Development of External Ablative Thermal Protection System for Composite Rocket Motor Case

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JAI KRISHNA MISHRA

(Roll No. 715039)

Supervisor (s):

Prof. C.S.P. Rao

Dr. P. Subhash Chandra Bose

Dr. N. Kishore Nath

DEPARTMENT OF MECHANICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

WARANGAL-506 004 (TS), INDIA.

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DECLARATION

This is to certify that the work presented in the thesis entitled “Development of External Ablative Thermal Protection System for Composite Rocket Motor Case” is a bonafide work done by me under the supervision of Prof. C.S. P. Rao, Dr. P. Subash Chandra Bose and Dr. N. Kishore Nath and was not submitted elsewhere for the award of any degree.

I declare that this written submission represents my ideas in my own words and where others’ ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea / data / fact /source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

(JAI KRISHNA MISHRA)

Roll No: 715039

Date:

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ABSTRACT

The large size rocket motor case designed with polymeric composite materials are ideally suited for launch vehicles due to its high specific strength and stiffness which results into less structural mass for high internal pressure. When launch vehicles, missiles accelerate through atmosphere, the external surface temperatures on rocket motor case increases due to high velocities and aerodynamic drag. The mechanical properties of polymeric composites materials start degrading at lower elevated temperature than metal alloys and hence, external surface thermal protection is essential for composite rocket motor case. The present research work is aimed for development of ablative thermal protection system for composite rocket motor external surface which need to function as a heat-insulating layer based on the working mechanism of ablation to limit the interface temperature within allowable limits. Ablative thermal protection functions are based on the ablation phenomenon in which physicochemical transformations take the place of solid substances by heat transfer mode of convection or radiation heat flow.

In present research work, the approach of ablative thermal protection system is considered as it is flexible and having good feasibility of process development considering compatibility with composite rocket motor case structural layer. In present work, Carbon roving impregnated tow, Carbon-Epoxy flat and ring specimens were manufactured and tested for mechanical properties at ambient temperature as per ASTM standards. The ring specimens were tested at elevated temperature for evaluation of carbon-Epoxy strength degradation temperature. The experimental studies for Phenolic and Silicone resins were carried out through Thermogravimetric analysis and Dry scanning calorimetry techniques for thermal stability evaluation. The silicone resin is selected for thermal protection system based on thermal stability results. The samples were manufactured with various reinforcements and by varying layers of thermal protection materials. These samples were subjected to thermal test of specific heat flux profile for evaluation of thermal protection system and interface temperature with composite structural layer. Based on thermal test results, the thermal protection system was finalized with two layers viz inner layer having Panox fabric-silicone resin and outer layer with glass-silicone resin. In next phase, missile sub scale model with thermal protection layers build up was manufactured. Missile model was subjected to flow test under wind tunnel for evaluation of thermal protection integrity with structural layer under shear. The model was also subjected to thermal test with measurement of interface temperature of thermal protection and structural layer. The test results confirmed excellent integrity of thermal protection layer with carbon-epoxy structural layer. The process development for external ablative thermal protection system for composite rocket motor

case was carried out considering lightweight, integrity with composite rocket motor case structural layer, manufacturing process parameters including curing aspects are prime fundamental requirements apart from thermal aspects. The hand lay-up and wet filament winding processes were selected and developed for inner and outer layer of thermal protection system for composite rocket motor case. The integrity of thermal protection layer with composite case structural layer were tested through non-destructive test methods (Ultrasonic and radiographic test). The composite rocket motor case with thermal protection layer were also subjected to hydrostatic pressure test for integrity evaluation.

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ABBREVIATIONS

SRM	Solid Rocket Motor
CRMC	Composite Rocket Motor Case
TPS	Thermal Protection System
HTPB	Hydroxyl Terminated Polybutadiene
CTPB	Carboxy Terminated Polybutadiene
NBR	Nitrile Butadiene Rubber
SBR	Styrene Butadiene Rubber
EPDM	Ethylene Propylene Diene Monomer
RCG	Reaction Cured Glass
TUFI	Toughened Unipeiece Fibrous Insulation
UHTC	Ultra-High Temperature Ceramics
ETPS	External Thermal Protection System
AETPS	Ablative External Thermal Protection System
CE	Carbon-Epoxy
DSC	Dry Scanning Calorimetry
TGA	Thermogravimetric Analysis
IR Heating	Infra-red Heating
ASTM	American Society for Testing and Materials

CHAPTER I

INTRODUCTION

1.1 General

Thermal protection systems are essential requisites for various aerospace applications like space crafts, launch vehicles, and missiles to protect the primary structure or subsystems from severe kinetic heating due to aerodynamic drags and high velocities. Apart from kinetic heating, thermal protection is also needed for the interaction of flames or plumes from engines & motor exhaust with surrounding surfaces and subsystems. In the preliminary stages of design iterations and configuration studies of launch vehicles & missiles, the need for various thermal protection systems is also conceived. Design and development considerations and inputs are derived for these thermal protection systems based on the overall configuration of launch vehicles, missiles and their mission objectives. There are various types of thermal protection schemes that are conceived and configured depending on mission objectives, trajectory, and application.

Launch vehicles and long-range missile systems configurations consist of various propulsion stages depending on mission objectives. These stages get separated one by one after the propellant of respective rocket motors gets consumed as per trajectory design, and motor cases are spent. The rocket motor casings are designed with high strength alloy steel and polymeric composite materials. In present scenario, the large size rocket motor cases are mostly designed with polymeric composite materials for achieving a high-performance factor with minimum structural mass. The large size rocket motor case designed with polymeric composite materials [4] are ideally suited for launch vehicles due to its high specific strength and stiffness which results into less structural mass for high internal pressure. When launch vehicles, missiles accelerate through atmosphere, the external surface temperatures on rocket motor case increases due to high velocities and aerodynamic drag [37]. The mechanical properties of polymeric composites materials start degrading at lower elevated temperature than metal alloys and hence, external surface thermal protection is essential for composite rocket motor case.

The ablative thermal protection system approach is a vulnerable option for such application as it is flexible and good feasibility of process development considering compatible with composite rocket motor case structural layer [40]. The lightweight, integrity with composite rocket motor case structural layer, manufacturing process parameters including curing aspects are prime fundamental requirements for the development of this external thermal protection system apart from thermal aspects [41]. The operational requirements of these rocket motor casings are needed only in the ascent powered phase of missile trajectory till motor burn time, followed by its separation. Due to such specific application, the generated heat flux and temperature rise on external composite case are relatively less, depending on missile configuration & trajectory, unlike extreme thermal conditions on ablative nozzle liners exposed to rocket motor exhaust & re-entry conditions. The present research work is aimed for development of ablative thermal protection system for composite rocket motor external surface which need to function as a heat-insulating layer based on the working mechanism of ablation to limit the interface temperature within allowable limits. Ablative thermal protection functions are based on the ablation phenomenon in which physicochemical transformations take the place of solid substances by heat transfer mode of convection or radiation heat flow. In other words, energy is managed through material depletion and pyrolysis.

1.2 Solid Rocket Motor (SRM)

Rocket motors falls under classification of non-air breathing type propulsion system i.e., atmospheric oxygen is not needed for combustion of fuel. The solid propellant stored in rocket motor contains fuel, oxidizer, binder and other ingredients as per formulation. A solid rocket motor is propulsion system [1] which operates on principle of energy conversion forms. The propellant contains chemical energy which gets converted to thermal energy through combustion process after grain ignition [41]. The high pressure and high temperature gases get generated inside chamber as combustion by product. These gases are expanded through a convergent-divergent nozzle and results into very high kinetic energy of exhaust gases at nozzle exit which in turn produces thrust. The Solid rocket motors are most widely used due to following advantages:

- Simple configuration and design
- Nil Preparation time
- Negligible moving parts/components
- Relatively less overall weight
- Design possibility for very high thrust for shorter action time
- Conducive for long period storage
- Design with thrust vector control is possible
- Combustion instability complexities are less
- Better production rate

Solid rocket motors are having vast application as propulsion stages for launch vehicles, long range and tactical missile systems to meet wide range of thrust magnitude. These are most specifically used as strap-on boosters apart from main booster of launch vehicles to achieve high initial thrust for high payload requirements and roll-stabilized upper stages propulsion to achieve higher incremental velocities and in turn long ranges. The design and configuration of the solid rocket motor involves various considerations like thrust profile & other mission specifications, load analysis (structural & thermal).

Solid Rocket Motors consists of five major sub systems [38] viz. Motor casing, Internal insulation system, Propellant grain, Nozzle, and Igniter as shown in Figure 1.1.

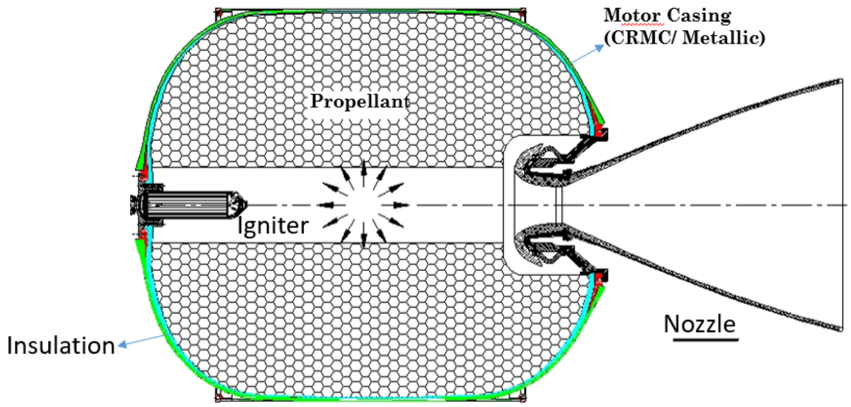

Figure 1.1: Solid Rocket Motor Elements

Motor case: It is very significant element structure of solid rocket motor. The motor case is combustion chamber designed to meet the specification of maximum expected operating pressure and other critical loads (flight, articulation and transportation) with adequate factor of safety. The motor case is designed with objective to meet all requirements with minimum structural weight through proper material selection. There are two class of materials for the solid rocket motor case: (1) Conventional metallic materials such as high strength low alloy steels, high strength aluminum and titanium alloys [39], (2) Composite materials having fibers as carbon, Kevlar and glass. Composite materials are ideal choice and are prime materials for design and manufacturing of recent rocket motor cases due to their unique properties especially high specific strength and specific stiffness [46].

