, maintenance, measurement, control and its utilization for scientific investigation of phenomena, techniques and concepts occurring at or pertaining to low temperature. As per National Bureau of Standard, Colorado, USA, any temperature below -150^0C(123K) comes under the preview of Cryogenics since the boiling point of permanent gases such as nitrogen, hydrogen, oxygen etc. fall below this temperature.

The cryogenics has reached application level of high impact in fertilizer, steel, petrochemicals, material science, gas purification, environmental science, agricultural chemistry, food science, biology, chemicals and pharmaceutical science besides such sectors as defence, atomic energy and space science etc. It is absolutely not possible to present the vast domain of cryogenics. An attempt is made to give a glimpse of this important branch of science and technology in the following sections.

1.1.1 Brief History of Development

A look into the history of the development of cryogenics revealed that the air we breathe was first liquefied in 1883 by a Polish scientist named Olszewski. After a decade or so, the liquid hydrogen was successfully produced by British Scientist, Sir James Dewar. Helium, the last of the so-called permanent gases, was finally liquefied by the Dutch physicist Kamerlingh Onnes in 1908. Thus by the beginning of the twentieth century, the door had been opened to a new world of experimentation in which all substances, except liquid helium, are solids and where the absolute zero is only a few micro degrees away.

Though UNESCO in its status report on cryogenics-1996 entitled Strategies for Developing India's National Capabilities in Cryogenic Science has stressed the need to spread of cryogenic R & D and education in India for economic growth of the country India still lags far behind chain and other advanced countries in the areas of cryogenic technology and education.

1.2 Composites materials

The definition of a "composite" is two or more materials with markedly different physical or chemical properties – categorized as "matrix" or "reinforcement" – combined in a way to act in concert, yet remain separate and distinct at some level, While other materials are technically composites, this term has come to refer to a combination of resin and fiber reinforcement, sometimes called "fiber-reinforced polymers" or FRP composites. This combination can produce some of the strongest and most versatile materials for their weight that technology has ever developed.

Moreover, the resin, fiber and additives that comprise composites can be adjusted to produce final parts and products with a wide range of physical properties, lending composites to a myriad of applications. While the resin used in composites is sometimes referred to as “plastic,” it is not to be confused with most plastics we see today, which are actually pure plastic, like toys and soda bottles.

1.2.1 Benefits of Composites

Composites provide unique benefits over traditional materials such as steel, aluminum, wood or concrete. This is owed to both the unique nature of the material, and our ability to adjust their components to change the characteristics of the final product. As a result, composites provide many advantageous physical properties and great design flexibility.

The benefits of composites include:

- Lightweight
- High strength
- Corrosion resistant
- High strength-to-weight ratio
- Directional strength - tailor mechanical properties
- High impact strength
- High electric strength (insulator)
- Radar transparent
- Non-magnetic

- Low maintenance
- Rapid installation
- Long-term durability
- Parts consolidation
- Dimensional stability
- Small to large part geometry – styling/design – sculptural form
- Customized surface finish

1.2.2 Composites in the manufacturing

Composites have the ability to open up a world of new possibilities for manufacturers, designers, and engineers. As many companies have learned, working with composites allows us to tailor the properties of fibers, resins , and additives to get the exact material properties and performance characteristics we need.

A composite material (also called a composition material or shortened to composite, which is the common name) is a material that is produced from two or more constituent materials.[1] These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions.

Typical engineered composite materials include:

- Reinforced concrete and masonry
- Composite wood such as plywood
- Reinforced plastics, such as fibre-reinforced polymer or fiberglass
- Ceramic matrix composites (composite ceramic and metal matrices)
- Metal matrix composites
- other advanced composite materials

There are various reasons where new material can be favoured. Typical examples include materials which are less expensive, lighter, stronger or more durable when compared with common materials, as well as composite materials inspired from animals and natural sources with low carbon footprint.[2]More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites,[3] which are known as robotic materials.[4]Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.[5][6] They are also being increasingly used in general automotive applications.[7]The most advanced examples perform routinely on spacecraft and aircraft in demanding environments.

1.2.3 Polymer composites

A polymer is a material consisting of very large molecules called macromolecules which are formed from repeating many small units called monomers through the polymerization process. Synthetic and natural polymers play essential roles in everyday life for their broad spectrum of properties, [8, 9] Polymers range from synthetic plastics such as polyethylene and polystyrene to natural biopolymers like DNA and proteins that are fundamental to biological structure and function. Because of their large molecular mass, they possess unique physical properties such as toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semi-crystalline structures. The degree of polymerization greatly influences the properties of the derived plastics.

Plastics are a wide range of synthetic or semi-synthetic materials that use polymers as a main ingredient. Plastics can be moulded, extruded, or pressed into solid objects of various shapes due to their plasticity. This uniqueness coupled with other properties, such as being lightweight, durable, flexible, and low cost has led to its wide use in domestic and many industrial sectors. Plastics typically are made through human industrial systems. Most modern plastics are derived from fossil fuel-based chemicals like natural gas or petroleum.

Plastics are broadly classified as thermoplastics and thermosetting plastics.

Thermoplastics do not undergo chemical change in their composition when heated and thus can be moulded repeatedly. Examples include polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). [10]

Thermosets or thermosetting plastics can be heated to melt and but can be shaped only once. After they have solidified, they stay solid. If reheated, thermosets decompose rather than melt as an irreversible chemical reaction occurs [11]. Vulcanization of rubber and Bakelite are typical examples of thermosetting plastics.

A polymer composite is a multi-phase material that is formed by impregnating fillers with a polymer matrix for reinforcement, resulting in synergistic mechanical properties that cannot be achieved from either component alone.

They can transfer loads between fibers of a matrix. Lightweight, high resistance to abrasion and corrosion, high stiffness, and strength along the direction of their reinforcements makes polymer composites for advanced industrial application including cryogenic and space technologies.

1.4 Need for the characterization of polymer composites for cryogenic applications

Fiber-reinforced polymer composites are used in many industries requiring extensive characterization and understanding of their behavior in ambient conditions. The response of the material can change drastically when exposed to extremities both within and beyond the Earth’s atmosphere that require structures to operate at ultra-low temperatures in the cryogenic range. Liquid propellant tanks for space programs, satellite launch vehicle structures; aircraft structures at cruising altitudes; support elements and devices operating at cryogenic temperatures, and arctic exploration structures are some of the areas where composite structures have to encounter extremely low temperatures.

Hence, it is necessary to characterize composites at cryogenic temperature to know the effect of low temperatures on composite materials towards designing the structural components based on polymer composites to be operated down to cryogenic temperature.

CHAPTER - 2

Properties
Of
Materials
At
Low Temperatures

CHAPTER-2

PROPERTIES OF MATERIALS AT LOW TEMPERATURES

2.1 Introduction

A knowledge of the properties and behavior of materials used in any cryogenic system is essential for proper design considerations. Often the choice of materials for the construction of cryogenic equipment will be dictated by consideration of mechanical and physical properties such as thermal conductivity (heat transfer along a structural member), thermal expansivity (expansion and contraction during cycling between ambient and low temperatures), and density (mass of system). Since properties at low temperatures are often significantly different from those at ambient temperatures, there is no substitute for test data. To help summarize the data that do exist and help estimate properties when no data are available, it is useful to have certain general rules in mind. That is the purpose of the following discussion.

2.2 Mechanical Properties

In any branch of engineering design, material choice is dictated by questions of safety and economy. The range of choice in cryogenic design is perhaps limited by the issue of low-temperature embrittlement. The purpose of this section is to show which materials retain their ductility from ambient to low temperatures. This determination requires an explanation of why ductility exists at all in some materials and not in others, and a knowledge of temperature mechanisms that govern ductility. Common indices of strength of materials are also explored, along with the temperature dependence of this important property [1].

2.2.1 Strength, ductility, and elastic modulus

When a bar of a structural solid is subjected to an elongating force, the first response is a slight stretching, which is directly proportional to the force producing it. If the elongating force is released during this initial period, the material will return very nearly to its original length. This is termed elastic behavior, which all solid materials exhibit in some measure. At some higher value of stress, however, the material will no longer behave elastically. It may break without further deformation (brittle behavior), or it will take on a permanent deformation (ductile behavior).

The ductile or brittle behavior of structural materials is usually determined by the familiar stress-strain test. In this test a steel bar of cross section A, on which a gage length L has been marked, is subjected to an axial tensile load P which gradually increases from zero value until the bar breaks. As the axial tensile load increases, values of elongation ΔL are taken. These measurements are related in the following manners**:**

$$\mathbf{S = P/A}$$

$$\boldsymbol{\varepsilon = \Delta L/L}$$

When S is defined as the stress and ε the strain. The relationship between S and ε is the stress-strain curve determined experimentally shown in figure 3.1a for a ductile material and for a brittle material fig 3.1b. In both figures, PL is the proportional limit defined as the maximum unit stress that can be developed without causing a deviation in the proportionally of stress to strain. The region from C to D is the yield point characteristics in a ductile material where deformation sets in without an increase in load. The maximum that can be developed in the material as shown by point F on fig 3.1a is known as the ultimate tensile strength. Brittle materials break at point F while ductile materials continue to stretch, or "neck down" from points F to G.

Another class of materials (nonmetals) is capable for extremely great elastic deformations. These are called elastomeric materials. Usually, materials exhibiting plastic deformation under stress are the more desirable for structures. Ductility is desirable so that accidental stresses beyond design values can be redistributed to safer levels by means of plastic flow.

Brittle materials have no such mechanism to protect them against excessive stress. When a local overstress occurs in a brittle material, the result is often failure of the material rather than a deformation. It is useful to know, therefore, which structural materials that are acceptable(ductile) at normal temperatures. This requires examining the structures of solids.

2.2.2 The Structures of Solids

The theory of elasticity treats solids as continuous elastic media. Solids are not continuous media but are composed of atoms bound together in more or less regular arrays. Essentially three different types of solid structures exist, represented by glasses, plastics, and metals.

Plastics. polymers that form plastics are composed of giant long-chain molecules. polymer molecules may have from hundreds to tens of thousands of atoms each and are essentially linear but generally lie in a tangled disarray. the intermolecular force that binds the polymer molecules to one another is a rather weak force, called the Van der Waals force. Some cross-linking among the polymer molecules may also be present. Cross-linking is actually chemical bonding between adjacent molecules and is much stronger than the Van der Waal forces. The more highly cross-linked polymers (thermosetting) form much more rigid solids than those that are only sparingly cross-linked (thermoplastics).

2.2.3 Low Temperature Ductility

The effect of temperature, on ductility is, to a first approximation, the effect of temperature on the response mechanisms discussed above-the crystal system (slip planes) and dislocation motion. This will be discussed first for metals, then for elastomers.

Since the number of slip systems is not usually a function of temperature, the ductility of face-centered cubic metals is relatively insensitive to a decrease in temperature. Metals of other crystal lattice types tend to become brittle at low temperatures. Crystal structures and ductility are related because the face-centered cubic lattice has more slip systems than the other crystal structures. In addition, the slip planes of body-centered cubic and hexagonal close-packed crystals tend to change at low temperatures, which is not the case for face-centered cubic metals. Therefore, copper, nickel, all of the copper-nickel alloys, aluminum and its alloys, and the austenitic stainless steels that contain more than approximately 7% nickel, all face-centered cubic, remail ductile down to the low temperatures, if they are ductile at room temperature. Iron, carbon and low alloy steels, molybdenum, and niobium, all body centered cubic, become brittle at low temperatures. the hexagonal closed packed metals occupy an intermediate place between fcc and bcc behavior. Zinc undergoes a transition to brittle behavior in tension, zirconium and pure titanium remain ductile.

The thermal vibration of atoms in the crystal lattice is strongly temperature-dependent and is less effective in assisting dislocation motion at low temperatures. The interactions of dislocations with thermal vibrations are complicated, but it is nonetheless satisfying to find that ductility usually decreases somewhat with a decrease in temperature.

The complete situation regarding brittleness in metal at low temperatures depends on more than just crystal structure. For instance, body-centered cubic potassium and beta brass remain ductile down to 4.2K, and the body-centered cubic metals, lithium and sodium, show to signs of brittleness down to 4.2K. In general, however, brittleness will not occur in face-centered cubic metals in which dislocations cannot be firmly locked by impurity atoms.

All plastics or elastomers except one become brittle at low temperatures. Polytetrafluoroethylene is unique in that it can still be deformed plastically to a small degree at 4K. Plastics and elastomers do not respond to stress as do metals. The less cross-linked elastomers yield by uncoiling their long-chain molecules and by sliding over one another. The thermal energy of material at room temperature facilitates this motion.

At low temperatures, however, the attractive intermolecular forces are more effective than the thermal energy “lubricant”, and the materials deform less readily. The effect is especially pronounced through the “glass transition” of the material during the temperature range at the onset of brittleness.

As mentioned, the tendency to show a ductile-brittle transition is corelated with the lattice type. Thus, the face-centered cubic metals show but few cases of this effect and for structural purposes may be regarded as almost uniformly well behaved. These include copper, nickel, aluminum, the solid solution alloys of each of these, and the austenitic stainless steels. In contrast, body centered cubic metals for the most part show brittle behavior (though the transition zones of some can be depressed to low temperatures). The ferritic steels are by far the most prominent of these. Prominent among the established structural metals with a different lattice are the hexagonal metals, magnesium, and titanium. The impact strength of magnesium is low at all sub-ambient temperatures, the indication being that the brittle transition zone is above room temperature. Tests on commercial titaniums indicate that ductility is retained in tension to low temperatures if the amounts of the interstitial solutes, carbon, oxygen, nitrogen, and hydrogen are small. However, notched-bar impact tests show a transition above ambient temperature.

For temperatures below 200K, it is the practice to use the face-centered cubic metals almost exclusively and especially where shock and vibration are encountered. However, less expensive steel can be used in many less critical applications, especially for temperatures above 150K to 200K. These generalities summarizing embrittlement at low temperatures are shown in the table.

2.2.4 Low-Temperature Strength of Solids

In general, the ultimate tensile strength of solid materials is greater at low temperatures than it is at ordinary temperatures. This is true for both crystalline and non-crystalline solids, and also for many heterogeneous materials as well (e.g., glass-reinforced plastics). For metals, the strength at 4K maybe two to five times that at room temperature. For plastics, the strength at 76K may be one and a half to eight times greater than the room-temperature value. Glasses show less change in strength at low temperatures; at 76K, glasses have between one and a half to two times their room-temperature strength [2].

Reduction of the thermal energy of the metal lattice at lower temperatures is responsible for part of the strength increases of metals. The decreased thermal vibration at low temperatures also results in stronger plastics, since it becomes more difficult for the long-chain molecules to slide over one another.

The change in strength of glass at low temperatures is not a strong as that of metals and plastics. The important cohesive forces of glasses are the chemical bonds between atoms (rather than the intermolecular forces of plastics). Such chemical bond forces are less affected by temperature.

There are exceptions to the above general rule. The thermal and mechanical history of a material, various solid-state phase changes, the form of the stress system, and the rate of application of this stress system can also affect mechanical properties. Some of the exceptions to the general rule of increasing strength with decreasing temperature can be explained qualitatively by phase change during deformation. some austenitic stainless steels undergo a partial transformation under strain from a face-centered cubic to an intermediate hexagonal close-packed phase and then to a body-centered lattice(martensite). The martensite form is stronger than the parent structure and contributes to the high strength of these materials. The tensile strength of austenitic steels shows the usual increase with decreasing temperature to some low temperature and then a decrease, reflecting a maximum in the phase transformation curve.

Plastics. Only a few plastics have been tested at temperatures below 200K. of these, only Teflon showed ductility down to the lowest test temperature, which was 4K. However, reinforced plastics such as the glass fiber laminates can have good properties, the tensile strength parallel to the laminations increasing at low temperatures and the modulus being approximately constant. Mylar breaks with fragmentation in a tensile test and is correspondingly brittle at low temperatures.

Yet in films of about $2.54x10^{-5}$m or less in thickness, Mylar shows remarkable flexibility in bending tests as low as 20K.

From figure, shows the tensile strength of several plastics. The increase in strength, as the temperature is decreased, is accompanied by a rapid decrease in elongation and impact resistance. The glass-reinforced plastics are the only plastics that retain appreciable impact resistance as the temperature is lowered.

2.2.5 Fatigue Strength

A simple reversed bending test is the usual method to measure fatigue strength. The fatigue strength is defined as the stress required to cause failure after a certain number of bending cycles and is given as S_f. some materials, such as carbon steel, have the property that the fatigue failure will not occur if the stress is maintained below a certain value, called the endurance limit S_e, no matter how many cycles have elapsed.