Insulation: Internal insulation for rocket motor is designed to meet the allowable interface temperature of motor case and insulation during action time. This insulation thickness protects the motor case structure until pressure –time curve tails off. The temperature of gases produced inside motor case ranges from approximately 2000 to3500 K and insulation system is very significant to meet functional objectives. The candidate materials for insulation have characteristics of low thermal conductivity, high heat capacity and undergoes ablation [42].

Igniter: The igniter is required to induce combustion reaction of motor propellant grain in controlled, predictable manner and at the specified rate. The ignition system imparts threshold heat flux and pressure to the grain surface needed to initiate combustion. There are mainly two types of ignition systems: 1) Pyro technique which are used for small rocket motors for tactical missile applications, 2) Pyrogen Igniters are small rocket motors mostly used for ignition of large size solid rocket motors. The igniter is fired through explosive chain consists of primary initiator (hot-wire resistor or bridge wire with charge mass) connected to the firing switch through the ignition circuit followed by another small booster charge as pellets or powder.

Propellant Grain: Solid propellant [2] is a mixture of main ingredients as fuel, oxidizer and binder as per formulation. The grain is ignited and undergoes combustion to produce gases at high pressure and temperature inside motor case. The grain formulations are tried in the initial phase and finalized with various functional considerations: (a) to meet specified burn rate (b) combustion by products with high temperature and energy (c) to meet mechanical and physical properties specifications like Tensile strength, Initial modulus, % Elongation and density [41]. The solid propellants are mainly classified as double base and composite propellants. The double-base propellant consists of two highly energetic compounds namely nitroglycerin and nitrocellulose. The basic function of nitrocellulose is for grain mechanical properties and nitroglycerin contributes for burn rate. Double-base grains are processed by mixing of all ingredients followed by pressing or extrusion into desired grain configuration. The composite propellant is mixture of oxidizer (Ammonium perchlorate, Potassium nitrate etc) as solid and binder (HTPB, CTPB etc) as liquid ingredient. The binder acts like fuel also apart from light metal powder like aluminum or beryllium powder as fuel. The composite propellant formulations are aimed to meet burn rate and mechanical properties specifications. Solid grains configuration design which includes grain shape, dimensions and structural integrity analysis are very crucial to meet mission objectives. The propellant grain will undergo combustion at its surface which is exposed to heat flux which generates threshold temperature to ignite the propellant.

Nozzle: The rocket motor nozzle is configured as convergent- divergent type in such a way that high pressure and high temperature gases inside chamber are expanded to attain high kinetic energy at nozzle exit to impart designed thrust to the vehicle. In general, nearly 65 -75 percent of total thrust [2] is the result of combustion products expansion in convergent portion up to nozzle throat to sonic velocity and balance thrust is developed in divergent cone. There are basically two types of nozzle configurations: 1) External Nozzle configuration (De-Laval nozzle which is external to the motor case), 2) Submerged-Nozzle configuration (convergent portion, throat, and partial divergent cone are submerged into the motor case). The submerged nozzle design is more challenging than the external configuration because the convergent submerged portion being inside the chamber are exposed to severe thermal environment and it need to be also designed considering external pressure. Thermal protection of submerged portion is also very critical. There are two basic configurations being used for divergent portion namely contoured and conical. The contoured nozzle is advantageous to reduce divergence losses and reduction in length for same area ratio than conical nozzle.

1.3 Rocket Motor Internal Insulation

Internal insulation in a rocket motor is thermal barrier material layer configured between the motor case internal surface and the propellant grain. The basic function of internal insulation is to inhibit heat transfer towards motor case and designed to limit case temperature with in allowable specifications to ensure its structural integrity. The insulation system also performs secondary functions given as follows:

- As inhibition on grain surface on which burning is not required as per design
- It reduces the transfer of case strain into the propellant due to less modulus
- It restricts the migration of chemical species within the motor propellant
- It faces particles impingement of combustion products and protect the case
- It acts like seals at case segment joints and other attachments to contain internal pressure and function as protection system against combustion products
- It is configured in case nozzle end dome to guide flow of combustion products into the nozzle as laminar flow

The design of rocket motor internal insulation involves [42]: (1) Selection of insulation material, (2) Prediction of insulation thickness in motor domes and cylindrical zones based on grain design & other specifications, and (3) Design of loose flaps in domes, motor segment joints, and other requirements needed for adequate insulation performance. The various features of internal insulation for solid rocket motor are shown in figure 1.2.

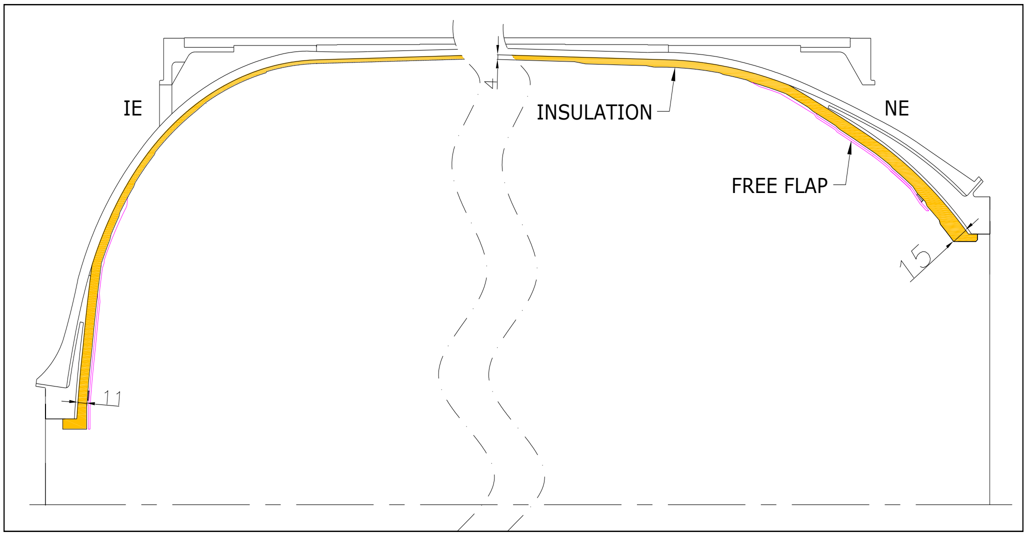

Figure 1.2: Solid Rocket Motor Internal Insulation Features

The most of the presently used insulation system for solid rocket motors works as heat barriers based on ablation phenomenon; i.e., the material when exposed to heat its temperature increases and physical state changes with material sacrifice due to pyrolysis [43]. The ablative insulation system divides the material into three zones when exposed to heat: (1) virgin zone, (2) decomposition zone, and (3) char zone. In the virgin-material zone, due to low temperature there are minimal changes in material and mode of heat transfer is by conduction. In the decomposition zone, the energy absorption takes place due to breaking and scission of molecules. The decomposition reactions are function of temperature and become very fast due to temperature increase with substantial material loss. In this zone, two modes of heat transfer are present: (1) conduction, and (2) pyrolysis. In general, majority of decomposition reactions are endothermic and small number may be exothermic. In the char zone also reaction mechanisms are similar to those in the decomposition zone, the main difference being the specific reaction involved. The reaction yields char (residue) which is mainly elemental porous carbon. In this zone decomposition of inorganic compounds and cracking of pyrolysis gas are main phenomenon. Insulation surface material gets eroded due to continuous exposure to hot gas flow motor environment. The phenomenon of surface erosion is termed as "surface regression" and there are various modes which include following: (1) Chemical effects (2) Physical effects (3) Combinations of chemical and physical effects

Insulation system materials [2] for solid rocket motors are having two main constituents viz. filler or reinforcement and matrix or binder e.g., Silicon/ NBR (Silicon is filler and NBR is binder) [42]. There are two types of materials which are used as binders for internal insulation: elastomers and thermosetting plastics. The elastomers are used in majority of insulation materials formulations. The main characteristics of elastomers which are functionally critical are as follows:

- Low elastic modulus and relatively soft
- High deformation with very high strains before failure (approx. 900-1000 %)
- Excellent resilience properties return quickly to its original length after load removal
- Non crystalline structure, having glass transition temperature well below expected operating temperature

The compound formulations with filled elastomers are highly suitable for internal insulation due to their excellent thermal properties and high strain capabilities to diffuse the effect of stress concentration from the case into the propellant. The main filler materials for elastomers are silica, asbestos and aramid and mostly these compounds are molded or manually laid up in motor case followed by curing in autoclave or oven at specified temperature, pressure and duration.

The Insulation materials are usually heat cured and compounds are made from binders or matrix of NBR, SBR, butyl, EPDM, polysulfide, silicone, and urethane masticated with a different type of fillers. The binders (polymers) are usually selected based on compatibility and other chemical requirements of propellant types. The various examples are as follows: NBR preferred with composite propellants; SBR- or NBR-phenolic with double-base propellants; and butyl, silicone, or EPDM elastomers in wide temperature ranges requirements with both class of propellant.

The performance of insulation system depends on various phenomenon: (1) Heat transfer to charred surface from the combustion by product gases, (2) Heat capacity of insulation material, (3) Transfer of mass produced from pyrolysis, (4) Energy recession from char surface into insulation, (5) Conduction of heat through decomposition zone, and (6) Char layer intactness with insulation.

The insulation material selection is based on its chemical compatibility with propellant and liner. The compatibility needs to be considered for both areas in rocket motor: (1) the cylindrical regions of case-bond where one side of insulation layer is bonded to the motor case and the other is with propellant, and (2) the motor domes loose flap regions where one side of insulation surface is bonded to the case or propellant and the other is un-bonded. In all the motor regions, every material needs to be compatible with every other material in contact.

Insulation system processing requirements are process intensive and stringent control is must at each and every stage. There are adhesive requirements at interface of case and insulation as well as between insulation to propellant. The motor case surface preparation, pot life of adhesive and application of specified adhesive thickness are very crucial for insulation layer lay-up. In most of cases bond strength depends on adhesive thickness, ambient temperature and cleanliness. The bond quality of elastomeric insulation to metal cases depends on variation in the chemical and physical properties of the elastomers. Due to processing conduciveness, sometimes plasticizers and antiozonants are added in the elastomer formulations which adversely affect the bond strength. To achieve good bond strength, the adhesive wetting characteristics and presence of reactive species chemically compatible with elastomer is essential. In case of composite case, the chemical compatibility between reactive species of insulation binder and composite case resin are relatively more complex and important due to their migration. The composite case surface preparations are more critical in comparison to metal cases; and the strain (at various life cycle phases of rocket motor) at bond line are higher than metal cases.