Fatigue strength data at low temperatures are not as common as yield strength data and ultimate tensile strength data, because the fatigue tests are more time consuming and hence more expensive to perform. As one would expect, however, the data that have been reported all show that fatigue strength increases as the temperature decreases, in the same manner as the yield and ultimate tensile strength.

Fortunately, at least for aluminum alloys, it has been found that the ratio of fatigue strength to ultimate strength remains fairly constant as the temperature is lowered. Therefore, the fatigue strength of these alloys varies with temperatures in the same manner that the ultimate strength varies with temperature. This fact may be used in estimating the fatigue strength for non-ferrous materials at cryogenic temperatures if no fatigue data are available. Representative data of fatigue strength for several materials at low temperature are shown in figure.

Plastics also increase in strength as the temperature is decreased, but this is accompanied by a rapid decrease in elongation in a tensile test and a decrease in impact resistance as the temperature is lowered. The glass reinforced plastics also have high strength-to-weight and strength-to-thermal conductivity ratios. Conversely, all elastomers become brittle at low temperatures. Nevertheless, many of these materials including rubber, Mylar, and nylon can be used for static seal gaskets provided they are highly compressed at room temperature prior to cooling [3].

The strength of glass under constant loading also increases with decrease in temperature. Since failure occurs at a lower stress when the glass surface contains surface defects, the strength can be improved by tempering the surface.

A cryogenic storage container must be designed to withstand forces resulting from the internal pressure, the weight of the contents, and bending stresses. Material compatibility with low temperatures, which has already been discussed, results in choosing among the fcc metals (copper, nickel, aluminum, steels etc.). Because these materials are more expensive than ordinary carbon steels, a design goal is to make the inner vessel as thin as possible. This constraint also reduces cool down time and the amount of cryogenic liquid required for cool-down. Thus, the inner vessel of cryogenic containers is nearly always of the thin-walled class. Relationships developed to determine the required thickness of cryogenic containers are detailed in this chapter.

2.3 Thermal Properties

The thermal properties of most interest at low temperatures to the process engineer are specific heat, thermal conductivity, and thermal expansion. Each of these important properties is discussed in this section. It will be shown that each of these properties depends upon the intermolecular potential of the lattice, and thus these properties are interrelated.

2.3.1 Specific Heat

Lattice Heat Capacity. Nearly all the physical properties of a solid (e.g., specific heat, thermal expansion) depend upon the vibration or motion of the atoms in the solid. Specific heat is often measured at low temperatures for design purposes. However, specific heat measurements are important in their own right, because the variation of specific heat with temperature shows how the energy is distributed among the various energy-absorbing modes of the solid. Thus, specific heat measurements give important clues to the structure of the solid. Finally, because other properties also depend on the lattice structure and its vibration, specific heat measurements are used to predict or correlate other properties, such as thermal expansion. Therefore, an understanding of the temperature dependence of specific heat not only gives useful design information, but also is helpful in predicting other thermal properties as well.

The specific heat of any material is defined from thermodynamics as

$$c_V=(\delta u/\delta T)_V$$

Where u is the internal energy, T is the absolute temperature and V is the volume.

2.3.2 Thermal Conductivity

The thermal conductivity, k_t, of any material is defined such that the heat transferred per unit time dQ/dt is given by

$$dQ/dt= -k_tA(dT/dx)$$

Where A is the cross-sectional area and dT/dx is the thermal gradient. To understand how thermal conductivity depends upon temperature, especially at low temperatures, it is useful to understand the basic mechanisms for energy transport through materials. There are three basic energy transports, and hence heat conduction through a solid. These are described below.

Lattice vibrational energy transport, also known as phonon conduction, occurs in all solids-dielectrics and metals. In nonmetallic crystals and some intermetallic compounds, the principal mechanism of heat conduction is by this lattice vibration mode, or the mechanical interaction between molecules. For single crystals at quite low temperatures, this mode of heat conduction can be very effective, equaling or exceeding the conduction by pure metals.

Energy transport in metals is dominated by electron motion. Metals, of course, also have a lattice structure and hence experience a lattice contribution to thermal conductivity. However, thermal conductivity in pure metals (particularly at low temperatures) is due principally to the “free” conduction electrons, those that are so loosely bound to the atoms that they wander readily throughout the crystal lattice and thus transfer thermal energy.

Molecular motion, such as noted in organic solids and gases, is another energy transport mechanism. This characteristic disorder as well as the lattice imperfections of organic solids introduce resistances to heat flow. Accordingly, disordered dielectrics such as glass and polymeric plastics are the poorest solid conductors of heat.

For the present, we are concerned with structural materials, and so we shall limit this overview to dielectrics (insulators) and metals. Furthermore, since dielectrics have only one heat transport mechanism (phonons), and metals have two (phonons plus electrons), we shall begin with heat transport in dielectrics.

2.3.3Thermal Expansivity

In the prior discussion of thermal properties, the atoms of the solid have been assumed to vibrate symmetrically about some equilibrium position in the solid. If this were the case, there would be no thermal expansion. Instead, the intermolecular potential energy curve (summing forces of attraction and repulsion) is not symmetrical. The general shape of the intermolecular potential is asymmetric. This results from a repulsive force that increases very rapidly as the two atoms approach each other closely (one atom is considered at rest at the origin), plus an attractive force that has a considerably smaller dependence on distance. Their algebraic sum provides a curve having a minimum at r_0, the classical equilibrium separation of the atoms at 0K. Increasing the temperature from 0K corresponds to raising the energy of the system slightly, and causing thermal vibrations to take place between r_1 and r_2. But because of the asymmetry of the potential well, the average distance no longer corresponds to r_0; it is slightly greater and results in the observed thermal expansion of materials. The rate at which the mean spacing of the atoms increases with temperature increases as the energy or temperature of the material increases; thus, the coefficient of thermal expansion increases as temperature is increased.

Both the specific heat and the co-efficient of thermal expansion originate from the concept of the intermolecular potential and accordingly these two properties and related. The present understanding of this relation is largely due to Gruneisen, who developed an equation of state for solids, based upon the lattice dynamics of Debye. The lattice showed that the dimensionless ratio (γ), should be a universal constant defined either as

$$\gamma = \alpha V/\beta_T Cv$$

or

$$\gamma = \alpha V/\beta_s Cv$$

Where is the volumetric coefficient of thermal expansion, β_T the isothermal compressibility, and β_s the adiabatic compressibility.

Here, the volumetric coefficient of thermal expansion is defined as the fractional change in volume per unit change in temperature under constant pressure conditions. The linear coefficient of thermal expansion λ_t is the fractional change in length per unit change in temperature while the stress on the material remains constant. For isotropic materials,

$$\alpha = 3\lambda_t$$

2.4 Conclusion

Properties of materials at low temperatures are often significantly different from those at ambient temperatures and there is no substitute for generated test data for a particular application. Basic theories of the physical and thermal properties of solids including plastics are discussed. The method of measuring such properties is highlighted. The knowledge is required to undertake the characterization of materials at low temperatures.

CHAPTER - 3

Characterization Of Polymer Composites
For
Cryogenic Applications-
A State-Of-Art Report
(Literature Survey)

CHAPTER-3

CHARACTERISATION OF POLYMER COMPOSITES FOR CRYOGENIC APPLICATIONS – A STATE-OF-ART REPORT (LITERATURE SURVEY)

3.1 Introduction

Cryogenics, the science and technology of low temperature starts below-150°C temperature and extends up to near absolute zero.

During cooling to cryogenic temperatures, polymers exhibit some peculiar characteristics that must be taken care of before undertaking any design of instruments or equipment to be operated in a cryogenic environment so that the finished device will serve the desired job.

The study of polymer materials at low temperatures has become a subject of much discussion with new developments in cryogenic liquid propulsion systems for space, superconducting magnets for diagnostic and motors, electronic and defense technologies, and also for large cryogenic engineering projects like International Thermonuclear Experimental Reactor (ITER), etc.

The chapter -3 begins with a brief description of methodologies of some important mechanical testing and then moves on to an overview of polymer composites and finally describes the change in properties like strength, modulus, toughness, brittleness, and thermal conductivity, etc. of polymer composite materials when they are exposed to a cryogenic temperature in comparison of their similar properties in relevance to the strength, modulus, toughness, brittleness, thermal conductivity, etc. Different characterization data on mechanical and thermal properties of polymer composites is also highlighted for assessing their suitability for cryogenic application which will serve as a comprehensive report on the effect of variation of temperature on modified polymer properties in the cryogenic temperature range so as to make one familiar with the properties and behavior of polymer composite materials at low temperature.

3.2 Significance of Some Important Mechanical Testing Terminologies

Impact testing is used to measure the impact toughness of the material used and is described as the toughness and the ability of the material to absorb energy due to sudden loading. The ductility and strength of the material are taken into account by toughness. Notched impact strength, as determined with a V-shaped notch, and the un-notched impact strength come under the purview of impact properties.

Fatigue is defined as the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle until it reaches a critical size leading to a complete fracture of the structure. Macroscopic cracks resulting from cyclic thermal stresses and strains due to temperature changes, spatial temperature gradients, and high temperatures are known as thermal fatigue which may occur without mechanical loads.

Fracture toughness is the critical stress intensity factor of a sharp crack where propagation of the crack suddenly becomes rapid and unlimited. A quantitative way of expressing a material's resistance to crack propagation is expressed by Fracture toughness.

The three-point bending flexural test provides values for the modulus of elasticity in bending, and flexural stress–strain response of the material and is performed in tensile testing machine testing. Results are sensitive to specimen and loading geometry and strain rate.

The tendency of a solid material to slowly move or deform permanently under constant stresses is regarded as Creep which measures the strain response due to constant stress.

3.3 Overview of Polymer and Polymer Composites

A polymer is a material consisting of very large molecules called macromolecules which are formed from repeating many small units called monomers through the polymerization process. Synthetic and natural polymers play essential roles in everyday life for their broad spectrum of properties [1, 2], Polymers range from synthetic plastics such as polyethylene and polystyrene to natural biopolymers like DNA and proteins that are fundamental to biological structure and function. Because of their large molecular mass, they possess unique physical properties such as toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semi-crystalline structures. The degree of polymerization greatly influences the properties of the derived plastics.

Plastics are a wide range of synthetic or semi-synthetic materials that use polymers as a main ingredient. Plastics can be moulded, extruded, or pressed into solid objects of various shapes due to their plasticity. This uniqueness coupled with other properties, such as being lightweight, durable, flexible, and low cost has led to its wide use in domestic and many industrial sectors. Plastics typically are made through human industrial systems. Most modern plastics are derived from fossil fuel-based chemicals like natural gas or petroleum.

Plastics are broadly classified as thermoplastics and thermosetting plastics.

Thermoplastics do not undergo chemical change in their composition when heated and thus can be molded repeatedly. Examples include polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) [3].

Thermosets or thermosetting plastics can be heated to melt but can be shaped only once. After they have solidified, they stay solid. If reheated, thermosets decompose rather than melt as an irreversible chemical reaction occurs [4]. Vulcanization of rubber and Bakelite are typical examples of thermosetting plastics.

A polymer composite is a multi-phase material that is formed by impregnating fillers with a polymer matrix for reinforcement, resulting in synergistic mechanical properties that cannot be achieved from either component alone.

A polymer matrix composite (PMC) is a composite material composed of a variety of short or continuous fibers bound together by a matrix of organic polymers. They can transfer loads between the fibers of a matrix. Lightweight, high resistance to abrasion and corrosion, high stiffness and strength along the direction of their reinforcements make polymer composites a versatile material for advanced industrial applications including cryogenic and space technologies.

3.4 Advances in the Characterization of Polymer Composites

Research and developmental works on polymer composites have gained tremendous momentum in recent years and its new areas of applications are being explored.

Polymer for Cryogenic application highlighting Methods, Mechanisms, and Perspectives is reviewed [5]. It is observed that polymeric materials become more brittle, and the adverse effect of thermal stress induced by temperature is significant. The research and development of thermoset and thermoplastic polymers related to the cryogenic compatibility of modified thermoset polymers and the improving mechanisms of the reported modification methods, the cryogenic application potential of some commercial thermoplastic polymers and the recent advance in the use of polymer, especially at liquid oxygen environment is explained. Moreover, the future scopes of research have been proposed with particular reference to aerospace engineering.

An investigation revealed that cryogenic treatment improves wear, abrasion, erosion, and corrosion resistivity, and durability and stabilizes the strength characteristics of various metals, alloys, plastics, and composites [6].

Carbon fiber reinforced polymer (CFRP) composites are widely used in aerospace crafts as a load-bearing component as they are lightweight but have reasonable mechanical strength. The effects of cryogenic temperature from 77 K to 298 K and cryogenic stability after 50, 100, and 150 cycles on the mechanical properties and failure modes of Carbon fiber-reinforced polymer composite laminates with various stacking sequences are investigated [7]. In-situ static tensile and three-point bending tests are performed. X-ray computed tomography (X-ray CT) results revealed significant degradation in tensile strength and modulus of laminates with the decrease in temperature because of changes in failure mode.

The flexural properties improved by over 50% and the degradation in properties of quasi-isotropy laminates is more significant than that of unidirectional due to the coupling effect of thermal expanding mismatch between material (fiber and matrix) and layer. Quasi-isotropy laminated exhibited greater micro-crack volume fractions (more than 6-fold after 150 cycles). The micro-cracks gradually expanded and nucleation occurred within the interfacial layers as thermocycling rises. The results provide important information regarding the structure design of cryogenic composite tanks under complex working environments based on temperature effect.

Polymer-based composites become brittle and micro-cracks are developed due to differential thermal coefficients of expansion (CTEs) between the polymer matrix and the impregnated filler materials. It is found that the use of single-walled (SWNTs) and multi-walled carbon (MWNTs) nanotubes could enhance the mechanical properties of polymer-based composites. The efficiency and effectiveness of stress transfer in the composites are normally affected by interfacial bonding properties. The viability of using coiled carbon nanotubes (CCNTs) and randomly-oriented Nano clay-supported nanotubes (NSCNTs) to enhance the mechanical properties of epoxy resin at the cryogenic temperature are explained in detail with experimental studies [8].

The polymer materials need to possess good mechanical and physical properties at cryogenic temperatures such as liquid helium (4.2 K), liquid hydrogen (20 K), liquid nitrogen (77 K), and liquid oxygen (90 K) temperatures, etc. Mechanical and physical properties of polymers and filled polymer materials at cryogenic temperature are highlighted with a details discussion on cryogenic tensile behaviors, shear strength, impact strength, fracture toughness, etc. Thermal creep and dielectric properties of polymers are also summarized [9].

The material properties such as tensile, compressive and shear strength, stress-strain behavior, mechanical and thermal fatigue response, fracture toughness, impact resistance, tribology thermal expansion and thermal conductivity and abrasion resistance of polymer composites are presented highlighting the challenges of cryogenic experiments towards characterization[10].

The tribological behavior of Poly Tetra Fluro Ethylene (PTFE) composites against steel at cryogenic temperatures is investigated. The results showed that the friction coefficient decreases with the temperature down to 77 K, but below 77K, It did not follow a linear evolution. The cryogenic environment has a great influence on the tribological performance of the polymer composites. SEM and AFM analyses revealed that the PTFE matrix composites investigated have transferred material onto the disc down to very low temperatures [11].

High strength, stiffness, and low weight propel composite materials and FRPs into new arenas. Due to the heterogeneous nature and anisotropic behavior of FRPs, a structural designer has faced challenges in predicting the integrity and durability of FRP laminates. Cryogenic fuel tanks for storing Liquefied Natural Gas (LNG) and liquid hydrogen are the unique structural applications of FRP at low temperatures. Micro cracks as well as delamination in the composites due to thermal residual stresses may develop which provide a pathway for the ingress of moisture or corrosive chemicals leading to loss of cryogenic fluids in the tanks. Matrix resins become brittle and do not allow the relaxation of residual stresses to take place. Polymers are well below their glass transition temperature and show little viscoelastic behavior when exposed to a cryogenic environment. Mechanical properties of FRP composites such as carbon, glass, and Kevlar fiber-reinforced polymers with different resin matrices at cryogenic temperatures are discussed [12].

The mechanical performance of carbon nanotube (CNT) reinforced polymer composites subjected to tension in a cryogenic environment is experimentally and numerically evaluated. Tensile tests are performed on CNT/polycarbonate composites to identify the effects of CNTs on tensile properties, and finite element computations are also conducted using a model for the representative volume element (RVE) of CNT reinforced composites for computing the effective composite elastic modulus and the stress state within the composites. The numerical findings are then correlated with the experimental results [13].

Thermal/mechanical response and damage growth in polymeric composites at cryogenic temperatures are investigated [14]. The research paper presents experimental data on the residual mechanical properties of a carbon fiber polymeric composite, IM7/PETI-5 both before and after cryogenic treatment. Tension modulus and strength are measured at room temperature, -196°C, and -269°C on five different specimen ply lay-ups,[0] 12, [90112, [-+4513s, [-+2513s and [45,903,-45,03,-45,903,45]. Specimens were preconditioned with one set of coupons being isothermally aged for 555 hours at 184 °C in an unloaded state. A microscopic examination of the surface morphology of the specimen after exposure to cryogenic temperature shows evidence of degradation along the exposed edges of the material.

The Characterization of cryogenic delamination growth behavior in woven glass fiber reinforced polymer (GFRP) composite laminates subjected to Mode II fatigue loading are reported in the literature by conducting tests at room temperature, liquid nitrogen temperature (77 K) and liquid helium temperature (4 K) using the four-point bend end-notched flexure (4ENF) test method, The research findings give an idea of the fatigue delamination growth mechanisms in the woven glass fiber reinforced polymer GFRP laminates under Mode II loading at cryogenic temperatures [15].

To assess the damage trends in cryogenically cycled (upto1000 cycles) carbon/polymer composites, (six carbon/polymer composites of three materials, two lay-ups each) are cycled by repeated submersion of 5 cm x 5 cm flat plates in liquid nitrogen. It is observed that reducing the ply thickness by 30% in the IM7/5250-4 delays surface ply micro-cracking by up to 200 cycles and the surface ply micro-crack densities are nearly equal by 100 cycles regardless of the ply thickness [16].

Thermal/Mechanical Response of a Polymer Matrix Composite at Cryogenic Temperatures is reported [17]. This paper presents experimental data on the residual mechanical properties of a carbon-fiber polymeric composite, IM7/PETI-5, both before and after cryogenic exposure. Tension, compression modulus, and strength are measured at room temperature, -196"C, and -269°C on five different laminate configurations. It is shown that trends in stiffness and strength that result from changes in temperature are not always smooth and consistent.

A yield-stress-based failure model is used to predict the temperature at which microcracking occurred in symmetrical cross-ply carbon-fiber/epoxy composite materials. Dynamic mechanical analysis was used to assess microcracking at cryogenic temperatures through the observation of discontinuities in the material properties during failure. The model accurately predicted the onset temperature for microcracking in three of the four cases. If the room-temperature properties of a fiber-reinforced polymeric composite laminate is appropriately modified to take care of property variations at low temperatures [18]. Low-temperature properties of a unidirectionally reinforced epoxy fiberglass composite are studied [19]. The tension, compression, and in-plane shear properties of a unidirectionally reinforced fiber/epoxy composite are measured at 295K, 76K and 4 K. The composite plate material is produced by the wet-filament winding method. The orthotropic material properties are dominated by the glass fiber properties if measured parallel to the direction of reinforcement and the epoxy resin matrix properties are dominated when measured transverse to the reinforcement. With the decrease in temperature, strength and elastic moduli are increased.

Effects of High and Low Temperatures on the Tensile Strength of Glass Fiber Reinforced Polymer Composites are studied [20]. The tensile strength of glass fiber reinforced polymer (GFRP) composites at high and low temperatures is experimentally determined. GFRP laminates are manufactured by the wet hand lay-up assisted by a vacuum bag to get average fibre volume fraction of 0.45. Using simultaneous heating/cooling and loading, glass fiber epoxy and polyester laminates are examined for their mechanical performance in static tensile loading. The tension mechanical properties; stress and modulus are reduced with increasing temperature from 250 C to 800 C. Results from room temperature to a minimum temperature of - 200 C, indicate that there is no considerable effect on the tensile strength but a slight decrease of tensile modulus is observed on the GFRP laminates. The experimental findings highlight the structural survivability at low and high temperatures of the GFRP at cryogenic environment.

The impact properties of glass fiber/epoxy composites in the cryogenic environment are experimentally determined [21]. GFRP samples are fabricated by vacuum infusion process with post-curing at 353 K for 3 h to ensure that a complete chemical reaction inside the samples is achieved. Samples are stored at room temperature (295 K), dry ice temperature (199 K), and liquid nitrogen temperature (100 K) conditions. The apparent damages and their size are visually examined and impact load, deflection, and energy absorption of each damage type are interpreted. Besides, the post-curing effect was also studied to verify its significance to the impact properties of composites. Experimental results show that post-curing could reduce the apparent damage and increase the energy absorption of GFRP composites.

3.5 Conclusion

Details of experimental findings by the researchers on the effect of low temperature pertaining to the structural properties including tensile strength, impact strength, thermal fatigue, creep, brittleness, etc. have been discussed, so that the designer can make a choice of the appropriate polymer composites for its application to a specific cryogenic field. It is observed that most polymers become brittle at low temperatures but their strength increases. Fiberglass-reinforced epoxy resin or graphite-impregnated PTFE can sustain low temperatures without cracking and hence their structural survivability at cryogenic temperature is manifested. In addition, PTFE offers self-lubricating properties.

CHAPTER-4

Aims and Objective Of The Present Study

Chapter-4

AIMS AND OBJECTIVE OF THE PRESENT STUDY

Polymers are excellent engineering materials and can be a substitute either fully or partially combined with metallic parts for the development of various types of equipment/components to be operated at cryogenic temperatures (below -150^0C). Fillers are selectively added to polymers resulting in polymer composites that enhance their mechanical strength and many desirable properties such as low thermal conductivity, electrical insulating property, vacuum sealing effect, self-lubricating property, and lightweight in comparison to metallic counterparts.

Most often the suitability of a large number of metals and alloys for their use at low temperatures has been studied but much less work has been reported in the field of characterization of polymer materials at low temperatures particularly that of different polymer resin-impregnated fiberglass composites. These polymer composites have a reasonable edge over many metallic components for cryogenic and allied applications Moreover, such composites are also used as non-conducting structural components in combination with metallic parts in the fabrication of cryogenic storage vessels, transfer lines, cryo stat, etc. The potential for these polymer composite materials in the low-temperature range still remains unexplored, particularly for the lack of adequate data on characterization and there lies tremendous scope to have in-depth studies of the behavior of such composites down to the boiling point of Liquid Nitrogen as well as their compatibility at cryogenic temperature as a parts with metallic components. In this regard, the characterization of polymer composites from the consideration of their utilization in the fabrication of cryogenic storage containers, plant components, cryostat, and other equipment being used at cryogenic temperature becomes the need of the hour.

The **objective present work** is to carry out rigorous study from theoretical and experimental points of view on the basis of the determination of some of the mechanical and physical properties of the glass fiber-reinforced plastic composites for cryogenic applications to finally arrive at the feasibility of the indigenous development of Glass Fibre fiber-reinforced plastic tube with necessary characterization /heat transfer consideration and its subsequent use as a neck of an indigenously built stainless steel liquid nitrogen vessel as well as a performance study of aluminized mylar as a Multi-Layer Insulation system. The work stresses to achieve material characterization, design, analysis, fabrication, and experimental run of the prototype cryogenic Dewar of 3 liter capacity developed.

CHAPTER-5

Preparation
Of
Glass-Fiber
Impregnated Epoxy Resin Tube
And
Investigation of its Physical and Mechanical Properties for its Use
As
a Structural Component
At
Cryogenic Temperature

CHAPTER-5

PREPARATION OF GLASS-FIBER IMPREGNATED EPOXY RESIN TUBE AND INVESTIGATION OF ITS PHYSICAL AND MECHANICAL PROPERTIES FOR ITS USE AS A STRUCTURAL COMPONENT AT CRYOGENIC TEMPERATURE

5.1 Introduction

Fiber-reinforced polymer composites in general and glass fiber-reinforced polymer (GFRP) in particular are used in many industries requiring extensive characterization and understanding of their behavior in ambient conditions [1-3]. The response of the material can change drastically when exposed to extremities both within and beyond the Earth's atmosphere that require structures to operate at ultra-low temperatures in the cryogenic range. Liquid propellant tanks for space programs, satellite launch vehicle structures; aircraft structures at cruising altitudes; support elements and devices operating at cryogenic temperatures, and arctic exploration structures are some of the areas where composite structures have to encounter extremely low temperatures.

Hence, it is necessary to characterize composites at cryogenic temperature to know the effect of low temperatures on composite materials towards designing the structural components based on polymer composites to be operated down to cryogenic temperature.

Composites are composed of two different materials having resultant properties far superior to that of individual materials. Composites are macroscopically homogeneous, i.e., the distinguishable behavior of the components cannot be seen through the naked eye and hence will act together as a unit [4, 5]. The main constituent of a composite is reinforcement which is responsible for load bearing.

whereas the matrix is the medium that binds the reinforcement and the interface is the common surface that contacts the reinforcement and matrix. Different composites can be categorized based on the type of matrix medium [6]. Glass-fibers and epoxy resin are considered for our composite preparation. Glass fibers are the most versatile industrial materials as they are readily available and possess some useful bulk properties such as resistance to any form of chemical attack, hardness, stability, transparency, and inertness. In addition, they also show good fiber properties such as stiffness, flexibility, and strength [7]. Epoxy resin is a kind of reactive prepolymer referred to as poly polyepoxides [8]. Glass fiber-reinforced polymeric (GFRP) composites are utilized in the manufacturing of composite materials [9]. The strength of the fiber and its modulus play a crucial role in the physical properties including chemical stability and mechanical behavior in the resultant composites. Matrix and the interface acting between the fiber and the matrix are responsible for the proper transfer of the stress [10].

The proper composition along with the orientation of the fibers made the GFRP properties comparable to steel, with stiffness higher than that of aluminum, and specific gravity one-quarter that of steel [11]. Mechanical properties of the composites can be improved by different glass fiber reinforcements like the woven mat, longitudinal, chopped mat, etc. [12]. Chapter -5 comprises the work on the fabrication of typical glass-fiber composite tubes for use at the neck of a cryogenic container followed by their characterization for determining physical and tensile properties and also testing its optimum strength before and after cryogenic temperature conditioning for different durations of time. Thermal stability, modulus, area of the elastic and plastic region, ductility, stiffness, strength at yield, and strength at break of the composites after liquid nitrogen conditioning are the main properties considered for the characterization.

5.2 Materials and Experimental Method

The special type of epoxy, EP3 is provided by a Fiberglass fabricator, Hoogly-712 233, India. The fabrication of composite tubes is done in collaboration with Industrial Molder and Fabricator, Howrah, India. The appropriate sample size is prepared by cutting one of the tubes with the help of ***Discoplan-TS***, a precision cutting and grinding machine for mineralogical, petrographic, and ceramic thin sections supplied by Aimil Ltd, New Delhi, India.

5.2.1 Glass Fiber Reinforced Polymer (GFRP)

Glass fiber is isotropic in nature [13, 14]. E-glass, S-glass, C-glass, and AR-glass are popular kinds of glass fibers. Lightweight, well resistant to water and chemicals, low cost, and high strength are the main characteristics of glass fiber. Relatively low cost compared with other types of FRPs makes glass fiber most suitable for composite making. GFRP laminates are manufactured from plain woven E-glass laminates. The chemical composition of glass-fiber in wt% is SiO_2 (55.0), Al_2O_3 (14.0), TiO_2(0.2), B_2O_3(7.0), CaO (22.0), MgO (1.0), Na_2O(0.5), K_2O(0.3) [15]. The major drawbacks of glass fiber are low elastic modulus, and low resistance to alkaline with long-term strength due to stress rupture. On the other hand, lightweight to the high strength of glass-fiber(E-glass) is a very attractive property for which E-glass will always be in demand for industry and researchers. Fig 5F.1(a) shows the geometrical illustration of the composite tube with its dimension. Fig5F.1(b) shows the top view (left one)) and side view(left one) of the GFRP-EP3 composite tube.

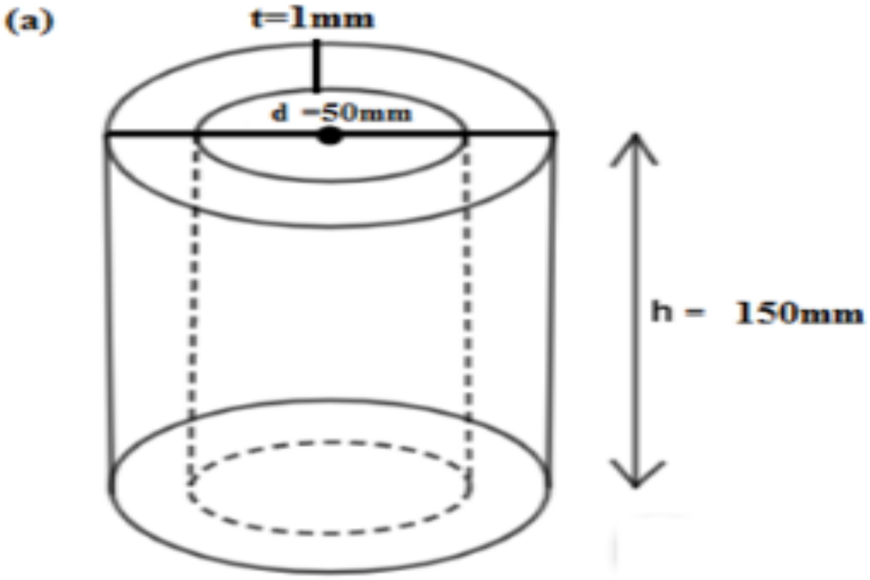

Fig – 5F.1(a) Dimension of the composite tube
Fig- 5F.1 (b) Pictorial top view(left one) and side view(right one) of the composite tube.

5.2.2 Epoxy Resin

Epoxy resins are the most commonly used substrates due to their good mechanical characteristic, thermal properties, corrosive resistance, versatility, and durability [16, 17]. EP3-type epoxy is used for fabricating the desired composites. It is a kind of synthetic resin that could be utilized as an adhesive, coating, casting plastics, and matrix resin for FRPs. EP3 is a breakthrough in epoxy adhesive technology featuring properties like high shear and high cure speed. It offers superior resistance to impact, thermal shock, corrosion, creep, vibration, and stress fatigue cracking while maintaining moisture and thermal resistance even for cryogenic application down to -196^{0}C (77K).

EP3 produces durable and exceptionally tough bonds which are remarkably resistant to serve thermal cycling and many chemicals including water, oil, and fuels. The hardened adhesive is a superior thermal insulator. EP3 offers the convenience of a heat cure with no mixing prior to use and uniquely favorable bonding performance for even the most difficult applications in the aerospace, composite, and chemical industries.

5.2.3 Fabrication of GFRP-EP composites tubes

Glass fiber is available in the woven form but for enhancing its mechanical strength at low temperatures and giving it a perfect shape with reasonable strength, glass fiber-impregnated resin is introduced [18,19]. The entire fabrication is accomplished with the help of a professional Industrial Moulder and fabricator. The epoxy used for the fabrication of the composite is EP3. The W/W ratio for the fabrication of reinforced glass fiber cloth is 70% fiber cloth with 30% Epoxy Resin.

The method of manufacturing experimental glass fiber composite tubes can be described as follows.

A male mandrill is first layered with epoxy resin and then wrapped with a glass fiber cloth. The packing is tightened followed by layering with epoxy resin and then clamping with a female mandrill. The sequence is repeated to achieve the desired thickness. The assembled system then undergoes a heat-curing process [20]. The composite tube is further allowed to be hardened at room temperature.

The composite is cut into the required size by an electrical saw in a thin and polished section preparation unit for tensile testing as per ASTM D638 standard [21]. After that, a piece of composite is weighed and then heated in a muffle furnace to ensure the desired percentage of Epoxy resin and glass fiber following ASTM D2584 standard [22].

The dimensions of the GFRP composite tube manufactured are given in Table 5 T. 1

Table 5T.1 Dimension of the composite tube

Dimension	Values
Length(mm)	150
Thickness(mm)	1
Inner Diameter(mm)	48
Outer Diameter(mm)	50

5.2.4 Physical properties

Knowledge of physical properties for determining the structural morphology of the sample is a very useful guideline to know the distribution of fiber in the matrix [23] and hence Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) are performed on the sample tube at room temperature are completed to ascertain the fiber and resin distribution in the matrix of the materials to be used for subsequent tensile testing with or without cryogenic conditioning .