During design of insulation, additional insulation thickness is catered to ensure structural integrity of motor against uncertainties: (1) heat conduction inside decomposition zone and virgin insulation, (2) Motor ballistic performance variations due to propellant lots among motors, (3) Performance variations in insulations materials among lots.

The various processing operations of insulation system, composite casing and propellant casting affect insulation mechanical properties, bonding characteristics and causes residual stresses. The process of mixing and blending of all ingredients of insulation material as per formulation is known as “compounding.” The major constituents of insulation material are elastomer and fillers. The type and proportion of filler material is prime source to tailor thermal, physical, and mechanical properties (tensile strength, elongation & modulus) and it also affects char characteristics, ablation rates, hardness and aging characteristics. Similarly, plasticizers and diluents are used in elastomer compound to achieve specific physical properties specifications to the elastomer to create specific desirable changes in physical properties. For example, in SBR, mineral fillers are added to coumarone resin to produce desired properties and in NBR, carbon black and silica is used to produce similar reinforcement effect [44]. The process by which curing agents, fillers, pigments, accelerators, and other additives are blended into the rubber compound is termed as mastication or milling. The stringent process control during mastication is key to produce insulation material compound having uniform properties to meet expected performance. The improper mastication produces compound with non-uniform properties which may result into varying erosion rate at different locations and even can lead to failures also. The compression molding and hand lay –up are most common processes used for fabrication of insulation system from un-vulcanized sheets of elastomers. The hand lay- up process is mostly adopted for large size rocket motor and it involves very few tools and provides flexibility to carry out lay –up of un-vulcanized elastomer sheets as per varying insulation thickness requirements viz., Igniter dome, nozzle dome and cylindrical zones of motor. The tolerance for insulation thickness needs to be relatively wider for hand lay –up process. The hand lay-up is carried out based on lay -up plan and accordingly templates are used to cut elastomer sheet sectors as per composite rocket motor case zones. Once lay -up gets completed for internal insulation, curing is carried out in autoclave after preparing vacuum bagging for rubber lined casing.

1.4 Rocket Motor Case

The missile and launch vehicle configurations consist of primary structures namely, metallic, composite airframe sections and rocket motors of each stage. The primary structures are always equipped with various subsystems and designed to meet all loads requirements. The primary objective while designing this structure is to select the materials with highest possible specific strength and specific stiffness. The development of such missile and launch vehicle structures are most fundamental requirements to achieve improved mission objectives in the aerospace field. The recent progress in various fields like composite materials, structural design & analysis is vulnerable to provide options to meet critical challenges. The rocket motor cases are major proportion of primary structures of missiles and launch vehicles and are considered as most sensitive element for mission performance as well as optimum design. Rocket motor cases are designed for high internal pressure and other structural load requirements of axial load and bending moment depending on overall mission objectives. Propellant is loaded in side case and ignited to produce high pressure which is expanded through nozzle to produce required thrust. The material is most crucial element in design of the rocket motor case and its selection involves considerations like high specific strength, high specific stiffness, machinability, weldability, availability, service conditions, and thermal properties. There are two types of materials in application for rocket motor case, viz., Metals and composite materials.

The rocket motor casings have been designed and manufactured using conventional metallic materials since beginning. Metal cases have been conducive for rough handling and also possesses certain advantages like good ductility permits yielding to occur before failure, can withstand relatively high temperature (700-1000) ˚C which reduces insulation requirements. The conventional metallic materials being used for rocket motor case are temper steels, low alloy low carbon steels, aluminum alloys and titanium alloys. The temper steels and Ni-Cr-Mo-V steels are most common for such application having strength up to 1500 Mpa. The Molybdenum and Chromium alloy steels are having good machinability and good heat resistance properties due to the presence of molybdenum and chromium. The Maraging steel is most preferred which is low carbon alloy steel with Ni-Co-Mo as alloying elements and high strength is achieved through aging at relatively low temperature [39]. The fracture toughness, weldability and machinability of Maraging steel is also excellent. The Aluminum alloys and Titanium alloys are also used for such applications.

Polymeric composite materials are ideal choice for rocket motor case due to their high specific strength and high specific modulus. The present research work is related to composite rocket motor case, hence composite materials basics, and manufacturing and other aspects are covered in detail.

1.5 Composite Rocket Motor Case:

Design of motor case with composite materials is boon as light weight structure with high strength is achieved which makes it ideal choice for rockets/aerospace applications. Polymeric composites consist of reinforcement and matrix. Reinforcements are principal load carrying elements and matrix acts as load transfer medium and keeps reinforcement at required locations and orientations [46]. Carbon & Aramid/Kevlar fibers having high strength and high modulus ideally suited reinforcement along with Epoxy resin as matrix materials for design of composite rocket motor case [3]. Composite case primary design load is internal pressure and depending on design requirements stress are critical in domes or cylinder. The dome shapes of composite casing are very important from wet winding and stress distribution point of view. Rocket motor casing is basically a pressure vessel with specially designed metallic end fittings namely polar bosses and skirts [47]. The end fittings are configured to suit the overall vehicle requirements for assembly/integration with adjoining airframe sections. The performance factor for composite case is high which contributes for overall high efficiency of propulsion system and drastic reduction in inert structural mass. If configuration constraints are not there, the rocket motor can be designed as a complete system and the casing can be designed to achieve the maximum efficiency with very high-performance factor. However usually there will be always configuration constraints from interface and other launch vehicle requirements which limits performance factor. In present scenario, the large size rocket motor cases in majority are made up of polymeric composite materials and hence basics of composite materials are covered in following sections.

Composite Materials: The composite materials [4] consist of two or more different constituents having individual properties and gets combined through various processes at macroscopic level to produce material with unique properties. The classification of composite materials are based on geometry of reinforcement or matrix type. Based on reinforcement geometry composites are classified as, particulate, flake, and fiber however based on matrix [6], composite types are: polymer matrix composites, metal matrix composites, ceramic matrix composites and carbon matrix composites [48]. The primary load carrying element is fiber in composites and overall mechanical properties of such materials mainly depend on fiber mechanical properties. There are various types of fibers being used viz., glass, Kevlar (aramid), carbon, boron, Ceramic, and metallic. The primary functions of fibers in composites are:

- To act as main load carrying element in structure.
- To contribute for the structural properties in the composites viz., mechanical (strength & stiffness), coefficient of thermal expansion etc
- To provide other properties like electrical conductivity or insulation based on fiber type

The matrix plays very vital role in composite structure and its primary functions are as follows:

• The matrix act as binder and holds fibers in required orientation and also function as medium to transfer load between fibers. Matrix is responsible for rigidity of the structure.

• The matrix keeps the fibers separated to act individually in structure and arrests any crack propagation.

• The matrix aids for required surface finish and helps to manufacture the net-shape or near-net-shape parts.

• The matrix protects the fibers from environmental effects and deterioration (wear or abrasion)

• The composite structure performance characteristics like ductility, impact strength, and toughness etc. are highly influenced by type of matrix.

• The mode of failures in composites strongly depends upon the type of matrix material and their compatibility with fiber.

• To exploit the fiber strength to maximum, the percentage strain at failure for matrix is preferred to be twice of that of fiber.

The polymer matrix is the most commonly used matrix type in aerospace applications including composite rocket motor cases. The polymer matrix are of mainly two types: Thermoset resins and Thermoplastic resins. Thermoset resins constituents namely basic resin, catalyst and hardeners are required to be mixed in specified proportion to facilitate for chemical reaction which is irreversible in nature. During curing process, the polymerization of chemical species takes place and due to their cross linking and three-dimensional molecular chains get formed. The thermosetting resins once polymerized cannot be re-melted and reshaped by heating due to presence of cross-linked non flexible molecular chains. Due to these cross-linking, the molecules are not flexible and cannot be remelted and reshaped. Thermoset resins are very conducive for composite processing being liquid at room temperature and provides better fiber or reinforcement impregnation during various processes such as filament winding, resin transfer molding, Vacuum assisted resin transfer molding and pultrusion. Thermoset resins possess excellent characteristics like good thermal and dimensional stability, rigidity, and mechanical properties. These are most preferred for structural application. The various types of thermoset resins are epoxy, polyester, vinylester, phenolics, cyanate esters, bismaleimides, and polyimides.

Thermoplastic resins are capable of undergoing repetitive reshaping and reforming as these materials gets melted by heating and again solidifies after cooling. These resin systems molecular species do not undergo cross-linking while polymerization, consequently are flexible and reformable. The thermoplastic resins are relatively more ductile and have higher toughness than thermosetting resins. The composites manufacturing using thermoplastic resins requires higher processing temperature and pressure than thermosetting composites. The thermoplastic resins viscosity is higher which is not conducive for various manufacturing processes like hand lay-up and tape winding process. The various thermoplastic resins are Nylons, Polypropylene, Polyether ether ketone (PEEK) Polyphenylene Sulfide (PPS).

Advantages of Composites: Composites are specially designed and produced for structures having weight critical applications in aerospace where high performance with minimum weight are fundamental requirements. The composites are advantageous over conventional materials as listed below:

1. Composite materials manufacturing provide potential to produce integrated parts. It is possible to replace several metallic parts by single composite entity.

2. In composite structures, there is possibility to have embedded sensors for recording and monitoring of structure health during service.

3. Composite materials possess a high specific stiffness (ratio of modulus and density). As a comparison, the Composites with one fifth of weight caters for same stiffness as that of steel materials.

4. The most significant characteristic of composites being their very high specific strength (ratio of strength and density). This specialty of composites makes them ideally suited for aerospace applications. As a comparison, the specific strength of typical composites are 3 to 5 times of steel and aluminum alloys. The biggest advantage of high specific strength and specific stiffness are light weight of composite structures.

6. The fatigue strength of composite materials is very high in comparison to conventional materials. In case of Steel and aluminum alloys, the fatigue strength is about 0.5 times their ultimate tensile strength however unidirectional carbon –epoxy composites offers fatigue strength as 0.9 times tensile strength.

7. The Composite materials are excellent in corrosion and chemical resistance.

8. The design flexibility is very unique advantage with composite materials, as based on application requirements the structure properties can be tailored through constituents and reinforcement orientation. For example, in space application to achieve dimensional stability, the composite structures with zero coefficient of thermal expansion (CTE) can be designed and manufactured by choosing suitable materials and ply sequence.

9. The composite parts/components manufacturing can be achieved net-shape or near-net-shape parts. This eliminates machining & other operations and consequently overall reduction in process cycle time and cost.

10. The manufacturing feasibility for complex parts using composite materials are much better than conventional materials

11. The feasibility of adopting techniques namely design for manufacturing and design for assembly is more suitable for composite materials.

12. The impact strength for composites materials are excellent.

1.5.1 Details of Composite Rocket Motor Case (CRMC)

The Composite materials are widely used in thermal and structural applications in launch vehicles and missiles due to their special material characteristics, high strength-to weight-ratio and excellent thermal protection through ablation.

The rocket motor case of each stage is primary structural element of launch vehicles or missile systems and composite materials with high strength and high modulus PAN based carbon fiber with epoxy resins are ideal. The design and manufacturing [3] of rocket motor cases with such materials offers capability for high internal pressure with least weight and high propulsion performance. The high performance of composite rocket motor case is evaluated through parameter performance factor, PF which is defined as PF = P V/ W, where P is rocket motor maximum expected operating pressure, V = volume, W= weight of the motor case. The performance factor of composite case can be 6 to 12 whereas for metallic case it is maximum up to 5 which is true indicator of composite case [49]. The design of composite rocket motor case includes design of composite structure and design of metallic igniter & nozzle end polar bosses.

Composite Motor cases are manufactured by the filament winding process in which hoop and helical plies are wound as per specified ply sequence and angle of winding based on design. The composite cases are consisting of cylindrical zone and domes at both ends, the shell thickness for these zones varies. The Composite motor cases are also designed with igniter and nozzle end metallic polar bosses and also skirts with metallic bulkheads to facilitate for integration of subsystems and vehicle interfaces. The constructional details of composite rocket motor case is shown in following figures 1.3 (a) and 1.3 (b):

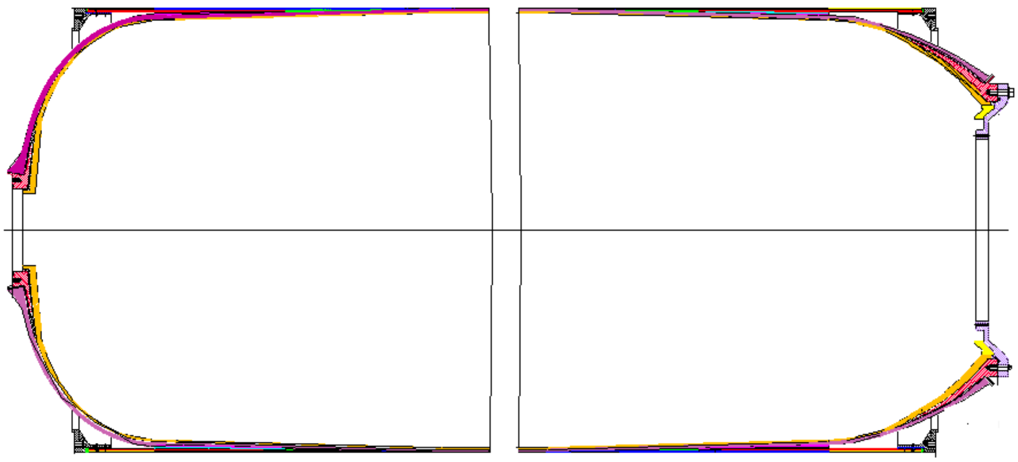

Figure 1.3(a) Composite Rocket Motor Case

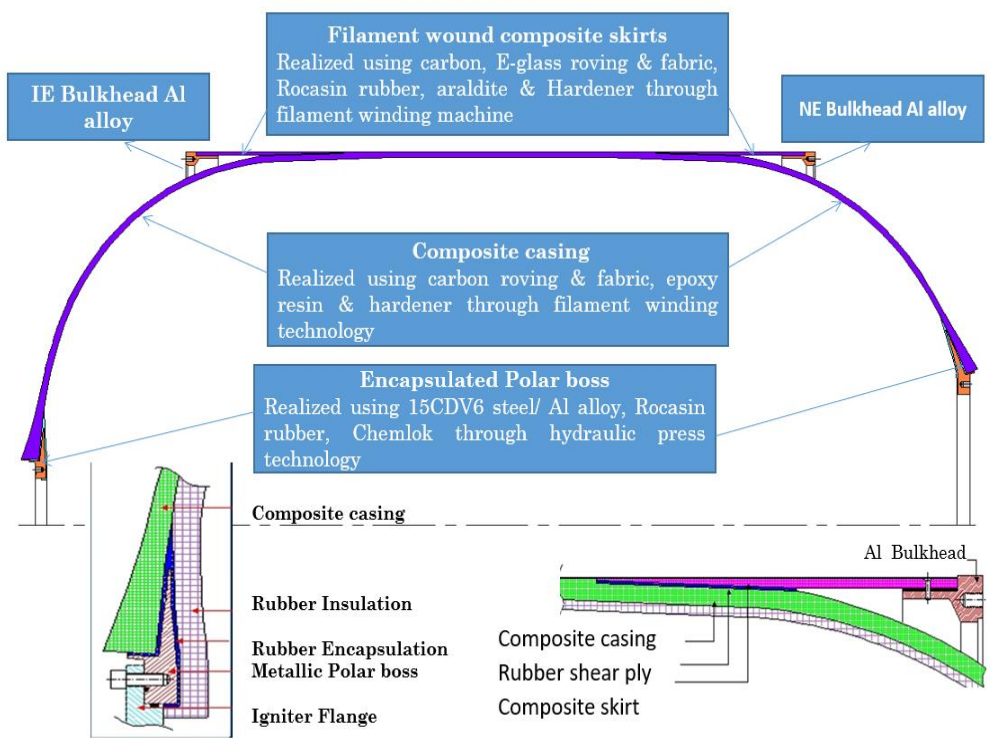

Figure 1.3(b) Composite Rocket Motor Case details

Composite Rocket Motor Case Materials:

Polymeric composites which are used for design of filament wound rocket motor case have main constituents as continuous fibers as reinforcement and polymeric resins as matrix [7]. The main fibres options meeting such requirements are Glass, Aramid/Kevlar & PAN Carbon. PAN Carbon fiber is having high modulus & high strength and used for present studies. Polymeric resins viz thermosetting and thermoplastic are options and Epoxy Resin which is thermosetting resin having good mechanical properties is used in present work. In present work, the composite rocket motor case is designed and manufactured with high strength PAN based carbon fiber and epoxy resin. The details and specification of materials used for composite rocket motor case in present studies are as follows:

Carbon Rovings: The reinforcement material for composite rocket motor case is carbon roving. The carbon roving is high strength and high modulus, detail specifications are given in following table 1.1.

Table 1.1: Carbon Roving properties

S.No	**Property**	**Specification**
1.	Tensile strength	4.2 GPa (Min.)
2.	Tensile Modulus	220 GPa (Min)
3.	Tow Size	12 K (No twist/ never twisted yarn)
4.	Tex	800 g/Km (nominal)
5.	Filament Diameter	6 to 8 microns
6.	Carbon Content	93 % (Min)
7.	Sizing	Epoxy compatible (0.8 % Min)
8.	% Elongation	1.2 to 2%
9.	Density	1.7 to 1.85 g/cc

Epoxy Resin: The matrix material for composite rocket motor case is epoxy resin. The epoxy resin is mixed with hardener in 100:24 (Resin: Hardener) proportion for polymerization. The detail specifications of resin and hardener are given as follows in table 1.2.

Table 1.2: Epoxy Resin & Hardener Properties

Sl. No	Property	Specification
1	Specific Gravity of Resin, at 25°C	1.15 to 1.20
2	Viscosity of Resin, at 25°C	15000 to 17000 cps
3	Volatile Content of Resin (% by wt.)	< 1.5 %
4	Epoxy Content of Resin (Eq/Kg of resin)	5.0 to 5.45
5	Specific Gravity of Hardener at 25°C	1.02
6	Viscosity of Hardener, at 25°C	152 cps
7	Initial mix viscosity of Resin & Hardener, at 25°C	6350 cps
8	Initial mix viscosity of Resin & Hardener, at 45°C	950 cps
9	Gel time of Resin mix at 100°C	140
10	Tensile strength	60 MPa
11	Tensile Modulus	2.4 GPa
12	% Elongation	4.2

1.5.2 Manufacturing of Composite Rocket Motor Case

The metallic end fittings namely igniter end and nozzle end polar bosses are machined from forging rings of Al alloy, alloy steel and Titanium alloy as per design. In present case, 15CDV6 low alloy low carbon steel material is chosen based on design for both end polar bosses. There are two metallic bulkheads also at both ends to facilitate for integration of composite rocket motor case with other airframe sections of missiles and launch vehicles. Theses bulkheads are also machined from Aluminum alloy AA 2014 forging rings as per drawing. The igniter end and nozzle end polar bosses are encapsulated with nitrile-based elastomer.

The mandrel and fixtures are very important for manufacturing of composite rocket motor case. Mandrel configuration, materials and finished dimensions especially both side dome contours are governing features for composite case inner surface. The mandrel preparation, machining and final dimensional inspection are done critically to ensure acceptable composite case after mandrel extraction. The encapsulated igniter end and nozzle end polar bosses are mounted on prepared mandrel which in turn gets loaded on winding machine.