5.2.4.1 Scanning Electron Microscope (SEM)

Surface morphologies of glass fiber-impregnated resin composite films are studied by means of a scanning electron microscope (SEM: JEOL Model JSM-6490) with an accelerating voltage of 15 kV. Fibrous mesh of glass fiber is mounted on aluminum stubs and gold coated to avoid electrical charging during the examination. All the SEM images are taken at the magnification of 5 KX. Fig 5F. 2(a) shows the epoxy resin embedded in the fiber of the matrix and Fig5F.2(b) exhibits the cross-sectional view of the fractured fiber after the tensile test.

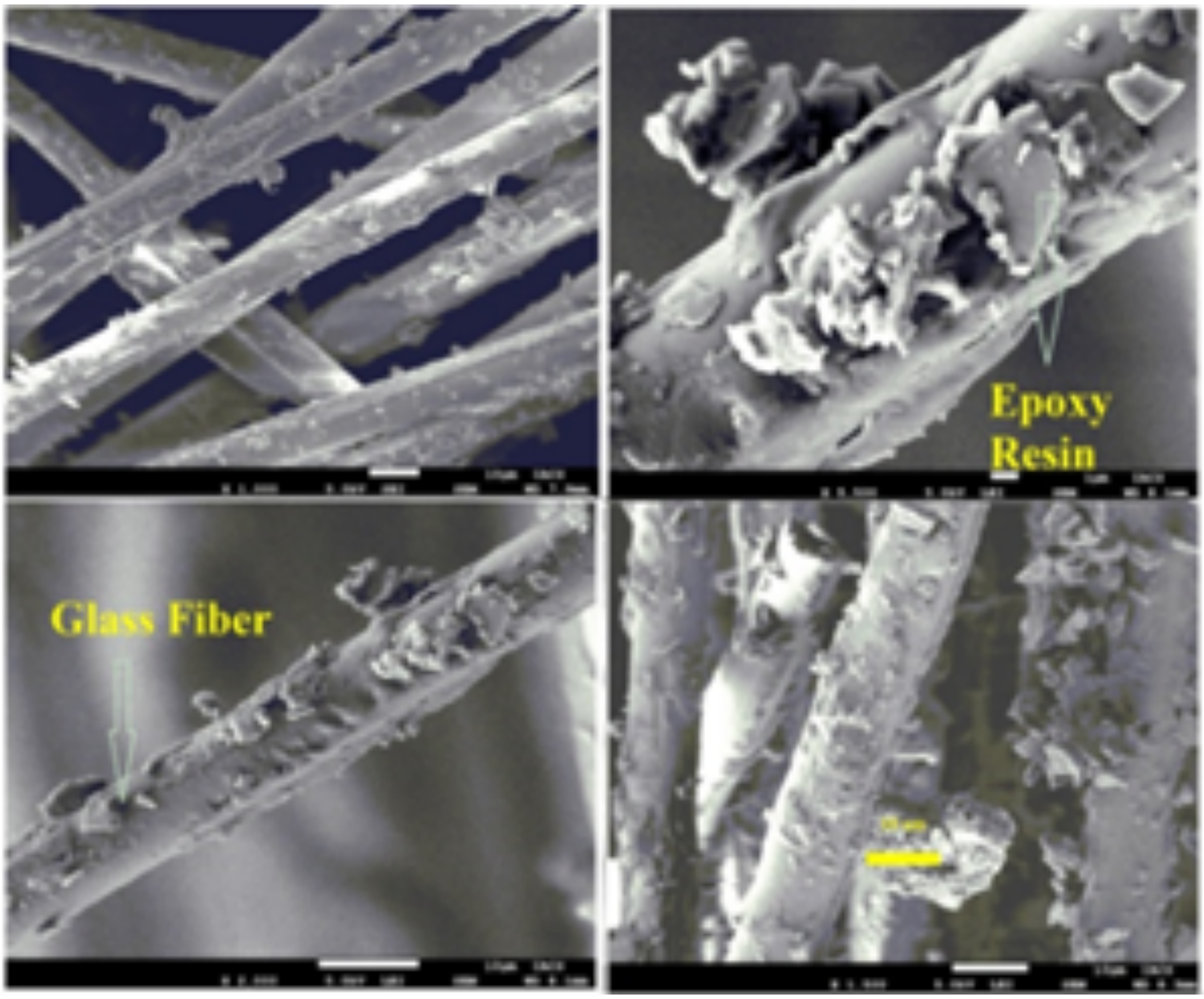

FIG-5F.2 (a) GFRP-EP3 composite, (b) SEM image on fibers orientation of the untreated samples(left one) and Cross-sectional view of fibers head of the untreated fiber composite after (right one) tensile test

5.2,4.2 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) study is carried out using PHILIPS SHIFFERT 3710 diffractometer supported by Lynx Eye super-speed detector and Ni-filtered Cu-Kα (λ=0.15406 nm) radiation is generated at 40 kV/ 40 mA. The diffractometer is operated with a scan speed of 0.5s for steps of 0.02 in 2θ (degree) at room temperature. Figure5F.3(a)&(b) show the GFRP with EP3 and normal GFRP.

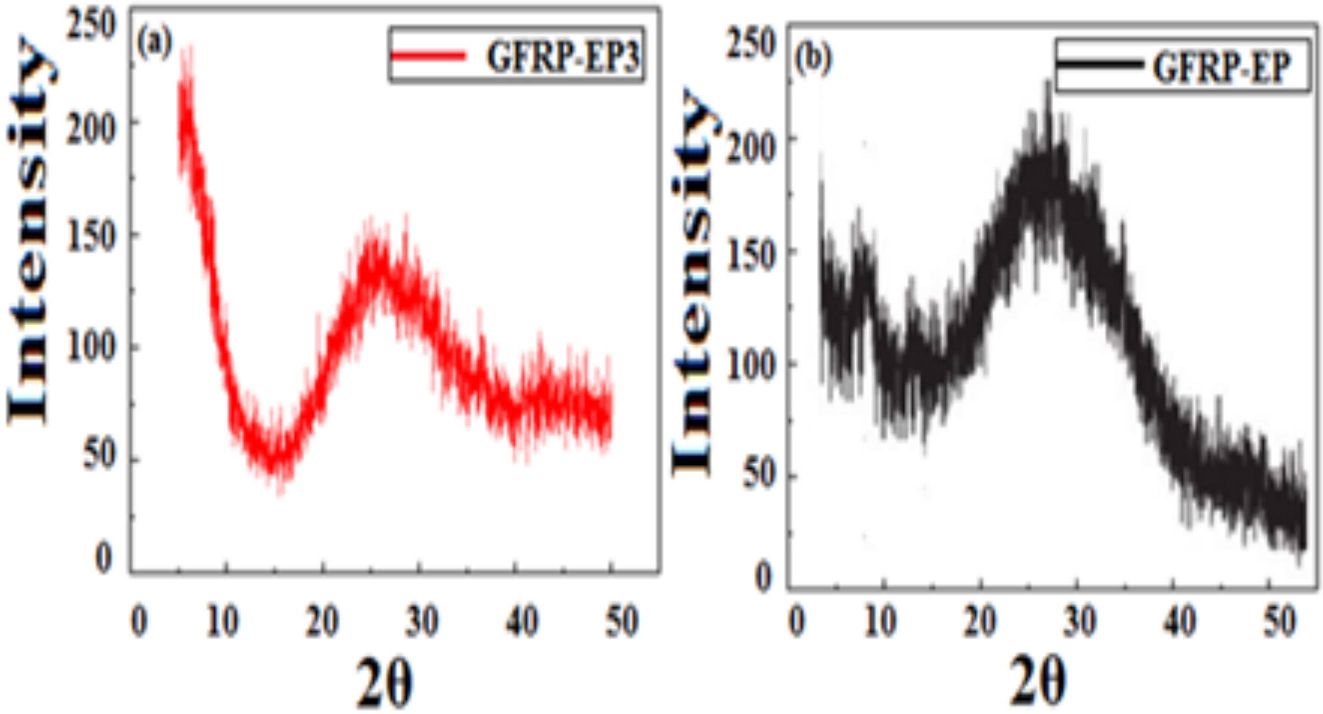

FIG-5F.3(a) GFRP with EP3 laminates (b) Normal GFRP laminates

5.3 Cryogenic conditioning

Five samples are prepared from one of the composite tubes for testing. The size of the specimen is 100mm x 20mm with a gauge length of 40mm. One sample is kept untreated at room temperature (RT)and other samples are immersed in liquid nitrogen in four different Dewar for cryogenic conditioning (CT) for 15, 30, 45, and 60 minutes to allow sufficient time for the change of properties [24]. Then the treated four samples are withdrawn from liquid nitrogen and kept in the desiccator so as to protect them from absorption of moisture. The conditioned samples are then promptly transferred to the testing system [25].

5.4 Tensile properties

The static tensile properties are obtained using a computer-controlled universal testing machine, INSTRON 5582 with a 100kN load cell as shown in Fig 4(a). ASTM D638 standard is followed for the testing. Room temperature (RT) is recorded as 25±3^{0}C and the specimens are loaded at a constant speed of 1mm/min until breaking.

To reduce the slippage problem, tabs from plane glass-fiber laminates are introduced on the GFRP-EP3 specimens. For data acquisition, Blue Hill 2 software is used. The tensile test is then performed to measure the characteristic curve, the modulus, and ultimate strength at yield and breakpoint [26, 27]. The average deformation energy for five samples is analysed with optical devices.

Fig5F.4(a) is the pictorial view of the Universal Tensile Machine

Fig 5F.4(b) shows the types of fracture developed in untreated composite specimens before (middle) and after tensile loading

FIG- 5F.4 (a) Universal Tensile Machine

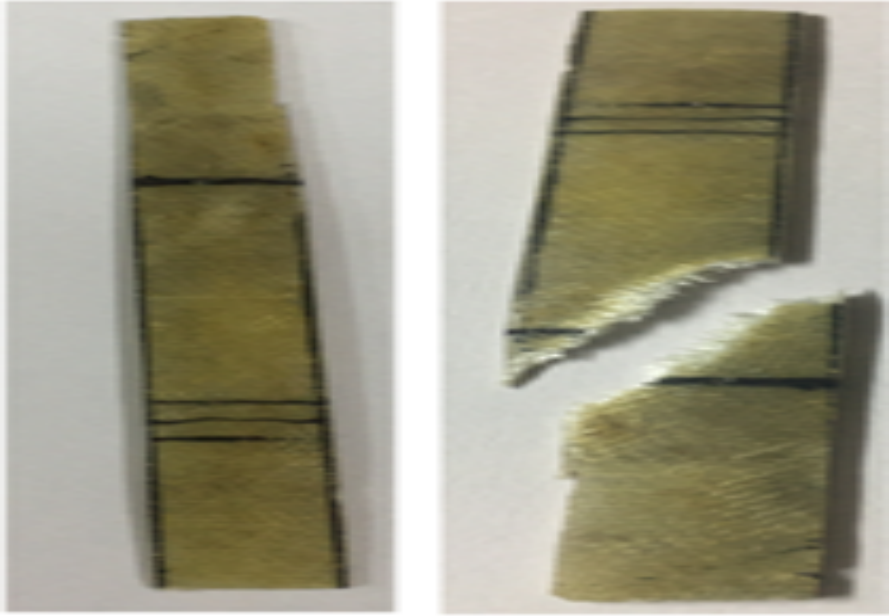

Fig 5F.4(b) Types of delamination and Fractured surface of the untreated composite before and after tensile loading of GFRP-EP3 composite.

Figure 5F.5 (b) represents Tensile stress vs Strain, and Figure 5F.5(a) represents Load vs. Deflection of the GFRP-EP3 composite without conditioning Figure5F. 6(b) to Figure -5F.9(b) represent Tensile stress vs Strain of GFRP-EP3 composite with conditioning for 15 minutes, 30 minutes, 45 minutes, and 60 minutes respectively. Figure 5F.6(a) to Figure -5F.9(a) represent the Load vs Deflection of GFRP-EP3 composite with conditioning for 15 minutes,30 minutes,45, minutes, and 60 minutes.

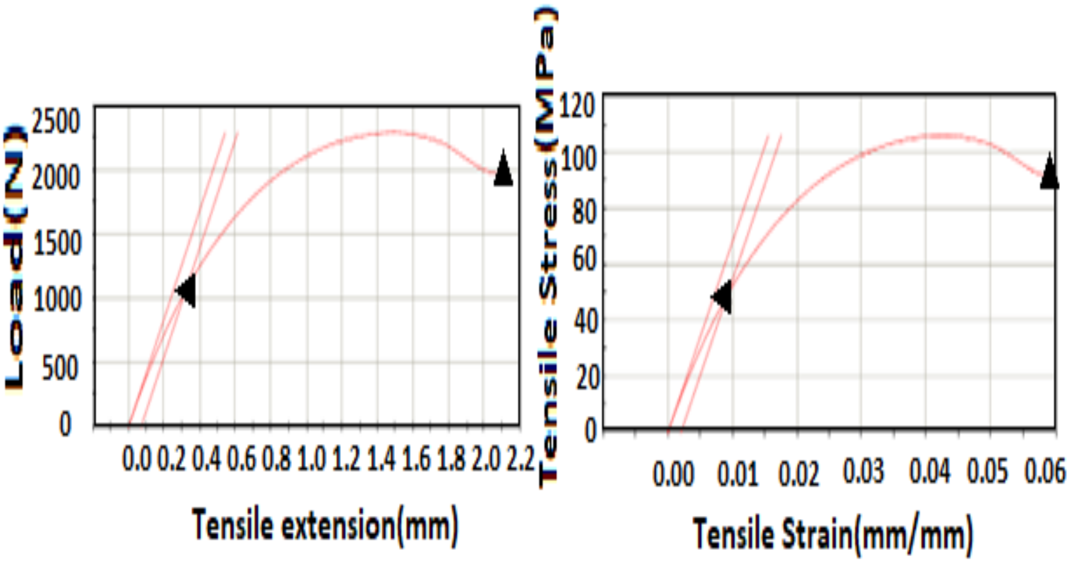

FIG-5F.5 (a) Load vs. Deflection of GFRP-EP3 composite without conditioning (b) Tensile stress vs Strain

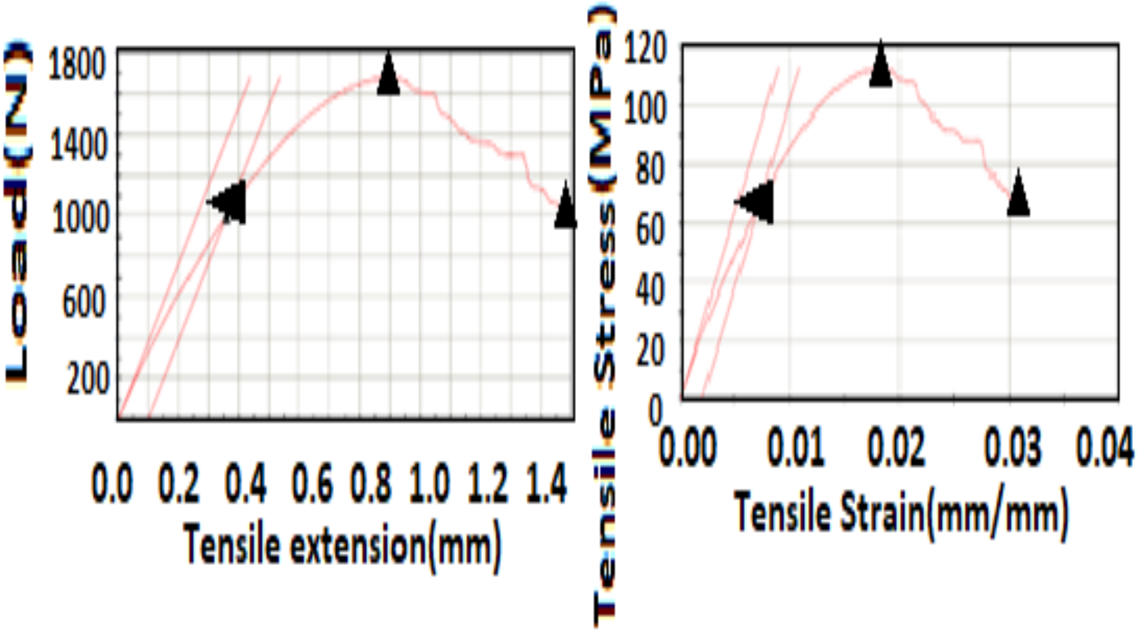

FIG-5F.6. (b) Tensile stress vs Strain, (a) Load vs. Deflection of GFRP-EP3 composite conditioned for 15 minutes