The composite rocket motor cases are manufactured using towpreg or roving /resin by filament winding process [8]. In present case, the composite rocket motor case is manufactured by wet filament winding process using carbon roving and epoxy resin materials. The set up for filament winding is shown in figure 1.4:

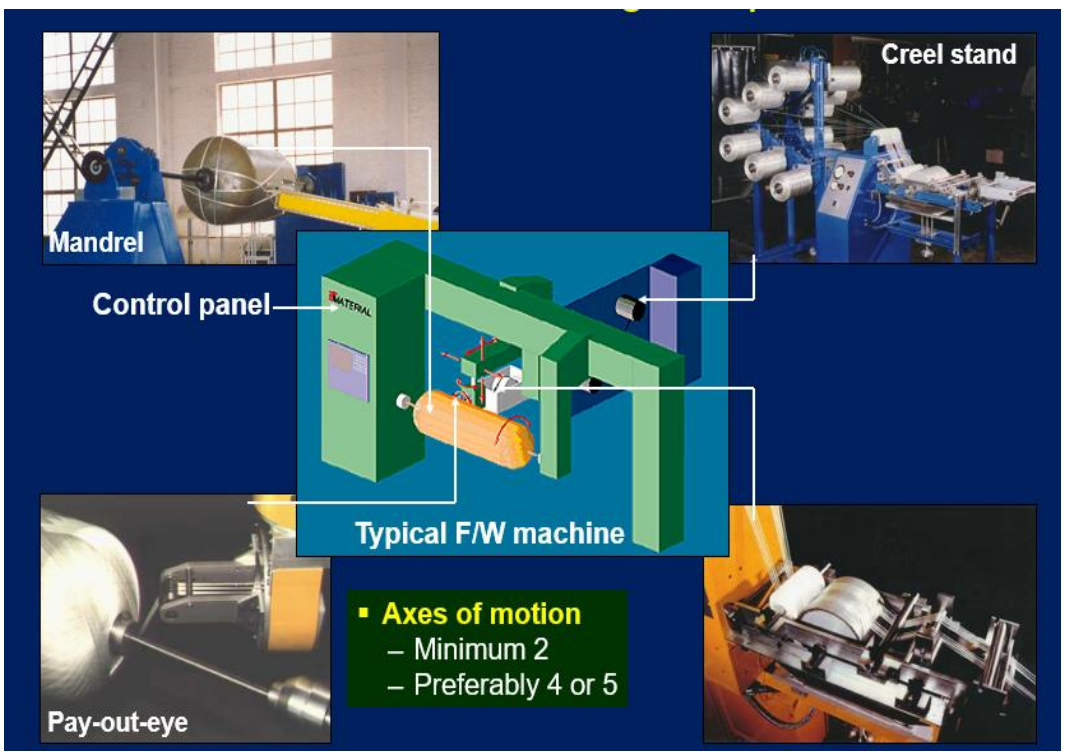

Figure 1.4: Filament Winding Process

The filament winding process requires filament winding machine which should be able to wind bands of resin-impregnated rovings under controlled tension on to a rotationally symmetrical mandrel as per desired geometrical fibre path [48]. The filament winding machine should be equipped for operations with following attachments and features:

- Application program that instructs the CNC system to control the various axis-movements of the machine to generate the desired winding patterns.
- Provisions to hold spools from which the bands of rovings are drawn on to the winding mandrel.
- Tensioning device to continuously control and display tension in the roving.
- Resin bath with doctor blades through which the rovings are drawn for impregnation.
- Pay-out-eye at the fiber laying carriage before being wrapped around the rotating mandrel.

The winding is carried out as per designed ply sequence[8]. The igniter end and nozzle end skirts are also wounded using fixtures. Once wet filament winding gets completed, it is kept in oven for curing as per specified curing cycle based on resin system. In present case, the resin system is epoxy resin and curing cycle for wound composite rocket motor case is given as follows in figure 1.5.

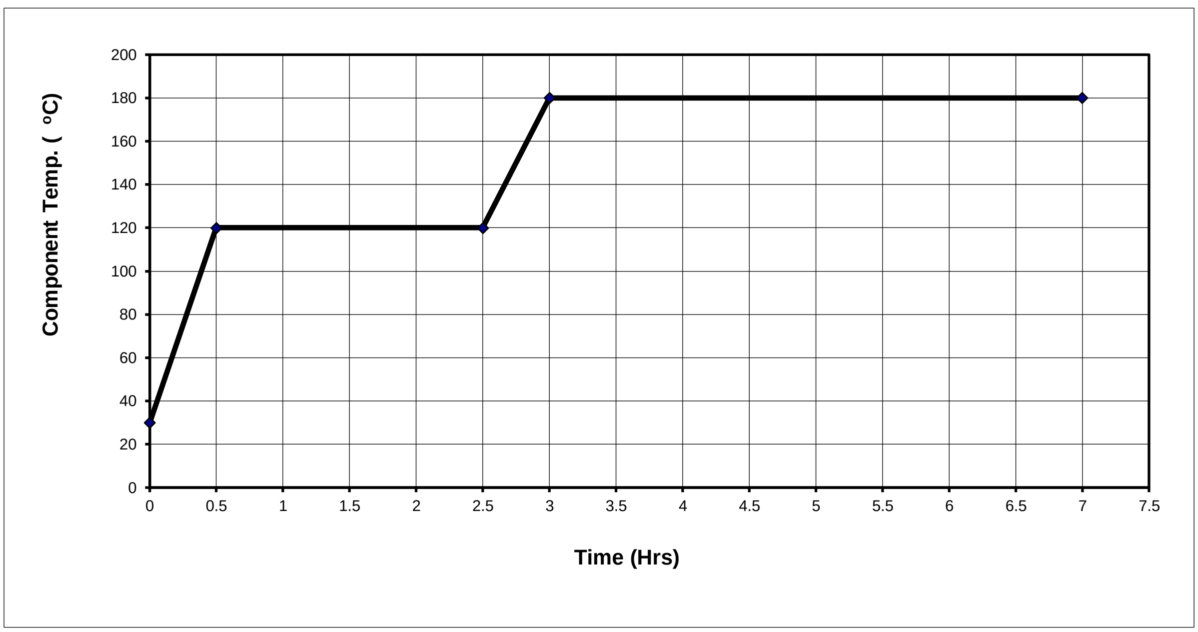

Figure 1.5: Composite Rocket Motor Case Curing Cycle

The mandrel is extracted after curing gets completed. The overall manufacturing of composite rocket motor case is shown in following figure 1.6 as process flow chart.

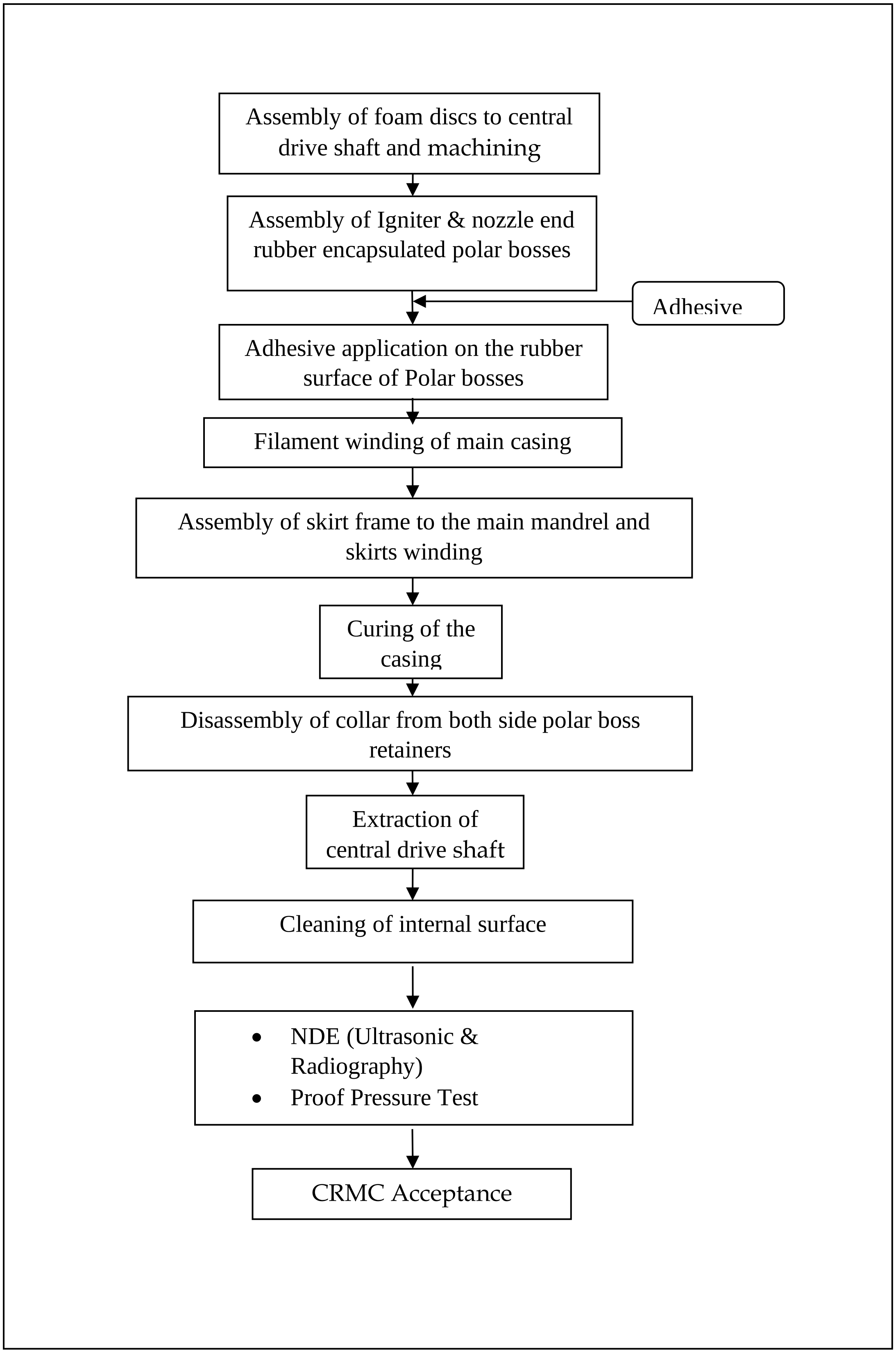

Figure 1.6: Composite Rocket Motor Case Manufacturing Process

1.6 Thermal Protection System

In aerospace field there will be various challenges pertaining to thermal protection requirements [9] which needs to be addressed during design stage of space crafts, launch vehicles and missile systems. One such case is encountered when a spacecraft, launch vehicle or missiles accelerates through the atmosphere at high speeds during ascent phase and re-entry, the aerodynamic drag generates heat. One more type of challenge occurs in the surrounding of the engines due to extreme heat in plume which can damage cable harness, fuel/oxidizer lines, avionics components and structural elements near to the base of the vehicle [9]. When the vehicles accelerate through the atmosphere there will be interactions of plume, plume with free stream air which leads to high pressure and recirculation of hot gases towards the base. These hot gases are shielded against entry into base section by thermal protection layer. In addition, the temperature of combustion products in plume are very high and enormous heat is radiated towards the engine area. This case is especially significant for solid rocket motors where the combustion products in plume contains molten metal (mostly Aluminum) particles which increases radiated heat. The thermal protection schemes for such cases are usually configured and designed locally near the nozzle exit in base section of vehicle.

There are various approaches for thermal protection schemes which prohibits heat transfer inside the space craft, vehicle and missiles. One such approach is to select the TPS material which absorb the heat and radiate it back to ambient. As a fundamental principle, all materials radiate heat when their temperature is more than ambient however based on materials characteristics only some can radiate heat very efficiently to allow no heat buildup and further transfer towards inside the vehicle. There is another approach for TPS working in which material absorbs heat and undergoes pyrolysis as well as decomposition [50]. The material forms residue (char) near to exposed surface which recedes due loss and erosion and protects the substrate material or structure. The term for such material working when exposed to heat is known as ablation.

It will be always the basic objective to design and configure thermal protection system (TPS) with minimum weight. A launch vehicles and missiles are designed for nominal launch weight to meet mission objectives. This launch weight consists of two major parts: the weight of the entire vehicle including propellant, fuels and all sub systems and the weight of the payload or war head. The design approaches will focus on to design of all subsystems or parts with minimum possible weight including thermal protection system in order to take advantage of carrying higher weight payload or enhancing ranges.

The approaches for thermal protection systems (TPS), development for spacecraft also depends significantly on risk with respect to crewed and non-crewed missions. The TPS design and development approach for crewed missions shall be very stringent to avoid loss of life. Whereas the development of TPS for non-crewed involves more risk. The basic objective of all TPS is to meet functional requirements efficiently with reliable performance. This is achieved through analysis of materials characteristics and adequate design for required applications. In general, the thermal protection system protects the vehicle primary structure and integrated critical subsystems including crew if any from external heat generated due to vehicle velocity in atmosphere including severe aero thermal conditions re-entry [51]. The functioning of TPS depends upon response of materials to the environment which in-turn is function of following:

- Material Properties (Physical, Thermal and Mechanical properties)
- Configuration of system (space craft, launch vehicles and missiles)
- Specific conditions (Heat flux, flow and dynamic pressure) based on trajectories and mission objectives

The thermal protection systems (TPS) are classified in two categories based on their usage: Reusable TPS and Ablative TPS. The basic criterion to meet functional requirements in terms of mach number and velocity for both class is given in figure 1.7as per NASA [10].

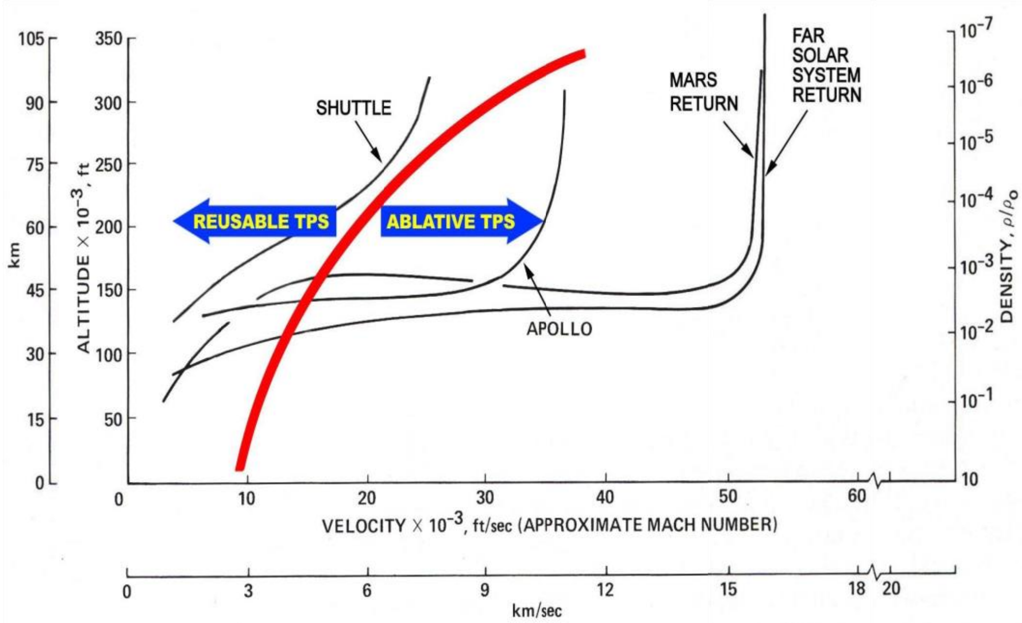

Figure 1.7: Reusable and Ablative TPS (Courtesy: NASA report)

1.6.1 Reusable thermal protection system (TPS):

The reusable thermal protection system (TPS) is mainly insulative type and in which basically heat management is through partial absorption or storage and remaining by re-radiation. In such TPS material are not changed as they can withstand. In case of such TPS, when surface experiences severe heating conditions during atmospheric entry, the surface temperature rises and heat is rejected in following two ways [11]:

• Re-radiation of heat from the surface and stored inside during severe aero thermal conditions

• Heat transfer through re-radiation and convection cooling during post-flight conditions after atmospheric entry

The working mechanism of insulative TPS is shown in following figure 1.8.

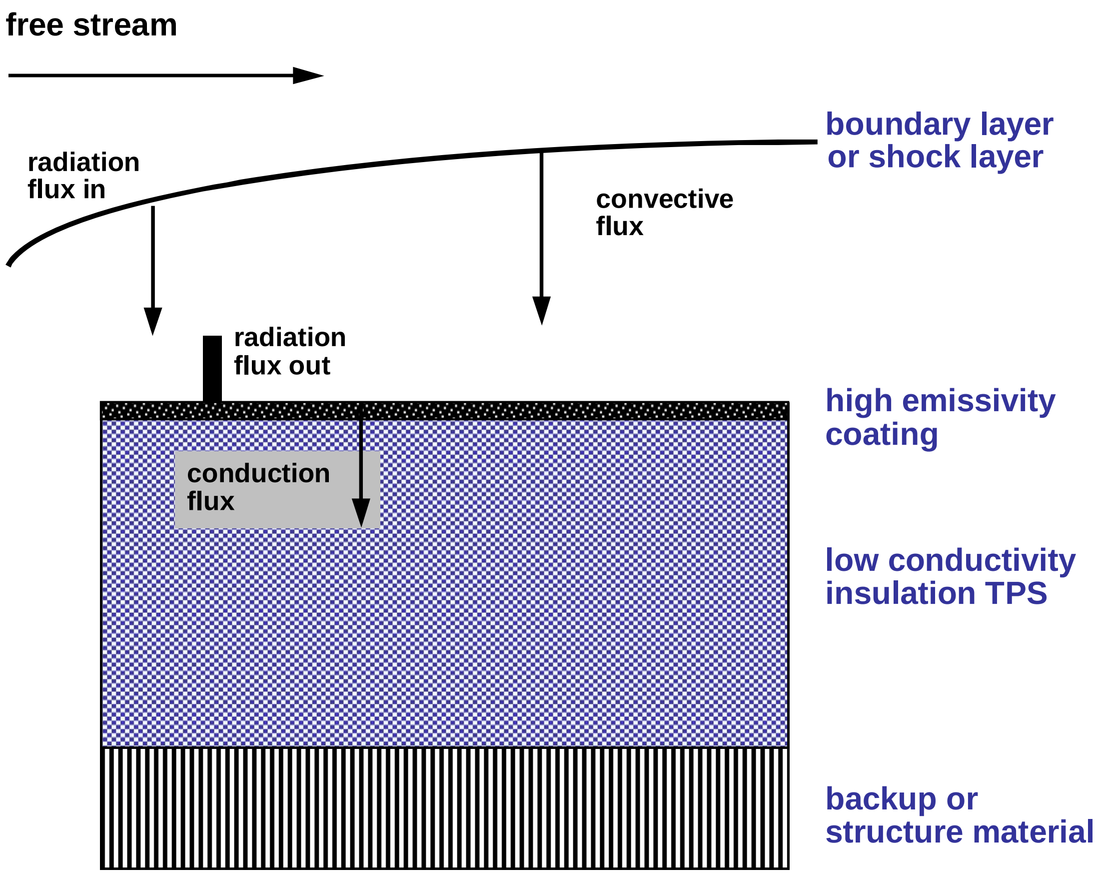

Figure 1.8: Reusable TPS working mechanism (Courtesy: NASA report)

There are various types of reusable TPS given as follows:

Reusable TPS Tiles:

The development of reusable TPS tiles were initiated way back by NASA [11]and these tiles are basically insulation materials which protect the shuttles airframe structure. These are made up of mainly with alumina fibers, high silica and alumino borosilicate. The micro structure of such materials is open porous and are used successfully for many NASA shuttle missions. The starting materials with their microstructures are given in figure 1.9 as follows:

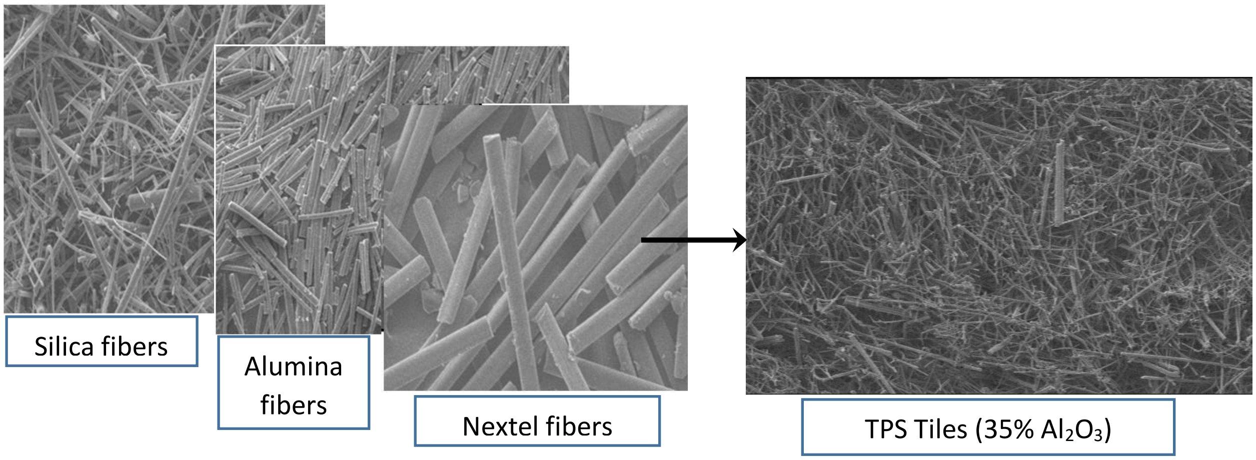

Figure 1.9: Starting material for Tiles (Courtesy: NASA report)

Tiles microstructure are heterogeneous which consists of regions with low density and cluster of fibers with some inclusions.