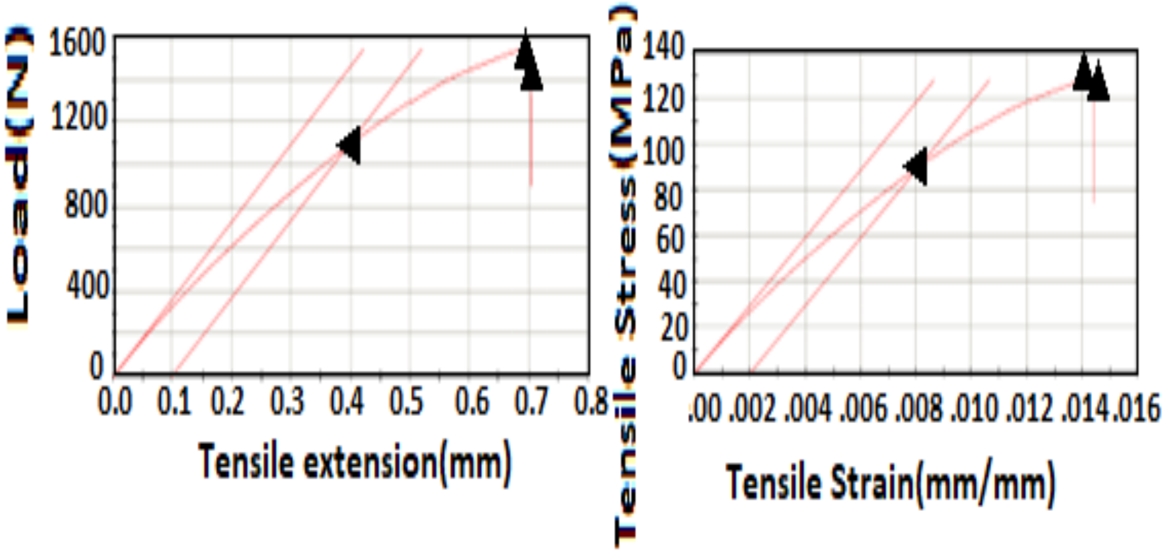

FIG-5F.7. (b) Tensile stress vs Strain, (a) Load vs. Deflection of GFRP-EP3 composite conditioned at 30 minutes

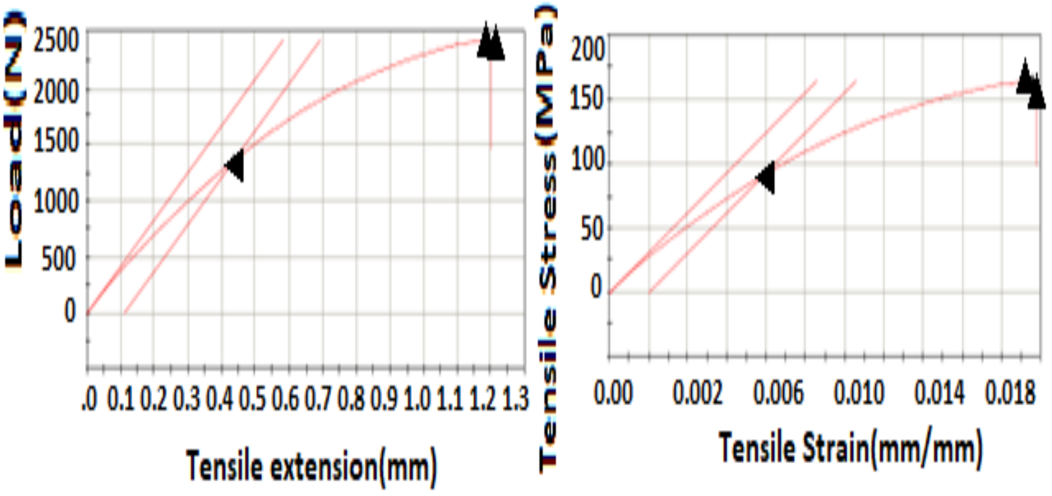

FIG-5F.8. (b) Tensile stress vs Strain, (a) Load vs. Deflection of GFRP-EP3 composite conditioned at 45 minutes

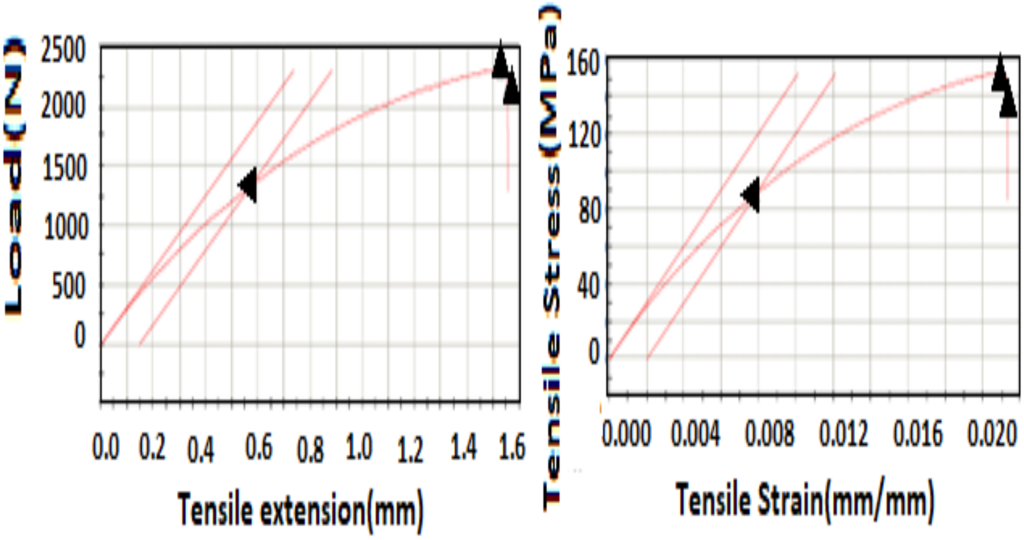

FIG-5F.9. (b) Tensile stress vs Strain, (a) Load vs. Deflection of GFRP-EP3 composite conditioned for 60 minutes

Tensile properties of the composite samples before and after cryogenic conditioning for 15, 30, 45, and 60 minutes are given in Table 5T. 2.

Table 5T.2 Tensile properties of the composite samples before and after cryogenic conditioning for 15, 30, 45, and 60 minutes

Composite sample (GFRP-EP3)	Young's Modulus (MPa)	Tensile Stress at Tensile Strength (MPa)	Tensile Extension at Break (mm)	Load at Break (kN)
Unconditioned	6835.82	90.85	2.08	1.97
Conditioned for 15 minutes	12699.14	113.65	1.48	1.00
Conditioned for 30 minutes	14885.56	128.39	0.70	1.49
Conditioned for 45 minutes	15532.91	164.15	1.20	2.35
Conditioned for 60 minutes	15112.47	152.21	1.55	2.13

5.5 Result and Discussion

SEM and XRD are carried out at room temperature for the composite material to ascertain its structural orientation with respect to resin and fiber before going for tensile properties determination.

Fig 5F.2(a) gives an SEM image where we clearly visualize glass fiber and the epoxy resin on it. The microscopy of the composites is performed using a scanning electron microscope and proper impregnation of glass fiber with epoxy resin. The retention of epoxy on glass fiber is observed on the bamboo shoots like fiber [28]. For characterization, fibers of the composite are dismantled from composite laminates. The traces of epoxy over glass fiber indicate the improved thermal stability of composites. This finding can also be confirmed by other thermal analyses like TGA, low-temperature thermal conductivity, etc. Generally, the thermal stability is improved due to the strong interface of epoxy resin with glass fiber. Even the resin reduces the void content from the reinforced matrix in the heat cure process. The matrix interface improves the mechanical properties of the composites. The developed composites (fiberglass-reinforced polymer) are ideal materials for applications in cryogenic temperatures. Fig 5F.2(b) shows the fracture type of the untreated composite (right one) before and after continuous tensile loading, and the nature of delamination of the fiber composite(right one).

The orientation and loading of glass fibers in the epoxy resin and the identification of peaks of reinforced glass fiber and its characteristics in the matrix are further studied using x-ray diffraction analysis, as shown in Figure 5F.3. Fig 5F.3(a) shows the glass fiber-impregnated resin and Fig 5F.3(b) shows plane glass fiber for comparison with examined reinforced polymer. X-ray diffractograms of oriented glass fiber Fig5F.3(a) are represented by the majority of elements. Fig 5F.3(a) also shows a peak at Bragg's s angle $2\theta=26^0$, affirming the crystalline silica in the composite. It can be seen that the glass fiber and epoxy resin do not have any other identifiable XRD materials that are amorphous in nature [29, 30]. This unidentifiable peak appears for composites' development of fiber loading and orientation with resin. Though Fig5F. 3(b) shows the sharp peak at $2\theta=27^0$ of silica it has a similarity with the examined reinforced polymer. Therefore, it is established that the dispersion of glass fiber is uniformly distributed in the matrix and hence no specific peak in Fig5F.3(a).

Tensile properties are investigated with cryogenic conditioning for different durations of time as well as for a sample without cryogenic treatment The results are discussed below.

After tensile loading, types of fractures to failures, and delamination of fibers are also studied. The influence of liquid nitrogen treatment on the strength of composites is studied. Table 5T. 2 shows the result of Young's modulus from the stress-strain curve of epoxy-based glass fiber-reinforced polymer before and after cryogenic conditioning for 15, 30, 45, and 60 minutes. The stress-strain curve and load-deflection curve of different temperatures are plotted which clearly indicate the enhancement of strength of the composite after cryogenic temperature conditioning (CT-C) for up to 45 minutes but beyond that duration, the modulus is slightly decreased for 60 minutes of conditioning and hence 45 minutes duration is considered as the optimum duration of treatment. It can be seen from Table-5T.2 that Young's modulus of GFRP/epoxy composites after CT-C is increased up to 45 minutes conditioned to a great extent from its strength at room temperature (RT). The possible mechanism may be due to the mobility of the molecules of the polymer chain when the temperature is decreased and the binding forces between the molecules increase at low temperatures, this happened when the samples are conditioned for 45 minutes. After CT-C, the relaxation polymeric chain of the composite seems to be completely arrested resulting in increased tensile properties, like modulus, stiffness, and strength. So, it is revealed that Young's modulus of GFRP-EP will be higher after CT-C at 45 minutes [31- 36].

Table- 5T.2 also exhibits the tensile strength and load at break from the load-tensile extension curve of epoxy-based glass fiber reinforced composite polymer tube, before and after CT-C at different times. Modulus, tensile strength, and load after CT-C at 77k are higher than at RT. The reason behind the increase in strength and load is the binding forces between the molecules of the epoxies which becomes stronger at 77k conditioning. So, compared to Epoxy Resin, GFRP, GFRP-EP and CFRP, the modulus and strength of the GFRP-EP3 composite after CT-C is higher [37-39].

5.6. Conclusion

The tensile properties of GFRP-EP3 laminates before and after CT –C at different durations have been evaluated in this article. The tensile-related mechanical properties are increased after cryogenic conditioning. At room temperature, the loss in tensile strength is mainly due to the epoxy resin softening of the composites, and the stiffness loss is attributed to the straightening of glass fibers as the epoxy resin softens. Results of low-temperature conditioning indicate that there is a considerable effect on the tensile strength between conditioned and unconditioned composites but there is a significant reason behind the duration of conditioning. The higher duration of the condition results in a higher modulus. It is clear that the increase of tensile modulus in the specimen with prior treatment with liquid nitrogen is two times higher than the unconditioned one and 45 minutes duration is considered as the optimum duration. The load at break is higher in case of 45 minutes of conditioning than 60 minutes of cryogenic conditioning. (table 2). In addition, treated laminates show brittle behavior. The stress-strain curve demonstrates that the area of the plastic region of the conditioned composite is larger than the unconditioned one, but its deformation is very abrupt due to increased brittleness in the treated specimen. The stress-strain, load vs. temperature, and load vs. deflection graphs reveal that for composites, after 45 minutes of cryogenic conditioning at 77K in a liquid nitrogen bath, the strength and modulus increase significantly with the increase of strain rate. Therefore, the present findings highlight the structural survivability of GFRP-EP3 at extremely low temperatures in the cryogenic range as well as at room temperature as results will be helpful in assessing the suitability of GFRP in the structural design of epoxy-based components for extremely low-temperature environments. Hence, GFRP-EP3 can safely be used for many industrial applications both at room temperature and cryogenic temperature including its use as a neck of cryogenic vessel.

CHAPTER-6

Study
Of
Aluminized Mylar
as
Radiation Shield in the Quest
of
an Effective Multi-Layer Insulation Development
for
a Laboratory Scale Cryogenic Dewar Vessel

CHAPTER -6

STUDY OF ALUMINIZED MYLAR AS RADIATION SHIELD IN THE QUEST OF AN EFFECTIVE MULTI-LAYER INSULATION DEVELOPMENT FOR A LABORATORY SCALE CRYOGENIC DEWAR VESSEL

6.1 Introduction

Cryogenic liquid can only be stored in a thermally insulated container and it has to be ensured that practically all modes of heat transfer such as conduction, convection, and radiation are eliminated. Ease of application and effectiveness of insulation is always taken into due consideration while selecting a particular cryogenic insulation. Vacuum insulation in cryogenic Dewar vessels essentially eliminates two components of heat transfer such as solid conduction and gaseous convection. Heat is transferred across the annular space of a vacuum-insulated vessel by radiation from the hot outer jacket to the cold inner vessel and by gaseous conduction through the residual gas within the annular space. Hence to minimize gaseous conduction, the annular space is degassed at an elevated temperature during the evacuation, and a very high vacuum (10^{-6} Torr)is maintained. In addition to the vacuum, the inner cold vessel is wrapped with several layers of aluminized mylar sheets as a radiation shield.

Multilayer insulation provides the most effective thermal protection available for cryogenic storage and transfer systems. It consists of alternating layers of highly reflecting material, such as aluminum foil or aluminized Mylar and a low-conductivity spacer material or insulator such as fiberglass mat or paper, glass fabric, or nylon net, all under high vacuum. When properly applied at the optimum density, this type of insulation can have an apparent thermal conductivity as low as 10 to 50 μW/m · K between 20k and 300 K. The prediction of heat transfer in MLI is very complex due to the anisotropic conductivity and combination of radiation and conduction modes of heat transfer. Radiation and conduction are the significant modes of heat transfer in MLI. Multilayer insulations are capable of maintaining hundreds of temperature gradients. The effective thickness of a typical MLI is within a few micrometers. The radiation energy from the inner vessel strikes the first reflective layer where a part is reflected back to the environment, and the remaining radiation energy heats up the first layer of MLI. As the temperature of the layer increases conduction and radiation take place to the next foil. Thus the second foil temperature will increase. The second foil reflects some radiation back to the first foil and the remaining energy is transferred to the third foil. This process continues up to the bottom layer. The performance of MLI depends on the number of layers. [1, 2]. Aluminized mylar of 12 microns is considered the optimum thickness of a single sheet The shape and structure affect the performance of MLI [3,4,5] .

6.2 Essential heat transfer equations for computation of MLI effectiveness in a cryogenic vessel

Several research works are reported in the literature using multilayer insulation for cryogenic systems both from theoretical and experimental situations[6- 22] but double-walled cryogenic storage vessel design using MLI needs special attention.

The outer side the of inner vessel, which is in contact with liquid nitrogen, is wrapped with several layers of Aluminised mylar as a radiation shield.

Heat transfer from the outer vessel to the shield = heat transfer from the shield to the inner vessel

$$Q_{2\text{-}S} = Q_{S\text{-}1} = \frac{\sigma(T_2^4 - T_S^4)}{\frac{1}{e_2}+\frac{1}{e_S}-1} = \frac{\sigma(T_S^4 - T_1^4)}{\frac{1}{e_2}+\frac{1}{e_S}-1} \text{-----------------(1)}$$

T_2=Temperature of the inner side of outer vesselT_2= Temperature of the inner side of the outer vessel

T_s= Temperature of the outer side of the shields

T_1=Temperature of the outer side of inner vessel = Temperature of liquid nitrogen = 77K (in the present case)

e_2=Emissivity of outer vessel

e_s= Emissivity of aluminized mylar shields

Heat is transferred across the annular space of a vacuum-insulated vessel practically by radiation only from the outer vessel at room temperature to the cold inner vessel as an annular space vacuum prevents heat transfer by solid conduction and gaseous convection. Sometime gaseous conduction to the residual gas within the annular space takes place in the event of degassing from the metallic surface under high vacuum.