Reusable TPS tiles are also given coatings, having main constituent as silica-based fibers with high volume fraction of porosity [11]. These coating are of mainly two types: Reaction cured glass (RCG) and Toughened unipiece fibrous insulation (TUFI). The RCG coatings are of low thickness, dense with high glass emissivity. These are having poor impact resistance and are usually provided on shuttle surface tiles. TUFI coatings gets penetrated into substrate material, having more porosity with high impact resistance. The RCG and TUFI coatings microstructures are shown in following figures 1.10 (a) and 1.10 (b) respectively.

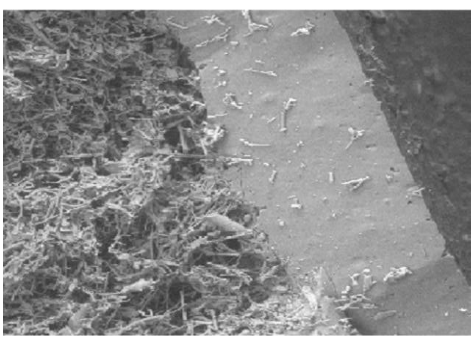

Figure1.10 (a): RCG Coating

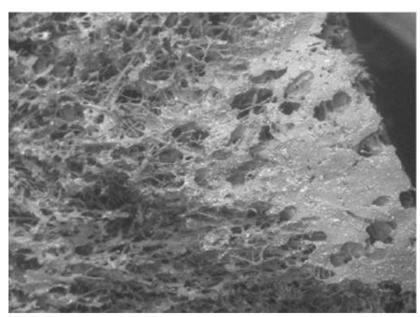

Figure1.10 (b): TUFI coating

(Courtesy: NASA report)

Toughened Unipiece Fibrous Oxidation Resistant Ceramic (TUFROC) TPS:

The TUFROC reusable TPS are ceramic materials which are having following advantages:

- Low weight TPS
- Excellent dimensional stability up to 1922 K
- High total Emittance (0.9)
- Thermal response through thickness is similar to single piece Shuttle-type fibrous insulation

The TUFROC TPS schematic is shown in following figure 1.11:

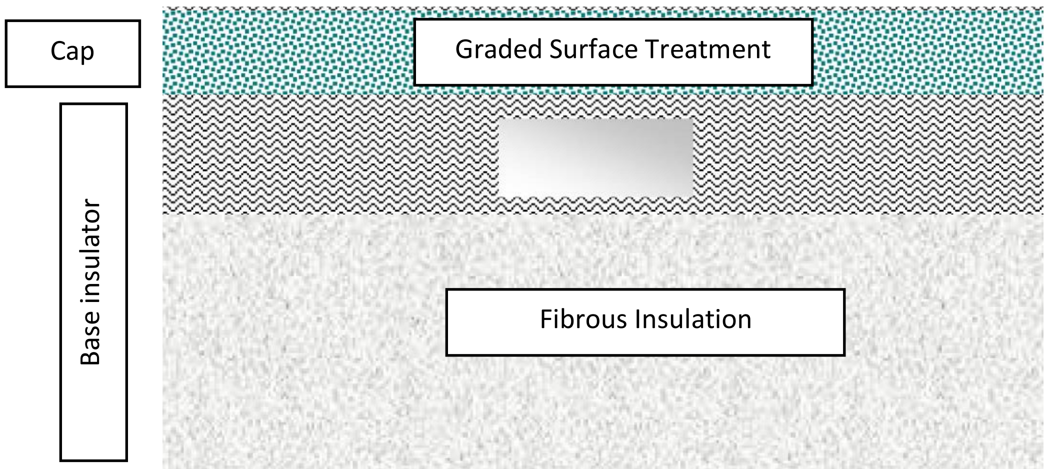

Figure 1.11: TUFROC TPS Schematic (Courtesy: NASA report)

Ultra-High Temperature Ceramics (UHTC):

The Ultra high temperature ceramics (UHTC) are mainly used for leading edges and sharp nose cone surfaces for thermal protection[11]. The thermal management by insulators and UHTC are different: Insulators function as heat sink until heat can be dissipated in same way as it entered and UHTC conducts heat through material and it is re radiated through cooler zones. UHTC consists of various materials options such as Borides, Carbides and Nitrides of elements. Some of their main characteristics are given as follows:

- High melting points
- Materials are having excellent hardness, mechanical properties and wear resistance
- Excellent thermal and chemical stability
- Microstructure is heterogeneous like composites

1.6.2 Ablative Thermal Protection System:

Ablative thermal protection systems (TPS) are unique applications in which materials are rated based on their degradation mechanisms and abilities. The ablative materials, used for thermal protection during ascent phase and re-entry of launch and space vehicles are examples of such materials [9]. The ablative materials sacrifice itself to protect the surface of launch and space vehicles from the enormous quantity of heat produced due to kinetic heating caused by atmospheric drag. The mechanism of ablative materials degradation involves endothermic reactions through which heat is absorbed by material and inhibits transfer to inside the vehicle. This phenomenon of material degradation is known as ablation process which involves heat transfer, chemical reactions and fluid flow [53]. The aerospace structures are protected against high external surface temperature most largely through ablation in highly effective and reliable manner. In the ablation process, the material sacrifices itself by dissipating heat fluxes through various endothermic reactions. The ablative material decomposition is complex which involves many physical and chemical phenomenon primarily driven by combined convection and radiation modes of heat transfer from to the surface of ablator [11]. In the beginning phase of decomposition, the heat is transferred within the ablative material through conduction and material gets swell due to thermal expansion as well absorbed moisture gets vaporized. Once the ablator material attains decomposition temperature, the pyrolysis for material starts through endothermic chemical reactions which generates comparatively cool gases and leaving behind residue known as char. The char is layer of porous and carbonaceous residue. The continuous exposure of heat flux causes increase of pyrolysis zone thickness with in ablator and also resulting in increased char thickness. This thick charred layer works like thermal barrier over virgin material as the high surface temperature drastically reduces the heat transfer with in ablator by convection and radiation. The inside generated pyrolysis gases will escape through the char layer resulting heat removal from char layer through convection. The surface temperature of the char layer continues to rise depending on heat exposure and re radiation from high temperature char surface will become predominant mode of heat transfer [11]. Depending on constituents of ablator, if it contains an element which undergoes melting will absorb additional heat due to heat of fusion and form layer on surface. This liquid layer reduces convection heat transfer into material and protects material. The char layer will attain temperature at which the char surface recession begins due to oxidation, sublimation and mechanical erosion due to continuous exposure of heat flux. The ablators produce porous carbonaceous char as result of endothermic degradation reaction which subsequently act as insulation layer. Ablative materials volumetric loss during degradation is very less. These charring ablators are most preferred thermal protection systems and are generally consists of polymeric resins like phenolic, epoxy, or silicon resins and glass, silica, felt fabric and short fibers as reinforcement.

The characteristics of ablative materials are very important for such application. As a thermal protection ablator, the thermal properties are most important viz ablation temperature, thermal conductivity, specific heat and density [10]. The preferred ablative material properties are high ablation temperature to sustain heat for longer time, low thermal conductivity to reduce heat transfer through material, and high specific heat in order to exhibit high heat capacity to absorb more heat while maintaining low surface temperature. In case of density of ablative material, there are two contradictory requirements i.e., high density for reduced recession rate and low-density reduction in inert mass. In launch vehicle and missile applications always minimizing inert mass is first objective hence low-density ablative materials are obvious choice. The ablative material decomposition mechanism must be based on endothermic reactions and more gases needs to be generated to absorb and block the heat incident on surface. The ablator material must have sufficient mechanical properties to resist high stress and vibrations.

To meet such specific characteristics, ablative materials are primarily composite materials having polymeric matrix and reinforcement fibers to withstand high temperature. As ablative thermal protection system, the fundamental function of polymeric matrix [13] is to undergo decomposition through endothermic reactions due to incident heat by forming char and since char is having less mechanical strength, the high temperature fibers will reinforce the porous char to avoid their removal. When ablative composite materials are exposed to heat, the degradation primarily have impact on matrix and to meet such specific requirements the polymeric resins are highly suitable as matrix [13]. The polymeric resins exhibit degradation through endothermic nature of reactions in non-oxidation atmosphere and possesses excellent properties like low density, low thermal conductivity, high specific heat and good mechanical properties. The matrix basically serves two functions in ablators: first to absorb incident heat and undergo decomposition, and second it needs to work as a binder for reinforcements. The various candidate resins for such application are phenolic, epoxies, silicones, and polytetrafluoro ethylene. There are various options for fillers or reinforcement based on application, for example low density fillers in weight critical zones and a reactive filler with fibrous reinforcement for porous char retention. The main options for fillers or reinforcement materials are carbon fibers, silica fibers, and other low-density felt fabric & balloons.

Ablative thermal protection functions based on ablation phenomenon in which physicochemical transformations takes place of solid substances by heat transfer mode of convection or radiation heat flow. In other words, energy is managed through material depletion and pyrolysis.

The detailed working mechanism of ablative thermal protection system [10] is briefly summarized as follows:

- Hot gases in the boundary layer heat the surface through convection
- Surface get heated by radiant flux from the shock layer
- Heat absorbed by surface is either re-radiated out or conducted inside
- Decomposition of polymer in the composite begins results into pyrolysis gases formation, carbon remains and a porous char layer begins to form on exposed side
- More decomposition of polymers occurs due to thermal front recession through the material
- The gases formed due to pyrolysis inside composite material are at lower temperature than gases at near char surface. When these gases flow through char takes away heat and temperature get reduced.
- The surface at which char formation takes place reacts through oxidation & sublimation with the boundary layer and material is depleted causing recession. This is due to exothermic or endothermic reactions.
- Convection heat transfer to surface is reduced due formation and movement of pyrolysis gases into boundary layer as these gases makes denser medium in vicinity

The working mechanism for ablative materials is shown in figure 1.12.