The radiant heat transfer rate between two surfaces is given by the modified Stefan-Boltzman equation[22]

$Q_r / A_1 = F_e \; F_{1\text{-}2} \, \sigma \; (T_S^4 \; \text{-} T_1^4 \;)$ --------------------- (2)

Q_r=heat transfer by radiation F_e = Emissivity factor

$F_{1\text{-}2}$ = Configuration factor/view factor = 1 (for cylindrical outer and inner vessels)

σ = Stefan-Boltzman Constant = $5.669\text{x}10^{-9}$ W/ m^2- k^4

A_1 = surface area of the inner vessel

T_S=temperature of the radiation shield

T_1=temperature of the inner vessel

Subscript 1 refers to the inner vessel (enclosed surface) and 2 refers to the outer vessel (enclosure). In addition, the emissivity factor for diffuse radiation for concentric spheres or cylinders is given by

$$\frac{\mathbf{1}}{\boldsymbol{F_e}} = \frac{\mathbf{1}}{\boldsymbol{e_1}} + \frac{\boldsymbol{A_1}}{\boldsymbol{A_2}}\left(\frac{\mathbf{1}}{\boldsymbol{e_2}} - 1\right) \text{ ---------(-3)}$$

Radiant heat transfer can be reduced by interposing a thermally isolated radiation shield between the hot and cold surfaces.

The emissivity factor with shield emissivity e_s is given by,

$$\frac{1}{F_e} = \frac{1}{e_1} + 2\frac{A_1}{A_S}\left(\frac{1}{e_s} - 1\right) + \frac{A_1}{A_S} + \frac{A_S}{A_2}\left(\frac{1}{e_2} - 1\right) \text{ ----------(4)}$$

Radiation through cylindrical portion:

$Q_{r1}=F_e\, F_{1\text{-}2}\sigma\, A_1\,(T_S^4 - T_1^4)$ -- --------------------(5)

Radiation through head portion:

$Q_{r2}=F_e\, F_{1\text{-}2}\,\sigma\, A_1\,(T_S^4 - T_1^4)$-----------------------------(6)

Total heat transfer by radiation $=Q_{tr.}= Q_{r1} + Qr2$ -------(7)

There is no heat transfer through support rods by conduction as no support rods are used and the inner vessel is suspended from the neck Gaseous conduction through residual gases is ignored.

The apparent thermal conductivity of a highly evacuated multilayer insulation can be determined from[22],

$K_a = (\frac{1}{N/_{\Delta X}})\ [h_s + \frac{\sigma\ e\ sT_2^3}{2-e\ s}\,(1+\frac{T_1}{T_2})^2\,(1+\frac{T_1}{T_2})\ ]$-------(8)

where N/Δx is the number of reflecting shields of per unit thickness, h_s is the solid conductance for the spacer material. It is evident that the apparent thermal conductivity can be reduced by increasing the layer density up to a certain point.

The effective thermal conductivity values generally obtained with actual cryogenic storage and transfer systems are greater than at least a factor of 2 with respect to the thermal conductivity values measured in the laboratory. This degradation in insulation thermal performance is caused by the presence of edge exposure to isothermal boundaries, gaps, joints, or penetrations in the insulation blanket required for structural supports, fill and vent lines, and the high lateral thermal conductivity of these insulation systems. The vacuum-deposited aluminum has an average emissivity of 0.030. The performance of multilayer insulation depends on the number of alternating layers of shields in the annular space. With more layers, radiant heat is reflected, and the insulating performance is higher but we must arrive at an optimum layers of shields.

The objective of the present study is to find the effectiveness of aluminized mylar sheets as multilayer insulation along with vacuum for an indigenously developed liquid nitrogen container of 3-litre capacity.

6.3 Materials and methods

Mylar is a Polyester film made from polyethylene terephthalate (PET) It has got high tensile strength, reflectivity, transparency, and electrical and thermal insulation properties which makes it a versatile reflecting material to be used as a radiation shield. Mylars are manufactured by using Thin Film Technology and aluminized mylar can be made by vapor deposition of a thin film of evaporated aluminum. This type of metal can reflect 99% of radiation heat transfer. The deposited side of the laminates appears shiny and the polyethylene side of such laminate appears dull.

Aluminized mylars in conjunction with high vacuum are used to make Multi-Layer Insulation(MLI) systems and are applied in developing cryogenic containers. The various dimensions of the indigenously designed cryogenic dewar of 3-liter capacity are given in Figure-6F.1. The inner vessel is wrapped with 10,20 32 and 42 layers of aluminized mylar (12 microns)with an interlayer of conductive spacer material. The performance study is conducted by pouring liquid nitrogen into the inner vessel and measuring the evaporation loss.

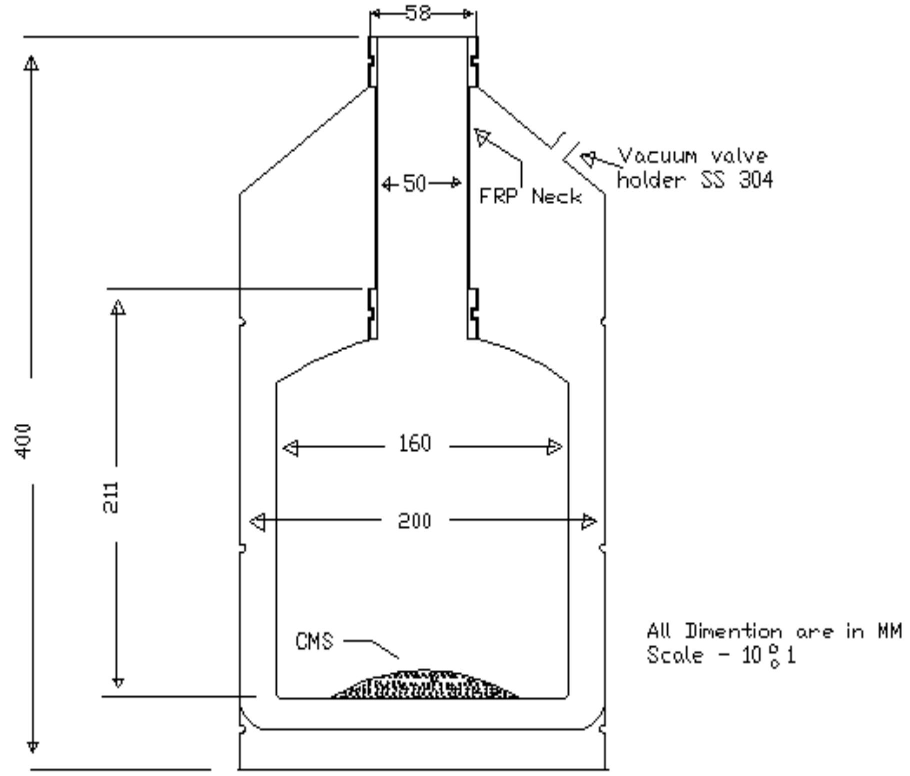

Figure 6F.1: Schematic diagram of the indigenous cryogen container of 3 liter capacity

Figure 6F.2 clearly shows the pictorial view of the experimental stage of wrapping the inner cylindrical vessel with several layers of aluminized mylar with non-conducting spacers in between two mylar sheets.

Figure 6F.2: Pictorial view of the inner stainless steel vessel after shielding with several layers of reflecting shields of aluminized mylar

Figure 6F.3 : Pictorial view of the inner stainless steel vessel and outer vessel before assembling

Figure 6F. 4 : Fabrication of FRP Neck with inner vessel with Eco-bond (Epoxy Resin)

Figure 6F. 5: Vacuum pump on-going

The inner vessel is then put into the outer jacket of stainless steel and suspended from the neck. an annular space is evacuated with the help of a mechanical pump and diffusion pump. Once the high vacuum is created, the dewar vessel is sealed through its vacuum port and is ready for testing with liquid nitrogen at 77K. The evaporation losses are tested for a varying number of shields of 12-micron aluminized mylar such as 10, 20, 32 and 42 layers.

6.6 Results and Discussion

3 liters of liquid nitrogen are poured into a cryo container under stable conditions for each case and holding times are noted.

The results of the performance of indigenous cryogen containers with varying numbers of reflecting shields are tabulated in Table 1

Table 6T.1: Performance of indigenous liquid nitrogen dewar with varying numbers of radiation shields

Number of reflecting shields	**Holding time of liquid nitrogen**
10	2 days
20	3 days
32	4 days
42	1.5 days

The graphical representation of the tabular results can be depicted as shown in Figure 6

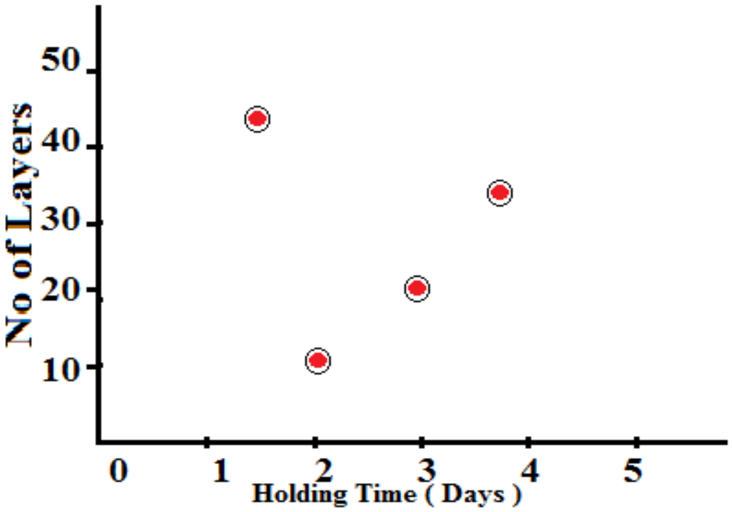

Figure 6F. 6: Graphical representation of the performance of the dewar with varying numbers of reflecting shields

The present case of investigation reveals that the holding time of liquid nitrogen increases with increasing the number of shields up to 32 layers and then abruptly falls to a low value may be due to an increase of contact points with an outer jacket as the annular space cannot accommodate a very large number of layers without touching the outer vessel. In this experiment, other causes of heat transfer are considered negligible and constant. Therefore, 32 layers of shields are taken as the optimum number of shields in our study.

Based on the number of layers, the conductivity of mylar shield can also be computed by equation (8)

The annular space gap is 20 mm as shown in figure-1. A gap of 4 mm between the last layer and the outer vessel is left blank so as to avoid direct contact with the outer jacket. Therefore, the total thickness of the shield becomes 16 mm.

T_2 – Ambient temperature (hot surface 300k)

T_1 - -196.6^{0}c (cold surface 77k)

$\sigma = 5.675 \times 10^{-8} w/m^2k^4$

The thickness of 32 layers = 16mm and

Number of shields with spacers per unit thickness = 32/16 = 2/mm

Average emissivity Mylar = 0.03

Thermal conductivity of fiberglass paper h_s = 0.03 W.m^{-1}/K

Thermal conductivity of shield assembly

$$K_a = \left(\frac{1}{N/_{\Delta X}}\right) \left[h_s + \frac{\sigma e T_2^3}{2-e} \left(1+ \frac{T_1}{T_2}\right)^2 \left(1+\frac{T_1}{T_2}\right) \right]$$

$$= \frac{1}{2} \left[0.03 + \frac{5.675\ X\ 10^{-8} \quad X 0.03\ X\ 300^2}{1.97} \left(1+ \frac{77}{300}\right)^2 \left(1 +\frac{77}{300}\right)\right.$$

$$= \frac{1}{2} \left[0.03 + \frac{15322.5\ X\ 10^{-8}}{1.97} (1.25)^2 (1.25)\right]$$

$= 0.5[0.03+7777.91 \times 1.95 \times 10^{-8}]$

$= 0.5[0.03+0.0001\ ] = 0.01\ w.m^{-1}/K$

6.4Conclusion

The results show that small cryogenic vessels can be super-insulated using multilayer insulation of aluminized mylar along with high vacuum. Aluminized mylar of 12-micron thickness with non-conducting spacers combination of 32 layers as optimum numbers of layers have successfully been used in the indigenously developed cryocan. The liquid nitrogen holding time is recorded as 4 days which indicates that small dewar can be used for laboratories. Further improvement of the cryo container is undertaken towards retentivity of high vacuum in the annular space for a longer period which will definitely increase the holding time with the same amount of radiation shields. The thermal conductivity of radiation shields as calculated is very low of the order of 0.01 $w.m^{-1}/k$ which is also desirable.

CHAPTER-7

Design
and
Prototype Development
of
3 Liter Cryogenic Containers followed
By
its Performance Study
in
Storing Liquid Nitrogen

CHAPTER -7

DESIGN AND PROTOTYPE DEVELOPMENT OF 3 LITER CRYOGENIC CONTAINER FOLLOWED BY ITS PERFORMANCE STUDY IN STORING LIQUID NITROGEN

7.1 Introduction

Since James Dewar invented double-walled silvered evacuated glass containers called after him “Dewar Vessels” in 1892, it became possible to use LN_2 for various low-temperature experimentation. However, such glass vessels are brittle, limited in size and can store cryogenic liquid for a few hours. They were gradually replaced by all metal double-walled vessels ranging from a small capacity of 1 litre for storing liquid nitrogen to very big sizes of capacity of 160000m^3[1-3] for temporarily storing liquid natural gas

Types of Cryogenic storage vessels may vary from low-performance containers, insulated with rigid foam or fibrous insulation to high-performance containers having multilayer insulation along with high vacuum in the annular space of the double-walled vessel. [1-2]

Thermal insulation is the most vital factor in the design of any cryogenic system to prevent all possible modes of heat leak. [1-4]

Sources of heat leakage into inner vessels are due to

a) Conduction through neck and inner vessel supports

b) Convection and conduction from annular residual gas in the vacuum interspace.

c) Radiation through walls.

d) Direct gas convection, and radiation through the mouth opening

Minimization of these sources of heat in leak into the systems gives minimum evaporation loss of cryogen during storage.

Provision should also be made for easy repeated evacuation service for removing slow evolution of gas from inner metal surfaces and/or repairs as and when needed. Minimum weight and maximum strength of the structure, ease of assembling, handling and transport, noncorrosive, indigenous availability, reasonable cost of materials for fabrication etc. are the other design considerations.

In general, cryogenic vessels are designed in accordance with ASME Section-VIII of the pressure vessel code [2].

The best design for fabricating a cryo-container is two concentric spherical vessels connected by a non-conducting neck. The entire load of the inner container is hung at the top of the outer vessel [3-4]. Considering the ease of fabrication and for small-size vessels, a cylindrical shape is the best choice and is adopted in the present case.

Aluminum cryogen containers are mostly available for storage and transport purposes but suffer from the following disadvantages compared to stainless steel construction:

1. Aluminium body is easily corroded but Stainless steel is not quite corrodible

2. Sufficient thickness of the sheet is necessary to offset the low structural strength making the weight as well as cost more comparable to stainless steel

3. Thin sheets of stainless steel used are comparable in strength and cost to aluminium shells and may be lighter than aluminium shells.

Considering the above and several other advantages we have designed and fabricated a prototype of LN_2 containers of capacities 3 litres from locally available 304 austenitic stainless steel sheets for making both the inner and outer shell of the container and glass fibre reinforced plastics tube for the neck of the inner container.

7.2 Design of Cryogenic Dewar Vessel

Various works on the design and development of cryogenic dewar are reported in the literature (5-21)

In designing a storage vessel for a cryogenic liquid, the important factors to be considered are a)duration of storage i.e., long duration -or short duration storage b)type of cryogenic liquid to be stored, c) permissible rate of cryogen loss d) mobile or stationary storage e) allowable cooldown time and cost f) the stratification in case liquid methane storage and pressure effects on the system g) type and thickness of the material required for the inner and outer vessels h)thermal conductivity of the material etc. Other important aspects include the optimum type of insulation and the design of inner vessel supports, fill and drain lines, vapor vents, vapour diffusers and safety devices. The performance of cryogen vessels may range from low-performance containers designed for short-term storage of a few hours to high-performance tanks, which allow less than 0.1% of the contents to evaporate per day.

The effectiveness of any cryogenic storage vessel depends upon how well it reduces the loss of the cryogen due to unavoidable heat in the leak and how well it maintains the purity of the stored liquid.

The basic design approach is to develop a vacuum-insulated doubled-walled container similar to that invented by James Dewar which has an inner vessel for storing the cryogenic liquid, and an outer vessel for serving as a vacuum jacket. To reduce the overall vessel weight and minimize the cool-down time, the wall thickness of both the inner and outer vessels should be made as thin as possible. It is desirable that the shape of a cryogenic container is selected in such a way so as to minimize the surface area to volume ratio and which will effectively reduce the heat in leak to the stored cryogen. A spherical vessel has the smallest surface area to volume ratio and hence is preferred for use in a fixed storage system as well as in mobile tanker ships. The surface area to volume ratio for cylindrical vessels is only slightly larger than that of the sphere but easier to fabricate and transport hence is widely used.

All sorts of cryogenic storage vessels both transportable and stationary, are normally designed for a liquid volume of 90% and a vapor volume or ullage space of 10%. The ullage volume is designed to take care of the pressure built up in the inner vessel due to heat inleak and may require later venting of some of the vapour formed above the liquid. In the laboratory, 1-5 litres of double-walled containers are used for the temporary storage of cryogenic liquid for a few hours to a few days.

7.2.1 Inner vessel Design

7.2.1.1 Material of Construction

The selection of suitable material for construction is the first factor to be considered while designing the inner vessel of a cryogen container. The material should conform to important criteria such as i)unreactive to the cryogen to be stored ii) ease of fabrication into the desired shape iii) low emissivity iv) resistance to cryogenic temperatures etc. Glass which is extensively used for laboratory Dewars, can meet most of these constraints, yet it has very low tensile strength and unsuitable for long term storage and for large vessels and hence it is gradually replaced by the metallic container.

For large vessels, 9% nickel steels are commonly used with higher boiling cryogens ($T_b > 75K$), whereas aluminum and austenitic steels can safely be used over the entire range of liquid temperatures. The thickness of the inner shell should be made as thin as practically possible and is only designed to withstand the maximum internal pressure which reduces cool-down time and lower the cost of cooling down of the container. Stiffening rings attached to the inner vessels are designed to support the fluid’s weight.

7.2.1.2 Computation of Volume of the Inner Vessel and its Dimension

The calculation of the volume of the inner vessel of 3 litres capacity cryogenic vessel and the corresponding dimensions such as diameter and height are presented below.

Cryogen storage capacity is considered to be 3 litres for our present design.

It is further assumed that the cylindrical portion of the inner vessel will take care of storing 3-litre cryogen and its cap /dome will take care of the ullage volume.

$$V = \frac{\Pi D^2}{4} \text{ x } h \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where,

V=Volume

D=Diameter of the inner cylinder

h= height of the cylinder

If h=D then this is the best design

h/D = 1 (h=D supposed)

From equation (1) putting h=D

$$V = \frac{\pi D^3}{4}$$

$\frac{\pi D^3}{4} = 3000$ [V= 3000 cm^3 for 3 litre container]

$D^3 = 3000 \text{ x } 4/\pi = 12000/\pi = 3821.6$

Therefore,

$D = \sqrt[3]{3821.6} = 15.63$ cm

If we consider h=D then

h = 15.63cm = 156.3mm

D = 15.63cm=156.3mm

For ease of fabrication and ease of design, we consider the cylindrical inner shel

Length (h) = 152mm

Diameter(D) = 160mm

7.2.1.3 Thickness of the Inner Vessel Shell

Section VIII of the ASME Boiler and Pressure Vessel Code should be followed for safety reasons when designing vessels larger than $0.2m^3$ [1, 2]. The code can be utilized for computing the thickness of the inner vessel.

Table 7T.1 represents the maximum allowable stresses and minimum tensile stresses for various metals at room temperatures [2] Weld efficiencies for Arc-Welded and Gas-Welded joints are given in Table 7T.2 [2]. Data available in these tables are very useful for the necessary design calculations.

Table 7T.1 Maximum allowable stresses and minimum tensile stresses for various metals at room temperatures

Material	Material Specification	Maximum tensile stress (MPa)	Minimum allowable stress(MPa)
Low alloy steel	SA 202 grade B	586	146.5
	SA 353 grade B(9%Ni)	655	163.7
	SA 410	414	103.4
Aluminum	SA-209(1100-0)	76	16.2
	SA-209(5083-0)	276	68.9
	SA-209 (6061-T4)	207	41.4
Copper	SB-11	207	46.2
Stainless steel	SA-240(304)	517	129.2
	SA-240(304L)	822	120.6
	SA-240(316)	517	129.2
	SA-240(410)	448	112.2
Monel	SB-12(ANNEALED)	482	128.2

Table 7T.2 Weld efficiencies for Arc-Welded and Gas-Welded joints

Type of joint	**Fully radiographed**	**Spot examined**	**Not Spot examined**
Butt joints with complete penetration	1.00	0.85	0.70
Single welded butt joint with backing strip	0.90	0.80	0.65
Single welded butt joint with no backing strip			0.60
Double full fillet lap joint			0.55

Though in the present case, we design a small vessel, we follow the code for over-safety and then make slight modifications from practical aspects. As per the ASME code, the minimum inner vessel shell thickness, t_{iw}, for a cylindrical vessel can be determined from

$$\mathbf{t_{iw.} = pD/\ 2(S_a\ \varepsilon_w - 0.6p) = pD_0\ /\ 2(S_a\ \varepsilon_w + 0.4p)}\ \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

D=160mm=0.16m

S_a=Maximum allowable stress for SS-304 grade = 129.2MPa from table-1

$=129.2\ \mathrm{x}10^3$ kPa

p= Internal design pressure=6 atm = 6 x 101.3 kPa =607.8 kPa

ε_w = Weld efficiency

For butt joint $\varepsilon_w = 0.60$ from table-2

D_0= Outside Diameter

$t_{iw} = (607 \text{x} 0.16) \ / \ 2(129.2 \text{ x } 10^3 \text{ x } 0.6 - 0.6 \text{ x } 607.8) = 48.56/(77520-364.68)$

$= 48.56/ 77155.32 = .0006 \text{ m} = 0.62\text{mm}$ (~24 SWG)

Actually, we have taken 0.6 mm (24SWG) as the thickness of the inner shell even for such a small vessel which will provide additional design safety.

7.2.2 Outer Vessel Design

An outer vessel is required to act as a jacket to the inner vessel.

7.2.2.1 Material of construction

The outer vessel is not in contact with cryogenic liquid and hence carbon steel can safely be used as the material of construction. In the present case, as the container is small, the same stainless steel 304 grade has been used for the outer shell also.

7.2.2.2 Dimension of the outer vessel

The diameter of the outer vessel is taken as 200mm and the total height is comfortably fixed as 400mm including the cylindrical portion, dome and conical portion so as to encapsulate the inner vessel. This will provide an annular space of 20 mm between the outside of the inner vessel and the inside of the outer vessel. This will facilitate wrapping the inner vessel with the required number of radiation shields before jacketing it with the outer vessel.

7.2.2.3 Thickness of outer vessel shell

The thickness of the outer shell of a storage vessel has to be designed to take care of the collapsing of the outer vessel shell due to the existing atmospheric pressure exerted on the outside of the outer shell and the vacuum provided on the annular space between the outer shell and inner shell. The failure mechanism has been incorporated also in the ASME Codes section-VIII based on the necessary calculation of a collapsing or critical pressure for various outer vessel designs. The ASME Code specifies that the critical pressure p_c is four times the allowable external pressure p_a on the vessel shell and atmospheric pressure is used as the external pressure for the computation of the thickness of the outer vessel.

The minimum shell thickness, t_{ow}, for a short cylindrical outer vessel is given by

$$\mathbf{t_{ow} = [p_c(1-\gamma^2)^{3/4}[(L/D_0)-0.45(t_{ow}/D_o)^{1/2}]/(2.42E)]^{2/5}D_0} \ldots\ldots\ldots\ldots\ldots \ \ldots\ldots \quad (3)$$

L is the distance between the two stiffening rings for the outer cylinder shell. The outer shell stiffening rings are used to support the weight of the inner vessel and its contents while maintaining the circular shape of the outer shell. For short vessels only two rings serve as the major support members and for very short vessels, stiffening can be totally eliminated. As in our design, no stiffening rings are used and the cylindrical vessel is very short hence L, is taken to be the length of the cylinder including the head.

Typical values of Young’s modulus and Poisson’s ratio for a few selected metals are given in Table 7T.3.

Table-7T.3 Typical Young’s modulus and poisons ratio for metals used in cryogenic vessel construction [2]

Metal	**Density(Kg/m^3)**	**Young's Modulus(GPa)**	**Poissons Ratio**
Aluminium	2700	69	0.33
Carbon Steel	7720	200	0.27
Low alloy steel	7830	200	0.27
Stainless steel	7920	207	0.28
Copper	8940	117	0.33
Monnel	8830	179	0.32

7.3 Fabrication of 3 liters double walled super-insulated cryogenic container

After completion of the basic design computation and finalization of the inner vessel and outer vessel thickness, radiation shield, neck of the inner vessel, and vacuum port joining resin as adhesive, the fabrication of the container is undertaken.

7.3.1 Necessary Machinery and Instrument

The fabrication unit must have standard metal sheet cutting, rolling, bending, seaming, beading machines, die press, gas welding, brazing and soldering equipment, etc. Other basic needs are a rotary-cum-diffusion high vacuum pump, high vacuum gauges, boosted with an LN_2 trap, shut-off valves, a small compressor for pressure testing the shells, a high vacuum leak detector, an ultrasonic metal flow detector, aluminized mylar foil of 12 microns thickness as super-insulating radiation shields, and a mechanical winding device.

Once the fabrication of the container shells, vacuum port, and polymer composite neck is finished, it has to be assembled to have the container as a whole. The container is to be fitted with a high vacuum system for creating a very high vacuum in the annular space between the outer vessel and the inner vessel.

7.3.2 Fabrication and assembling of the cryogenic container

The fabrication of the 304 austenitic stainless-steel outer, inner shells and neck is carried out with the help of an industrial manufacturer. The inner vessel is hung from the mouth of the cone-shaped outer vessel. There is no physical conduction in-between inner and outer vessels except the neck which is made of thermal insulating polymeric composite (GFRP).

The evacuation port is made of a new design and closed by a screw-threaded o-ring sealed piston working through an o-ring sealed coupler joint.

The various types of insulation used in the storage and transfer of cryogenic liquid can be conveniently subdivided into five categories: vacuum, multi-layer insulation, powder and fibrous insulation, foam insulation and special-purpose insulation. In the present case, super insulation i.e., several layers of aluminised mylar with 12-micron thickness is used as a reflecting shield along with a vacuum in the annular space.

Practically, the inner vessel is wrapped with 32 layers of a 12-micron thick aluminised Mylar sheet as a radiation shield. The Mylar brand trade mark belongs to DuPont Tejjin Films for a specific family of plastic sheet products prepared from Polyethylene Terephthalate resin. During evacuation, the inner vessel is heated to 100^0C with an internal heater and the outer wall to 80^0C in a surrounding heating chamber. The activated charcoal and shells are thoroughly degassed using an LN_2 trap in a diffusion vacuum circuit. Both the mechanical pump and diffusion pump are made operative for several hours to a achieve a high vacuum of the order of 10^{-6} Torr. Finally, the vacuum port is closed by the plunger at a pressure of 10^{-6} mbar and the container is ready for use in the laboratory once a lid is installed in the mouth and a handle is fitted.. When the container is filled with LN_2, the residual gas pressure in a short time will fall below 10^{-7} mbar, keeping in mind that the interlayer gas in the super insulation will take appreciable time to be absorbed by the activated charcoal pocket.

The mouth of the container is fitted with a lid made of an ebonite guard and a stainless steel cap which fits the container easily. A stainless steel wire ring-type handle with a wooden grip is attached to the neck to carry the container. The schematic view of the developed Cryo container along with its details dimensions is given in Figure 7F.1. which is similar to earlier Figure 6F.1.

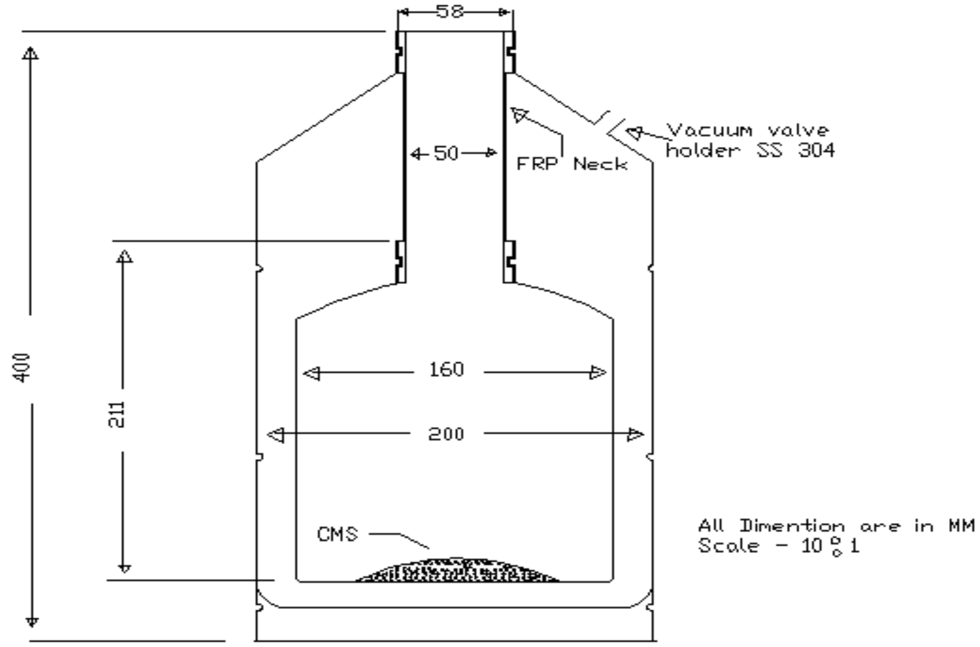

Figure7F. 1 Dimensional Sketch of a 3-litre cryo container

The complete pictorial view of the assembled cryo container developed along with various parts shells before assembling is shown in Figure 7F.2.

Figure7F. 2 Pictorial view of the cryo container developed (left side) and pictorial view of dome and shell before assembling (right side)

7.4. Results and discussions

The developed cryo container is filled with 3-liter liquid nitrogen by opening the lid. The mouth of the container is then closed with the ebonite lid which allows normal evaporated nitrogen to escape. The container is kept on the table and its holding time for liquid nitrogen is noted. The evaporation rate is calculated based on the holding time. The same empty cryo container is now attached again to the mechanical pump and diffusion pump circuit through its vacuum port The pumps are made on and the annular space vacuum of the cryo container is raised to 10^{-6} mbar(torr). Now without sealing the vacuum port, liquid nitrogen is filled in the cryogen container up to its capacity of 3 litre and is made stabilised. The mouth of the container is then closed. Observation for holding time is started in situ. The total time for evaporation of the entire liquid nitrogen is noted in continuous evacuation mode of the annular space of the cryo container. The results are represented in table- 7T.4

Table 7T.4 Performance of indigenous cryo container in terms of evaporation rate

Different positions of the cryo container filled with 3 litres of liquid nitrogen	**Holding time of liquid nitrogen in days**	**Evaporation rate**
Cryo container detached from High Vacuum System after a vacuum of 10^{-6} Torr is reached and the Vacuum port is sealed	4 days	0.75 litre/day (25%)
Cryo container attached with vacuum line for ensuring high vacuum of the order of 10^{-6} Torr in the annular space i.e.; in situ experimentation.	7.5 days	0.4 litre/day (13.33%)

The results show that the liquid nitrogen holding time for the cryo container kept in the table is 4 days which is equivalent to an evaporation rate of 0.75 litre/day (25%). It is observed that the holding time is increased to 7.5 days, which amounts to an evaporation rate of 0.4 litre/day (13.33%), when the observation is made in situ i.e.; the annular space of the dewar is in continuous evacuation mode ensuring no loss of the vacuum.

It indicates that in the finished cryo container, the high vacuum somehow deteriorates with time assuming other factors remain constant.

7.5. Conclusion

The result is encouraging since the 4-day holding time of liquid nitrogen at -196^0 C(77 K) is quite compatible with laboratory-range uses of liquid nitrogen for low-temperature experimentations.

As the holding time substantially increases with the maintenance of annular space high vacuum in situ observation, it is possible to further improve the performance of the cryo container by improving the fabrication technique and preventing fine leaks to the annular space.

Therefore, it is concluded that a cryo container of 3-litre capacity is successfully developed to cater the need of laboratories for low-temperature experimentations.

CHAPTER-8

Summary
and
Conclusion

CHAPTER-8

SUMMARY AND CONCLUSION

8.1 Summary

Advances in the development of materials play a crucial role in the progress of cryogenic technologies. Polymers are excellent engineering materials and can be a substitute either fully or partially combined with metallic parts for the development of various types of equipment/components to be operated at cryogenic temperatures (below -150^{0}C). Fillers are selectively added to polymers resulting in polymer composites that enhance their mechanical strength and many desirable properties such as low thermal conductivity, electrical insulating property, vacuum sealing effect, self-lubricating property, and lightweight in comparison to metallic counterparts.

Most often the suitability of a large number of metals and alloys for their use at low temperatures has been studied but much less work has been reported in the field of characterization of polymer materials at low temperatures particularly that of different polymer resin-impregnated fiberglass composites. These polymer composites may have a reasonable edge over many metallic components for cryogenic and allied applications e.g. in a cryogenic container, LNG tank, high vacuum application, expansion turbine rotors, expansion engine parts, space rocket shells, etc. Moreover, such composites are also used as non-conducting structural components in combination with metallic parts in the fabrication of cryogenic storage vessels, transfer lines, cryo stat, etc. The potential for these polymer composite materials in the low-temperature range still remains unexplored, particularly for the lack of adequate data on characterization and there lies tremendous scope to have in-depth studies of the behavior of such composites down to the boiling point of Liquid Nitrogen as well as their compatibility at cryogenic temperature as a parts with metallic components. In this regard, the characterization of polymer composites from the consideration of their utilization in the fabrication of cryogenic storage containers, plant components, cryostat, and other equipment being used at cryogenic temperature becomes the need of the hour.

The present work is a rigorous study from theoretical and experimental points of view on the basis of the determination of some of the mechanical and physical properties of the glass fiber-reinforced plastic composites for cryogenic applications which finally establishes the feasibility of the indigenous development of Glass Fibre fiber-reinforced plastic tube and its subsequent use as a neck of an indigenously built stainless steel liquid nitrogen vessel as well as a performance study of aluminized mylar as a Multi-Layer Insulation system of a cryogenic vessel. The work stresses material characterization, design, analysis, fabrication, and experimental run of the prototype cryogenic dewar developed.

Chapter 1 defines cryogenics and its history of development along with polymer composites and the need for characterization for cryogenic applications.

Chapter 2 highlights the mechanical and thermal properties of solid materials including plastics at low temperatures in the cryogenic range.

A knowledge of the properties and behavior of materials used in any cryogenic system is essential for proper design considerations. Often the choice of materials for the construction of cryogenic equipment will be dictated by consideration of mechanical ,physical and thermal properties such as thermal conductivity (heat transfer along a structural member), thermal expansivity (expansion and contraction during cycling between ambient and low temperatures), and density (mass of system).

Properties of materials at low temperatures are often significantly different from those at ambient temperatures and there is no substitute for generated test data for a particular application. Basic theories of the physical and thermal properties of solids including plastics are discussed. The methods of measuring such properties are highlighted.

Chapter 3 presents a state-of-the-art report on the progress of polymer composite materials for low-temperature applications.

The effect of low temperature pertaining to the structural properties including tensile strength, impact strength, thermal fatigue, creep, brittleness, etc. have been discussed. These are essential for the designer to make a choice of the appropriate polymer composites for their application to a specific cryogenic field. It is observed that most polymers become brittle at low temperatures but their strength increases. Fiberglass-reinforced epoxy resin or graphite-impregnated Poly Tetra

Fluoro Ethylene (PTFE /Teflon) can sustain low temperatures without cracking and hence their structural survivability at cryogenic temperature is manifested. In addition, PTFE offers self-lubricating properties.

Chapter 4 is dedicated to explaining the aims and objectives of the present study. The main aims and objective of the present intensive study is to first polymer composites characterization and then to establish the feasibility of the indigenous development of Glass Fibre Reinforced Plastic-based tube and its subsequent use as a neck of an indigenously built liquid nitrogen vessel as well as performance study of aluminized mylar as a Multi-Layer Insulation system of a cryogenic vessel. It is further intended to emphasize innovative design, analysis, fabrication, and experimental run of the prototype tube of GFRP and prototype cryogenic Dewar developed.

Chapter 5: Various components made of polymer composites are much lighter than their metallic counterparts but have equivalent strength for ultra-low temperature applications.

Chapter 5 is devoted to the preparation of a glass-fiber-impregnated epoxy resin tube and the investigation of its physical and mechanical properties as well as an in situ experiment in immersing it in liquid nitrogen to assess its eventual use as a structural component such as a nonconducting neck of cryogenic dewar.

In this chapter, the tensile properties (before and after cryogenic treatment) of an indigenously prepared unidirectional cylindrical hollow composite tube made of

GFRP-EP3 have been investigated. XRD and SEM of the tube material are performed before cryogenic conditioning of the material to ascertain the fiber and resin distribution in the matrix. Both, the strength, and modulus increase significantly with the increase in strain rate and reach the optimum value for 45 minutes of cryogenic conditioning.

The results established the viability of GFRP-EP3 in the structural design of epoxy-based components for cryogenic applications, including its use as a nonconducting neck of a cryogenic vessel.

Chapter 6 has successfully established aluminized mylar as a radiation shield in the development of an effective multi-layer insulation system for any laboratory-scale cryogenic Dewar vessel etc.

Storage and transfer of cryogenic liquid require very low heat leaks so as to prevent evaporation loss of cryogen for various low-temperature applications including cryogenic fuel storage for space missions as propellant. Multilayer insulation provides the most effective thermal protection available for cryogenic storage and transfer systems. Heat is transferred across the annular space of a vacuum-insulated double-walled vessel mainly by radiation from the outer vessel at room temperature to the inner vessel at cryogenic temperature as the annular space vacuum prevents heat transfer by solid conduction and gaseous convection

In this context, extensive studies on the performance of aluminized mylar sheets with fiberglass paper as spacers for the multilayer insulation system are done. Mylar is a special kind of polymer (Polyester film) made from polyethylene terephthalate (PET) having high tensile strength, reflectivity, transparency, and electrical and thermal insulation properties. Aluminized mylar can be made by vapor deposition of a thin film of evaporated aluminum.

The chapter described relevant heat transfer equations for computing heat transfer as well as finding effective thermal conductivity of the shields from a heat transfer equation involving a number of shields per unit length, solid conduction of spacer, emissivity of shield and surrounding metal surface, etc. The thermal conductivity of radiation shields as calculated is very low of the order of 0.01 $w.m^{-1}/k$ which is a very interesting result.

The optimum number of layers of radiation shields required for cryogenic storage vessels is also computed and found to be 32 layers of aluminized mylar(12 microns). The liquid nitrogen holding time in the Dewar is recorded as 4 days for 3 litters, using such a multilayer system indicating the efficiency of such radiation shields.

The successful design and prototype development of a 3-liter cryogenic container using glass fiber-reinforced polymer tube neck and aluminized mylar as a reflecting shield is finally achieved in **Chapter 7.**

In designing a storage vessel for a cryogenic liquid, the important factors to be considered are a) time of storage i.e., long duration -or short duration storage b) type of cryogenic liquid to be stored, c) tolerable rate of cryogen loss d) mobile or stationary storage e) allowable cooldown time and cost f) the stratification in case liquid methane storage and pressure effects on the system g) type and thickness of the material required for the inner and outer vessels h) thermal conductivity of the material, etc. Other important aspects include the optimum type of insulation and the design of inner vessel supports, fill and drain lines, vapor vents, vapor diffusers, and safety devices. The performance of cryogen vessels may range from low-performance containers designed for short-term storage of a few hours to high-performance tanks.

The effectiveness of any cryogenic storage vessel depends upon how well it reduces the loss of the cryogen due to unavoidable heat in leak and how well it maintains the purity of the stored liquid.

The basic design approach is to develop a vacuum-insulated doubled-walled container similar to that invented by James Dewar which has an inner vessel for storing the cryogenic liquid, and an outer vessel for serving as a vacuum jacket. To reduce the overall vessel weight and minimize the cool-down time, the wall thickness of both the inner and outer vessels should be made as thin as possible. It is desirable that the shape of a cryogenic container is selected in such a way so as to minimize the surface area to volume ratio which will effectively reduce the heat in leak to the stored cryogen.

All sorts of cryogenic storage vessels both transportable and stationary, are normally designed for a liquid volume of 90% and a vapor volume or ullage space of 10%. In the laboratory, 1-5 liters of double-walled containers are used for the temporary storage of cryogenic liquid for a few hours to a few days.

Various types of small cryogenic vessels, especially liquid nitrogen containers, with body shells fabricated from aluminum, are being manufactured under foreign know-how by different industrial organizations. A unique design of a cylindrical shaped cryo container of 3-liter capacity, made from austenitic stainless steel of 304 grade with neck indigenously made from glass fiber impregnated epoxy resin of comparable weight, strength, and efficiency to aluminum vessels, serviceability, long life, especially suitable for the laboratory use and transport of LN_2 frozen bull semen to rural areas for animal husbandry purposes, LO_2 for health services and metal fabrication work and LCH_4 for supplying a high-grade non-pollutant fuel, has been designed and constructed. Details of the design, fabrication, and material of construction for a 3-liter liquid nitrogen container using a stainless steel body and glass fiber-reinforced plastic as its neck are discussed in the chapter. Section VIII of the ASME Boiler and Pressure Vessel Code followed for computing the thickness of the inner vessel.

The thickness of the outer shell of a storage vessel has also been designed as per ASME Codes section-VIII to take care of the collapsing of the outer vessel shell due to the existing atmospheric pressure exerted on the outside of the outer shell and the vacuum provided on the annular space.

The inner shell, outer shell, glass fiber-reinforced polymer tube, vacuum port, and other different parts are fabricated and then assembled to develop the dewar as a whole.

It is then attached to the high vacuum system to evacuate the annular space (10^{-6} Torr)vacuum. The vacuum port is sealed and the Dewar is detached from the vacuum pump and is made ready for testing.

The indigenously built container is tested by filling it with liquid nitrogen and noting the evaporation loss. The result is encouraging since the 4-day holding time of liquid nitrogen at -196^0 C(77 K) is quite compatible with laboratory-range uses of liquid nitrogen for low-temperature experimentations.

As the holding time substantially increases with the maintenance of annular space high vacuum in situ observation, it is possible to further improve the performance of the cryo container by improving the fabrication technique and preventing fine leaks to the annular space.

Therefore, it is concluded that a cryo container of 3-liter capacity is successfully developed to cater to the need of laboratories for low-temperature experimentations as well as for rural transport of liquid nitrogen/liquid methane..

8.1 Conclusion

The results found in each part of the work are very encouraging which justifies that the overall work plan for the thesis is successfully executed.

Therefore, it can finally be concluded that the present work is systematically performed starting from material selection to characterization and from theoretical analysis to practical design/fabrication/prototype development followed by testing of equipment resulting in the successful development of glass fiber-impregnated polymer component suitable for low-temperature application as well as a prototype stainless steel cryogenic dewar using non conducting GFRP neck and aluminized mylar reflecting shield. The performance of the Dewar is adjudged by storing liquid nitrogen and hence can be practically used for storing liquid nitrogen. There lies tremendous possibility for further improving its performance. The present work will help cryogenic hardware development for the country in which India lags far behind China and other advanced countries.

CHAPTER-9

Scope

Of

The Future Work

CHAPTER-9

SCOPE OF THE FUTURE WORK

The present work will open up avenues for further studies in diversified fields. Some of the important fields of research which could be undertaken are listed below:

1. In the present work, a liquid nitrogen Dewar vessel of 3-liter capacity is practically developed in **polymer composite- mylar(a polymer) -a metal hybrid mode** which successfully stored liquid nitrogen at -196^0 C. and as the vessel is designed following ASME Section VIII Boiler and pressure vessel code, the same methodology/design procedure can be extended for upscaling i.e for designing and manufacturing larger volume cryogenic tanks in industrial scale.
2. Development of Liquid Natural Gas (LNG) (-162^{0}C) fuel tanks for automobiles which are more efficient than Compressed Natural Gas(CNG) fuel tanks[1].
3. Liquid hydrogen storage vessel for liquid propellent (liquid hydrogen, liquid oxygen) for the space program.

Indian Space Research Organization (ISRO) normally stores huge amounts of liquid hydrogen (-254^0 C) in metallic cryogen tanks for their all launch vehicles.

4. In the present case, the cryogenic Dewar is developed using a polymer composite neck and stainless steel for the shell. Research and development can be undertaken based on knowledge gathered to design and development of cryogenic vessels entirely using a polymer composite such as fiberglass reinforced plastics or carbon fiber-reinforced polymers(CFRP). If this happens the storage vessel will be lighter and there will be a huge cost reduction for the same capacity tank. NASA is in the process of developing a nonmetallic composite tank (1) .Cryogenic propellants, such as liquid oxygen(-183^{0C} C) and liquid hydrogen (-154^{0}C) are used to provide the enormous thrust needed for large rockets and space shuttles. Propellant tanks are normally fabricated out of metals.If composite tank fabrication becomes successful on a commercial scale, it will significantly reduce the cost and weight of launch vehicles and other space missions.

5. The present research can be extended for cryogenic transfer line design using metal and polymer composite combinations

6. Cryogenic valves play a critical role in using/transferring large-scale cryogenic liquids. The cryogenic valve can be designed using Teflon(Polly Tetra Fluoro Ethylene) as a sealing material in the gasket.

7. Possibilities of using Liquid nitrogen for developing automobile air-conditioning can easily be attempted with zero carbon dioxide emission and CFCs

8. The Government of India approved a ₹19,744 crore National Green Hydrogen mission that aims to make India a ‘global hub’ for using, producing,

and exporting green hydrogen in which liquid hydrogen storage in cryogenic storage and transfer system will play a major role[2].

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PUBLICATION ARISING OUT OF THIS PRESENT STUDY IN THE NATIONAL/INTERNATIONAL JOURNALS AND PROCEEDINGS

Publication in International Journal/Proceedings

- "**Progress in Polymer Composite Materials for Cryogenic Application**", **S. Ghosh**, S. C. Sarkar, **International Journal of Research in Engineering and Science (IJRES)**, Volume 11 Issue 1 ,2023, 382-386.

- "**Investigation on the Tensile Properties of Glass Fiber Reinforced Polymer composite for its use as a Structural Component at Cryogenic Temperature"**, **S. Ghosh**, S. C. Sarkar, Progress in Superconductivity And Cryogenics (PSAC)", Vol.25, No. 3, pp 43-48.

- **"Performance study of Aluminized Mylar as Multi-Layer Insulation in an Indigenously Developed Cryogenic Dewar Vessel", S.Ghosh,** S.C.Sarkar, Peer Reviewed Proceedings of 27th National and 5th International Heat and Mass Transfer Conference, IHMTC 2023.

- "**Design and Development of Cryogenic Dewar Using Glass Fibre Reinforced Polymer Tube Neck", S.Ghosh,** N.R.Chakrobarty ,S.C.Sarkar is under review.

- **"Efficiency Evaluation of a Laboratory Scale Cryogenic Dewar through evaporation Loss", S. Ghosh**, S. C. Sarkar, being communicated.

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- **Performance study of Aluminized Mylar as Multi-Layer Insulation in an Indigenously Developed Cryogenic Dewar Vessel**, S.Ghosh,** S.C.Sarkar, 27th National and 5th International ISHMT-ASTFE Heat and Mass Transfer Conference(IHMTC 2023), **IIT PATNA**, 14th-17th Dec, 2023 .

- Characterization of fiberglass reinforced resin tube for its application in a cryogenic container, **S.Ghosh,** N.R.Chakrobarty, S.C.Sarkar, National Symposium on Cryogenic and Superconductivity(NSCS), **IIT-KHARAGPUR**, 18th -22th Oct, 2022.

- Study on Evaporation Loss of Liquid Nitrogen from an Indigenously Built Cryogenic Vessel, **S.Ghosh**, G.P.Mandal, S.C.Sarkar. International Conference on Futuristic Advancements in Materials, Manufacturing and Thermal Sciences, ICFAMMT 2024, Space Society of Mechanical Engineers (SSME), Space Applications Centre, **ISRO AHMEDABAD**, 2024.

WORKSHOPS ATTENDED:

1. CRYO 18, National Workshop on Cryogenics, Centre for Rural & Cryogenic Technologies, Jadavpur University, 14th March, 2018.

2. 28th West Bengal State Science &Technology Congress, Bidhannagar Gov. College, 28th-29th December, 2018.

3. CRYO 19, National Workshop on Cryogenics, Centre for Rural & Cryogenic Technologies, Jadavpur University, 29th March, 2019.

4. 29th West Bengal State Science &Technology Congress, Maulana Abdul Kalam University of Technology, 5th-6th December, 2019.

5. 31th West Bengal State Science &Technology Congress, Calcutta University, 21th-22th December, 2023.