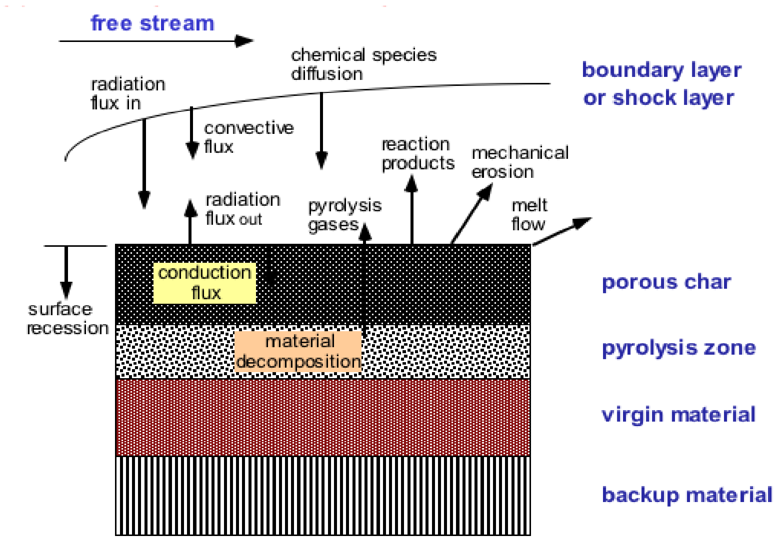

Figure 1.12: Ablative Mechanism

The ablative TPS is most suitable for external thermal protection of composite rocket motor casing based on functional and various process requirements in case of present work. The operational requirements of composite rocket motor case are for single time use and low density ablative thermal protection is highly suited.

1.7 Research Work Plan

Present research work is carried out as per plan given in following flow chart:

Identification of research area as “Development of external ablative thermal protection system for composite rocket motor case”

↓

Literature review: Composite materials, composite processes, Thermal protection systems, ablation, ablative materials, thermal tests

↓

Testing and evaluation of carbon epoxy composites: manufacturing of samples, Mechanical properties at ambient and elevated temperature, Glass transition temperature

↓

Experimental studies on resins for ablative thermal protection system by Thermogravimetric analysis (TGA) and Dry scanning calorimetry (DSC) for Resin selection

↓

Thermal experimental studies for thermal protection system (TPS) to finalize TPS material and configuration: manufacturing of samples and missile sub scale model, thermal tests on samples and model, wind tunnel tests on model

↓

Process development for external ablative thermal protection system over composite rocket motor case and verification and validation of developed process through Ultrasonic, radiography and internal hydrostatic test

↓

Completion of present research work scope by “Development of external ablative thermal protection system for composite rocket motor case”

1.8 Objectives of Present Research Work

The present research work is aimed for development of external ablative thermal protection system for composite rocket motor case is planned in four major experimental studies in form of following research objectives.

1. Generation of mechanical properties for Carbon-Epoxy composite at ambient and elevated temperature through experimental testing and evaluation. This carried out with aim to generate test data which ia required for thermal protection scheme.
    - Laminate, flat and ring specimens manufacturing
    - Mechanical testing of Carbon roving, Flat specimens, Filament wound Ring specimens
    - Ring specimen tensile strength testing at elevated temperature
    - CE composite and Epoxy Resin testing for Tg and Cure Characteristics
2. Evaluation of thermal characteristics of resins through experimental studies and their comparison to select suitable resin for ablative thermal protection system.
    - Selection of Phenolic Resin and Silicone Resin
    - Samples preparation
    - Thermogravimetric analysis (TGA) and Dry scanning calorimetry (DSC) studies on both Resins for thermal stability characteristics
3. To finalize configuration of thermal protection layer and material, experimental studies on TPS samples by IR thermal test were planned
    - Manufacturing of Samples
    - Thermal Testing
4. To simulate flow conditions in flight and integrity verification, the experimental studies on ablative external thermal protection layer under shear and flow were conceived.
    - Manufacturing of Subscale missile model with CE and external thermal protection layer
    - Clod blow down test in wind tunnel for virgin model
    - IR thermal test on model and post thermal soaking wind tunnel test
5. Process Development of Ablative external thermal protection layer on composite rocket motor case

- Process development: hand layup for inner layer and filament winding for outer layer
- Process validation through testing and evaluation of integrity between external thermal protection and composite rocket motor case

1.9 Organization of the Thesis

Organization of present research work thesis is given as follows:

- Chapter-I, Introduction: This chapter includes introduction of solid rocket motor, Composite rocket motor case (CRMC), Composite materials, thermal protection system, present research work objectives and organization of thesis.
- Chapter-II, Literature Review: This chapter includes brief of various published research papers in field of rocket motor, Polymeric composites, composite materials, composite processes, thermal protect systems (TPS), Ablation, Ablative TPS, Ablative materials, TPS materials testing, TPS thermal tests, Thermogravimetric analysis (TGA) and Dry scanning calorimetry (DSC) test methods
- Chapter-III, Testing and evaluation of Carbon Epoxy Composites: This chapter includes objectives, mechanical properties testing of PAN based carbon roving by impregnated tow test, manufacturing of CE composite Uni-Directional laminate & specimens, mechanical testing of longitudinal & transverse specimens, manufacturing of filament wound ring specimens, tensile testing of ring specimens at ambient, tensile testing of ring specimens at elevated temperature to determine strength degradation temperature, mechanical testing of neat Epoxy resin, Glass transition temperature (Tg) evaluation for CE composite by (Dry scanning calorimetry) DSC method, summary of test results
- Chapter-IV, Experimental Studies of Resin Systems for ablative thermal protection system (TPS): As resin plays functionally critical role in TPS, this chapter includes objectives, TGA & DSC studies on Phenolic and Silicone resins to determine initial decomposition temperature, ten percent weight loss temperature and char yield, Selection of Resin based on thermal stability characteristics, determination of thermal conductivity of glass silicone and glass phenolic composite specimens.
- Chapter-V, Thermal experimental studies for thermal protection system (TPS): This chapter includes objectives, manufacturing of Carbon Epoxy samples with external thermal protection layer of Kevlar, glass and panox as reinforcement and silicone resins, test set up

details, heat flux profile, thermal test results, finalization of external thermal protection (ETP) layer, Experimental studies on ablative external thermal protection (ETP) layer under shear and flow, manufacturing of sub scale missile model with CE layer and ETP layer, Clod blow down test of virgin model in wind tunnel, Model Infrared thermal test, Repeat cold blow down test after thermal soaking of model, evaluation of test results

- Chapter-VI, Process Development of ablative external thermal protection layer : This chapter includes curing cycle of external protection layer on composite case, details of process for inner layer made up of Panox silicone and outer layer made up of glass silicone, External thermal protection and Composite rocket motor case interface integrity evaluation (by ultrasonic test and radiographic test), Process validation of external thermal protection layer through internal hydrostatic pressure test and results evaluation.
- Chapter-VII, Conclusions: This chapter includes conclusions based on studies carried out for all research work objectives and test results.

CHAPTER 2

LITERATURE REVIEW

2.1 General

The launch vehicles accelerate through earth atmosphere after liftoff with very high velocity, similarly spacecrafts also enter planetary atmosphere usually at extremely high speed. The kinetic heating due to extremely high velocity flights and aerodynamic drag leads to severe aerothermal conditions on vehicle exteriors [9]. The design provisions for vehicle configurations to protect structure and external surface to sustain against such extreme thermal environment are known as thermal protection systems (TPS). Thermal protection systems are essential requisites for various aerospace applications like space crafts, launch vehicles and missiles to protect the primary structure or sub systems from severe kinetic heating due to aerodynamic drags and high velocities. Apart from kinetic heating, thermal protection is also needed for interaction of flames/plumes from engines & motor exhaust with surrounding surfaces and subsystems [10]. In preliminary stages of design iterations and configurations studies of launch vehicles & missiles, the need of various thermal protection systems is also conceived. Design and development considerations and inputs are derived for these thermal protection systems based on overall configuration of launch vehicles/ missiles and their mission objectives. There are different types of functional requirements which needs to be considered for evolving thermal protection schemes during design of spacecraft, launch vehicles& missile systems. These thermal protection schemes will depend on structure configurations, trajectory phases and aerodynamics. One type of challenge occurs during ascent phase when a spacecraft, launch vehicles/ missiles moves through the atmosphere at very high speeds including most severe aero thermal condition during re-entry to the atmosphere again at extreme speeds. These critical aero thermal conditions need to encountered by designing adequate thermal protection to ensure fulfilment of mission objectives otherwise without proper thermal protection, atmospheric kinetic heating generates enough heat which can lead to failure specially during re-entry. A second type of challenge occurs in the surrounding of the engines, auxiliary propulsion systems, reaction control systems during launch and flight[11]. As the vehicle/missile accelerates through the atmosphere, interactions among plumes and interaction between free air and plume generates high pressures that recirculate some of the hot gases towards the airframe section base. These hot gases are prevented from entering the engine compartment and other passages by a thermal shield across the section base. This thermal barrier needs to withstand extreme conditions for intended action times are another type of thermal protection system. Apart from this, radiation of enormous heat of hot gases from propellant combustion is also takes place towards engine compartment.

The non-reusable TPS made up of ablative materials were used on earlier vehicles and space crafts, like Mercury, Gemini and Apollo. In such ablative TPS, the material absorbs heat on exposed surface undergoes ablation phenomenon thus inhibits heat entry in side vehicle [12]. The concept of ablative TPS is very significant even in present manned missions like Russian Soyuz capsules. Thermal protection systems made up of ceramic tiles which can withstand high temperature and blankets consists of insulators which inhibits heat transfer towards vehicle interiors are also being used like in space shuttle Orbiter. The ceramic tiles are brittle and when used as TPS on vehicle exterior are prone for failure even at low impact load. The metallic Armor TPS was developed by NASA [12] to mitigate such disadvantages of ceramic tiles and used in the Venture Star program. In this TPS, the external surface was designed to sustain aerodynamic loads during flight. The external surface is made up of sandwich panels with metallic honeycombs and also consists of insulation materials with fibrous ingredient to inhibit heat transfer towards vehicle interior. The load carrying capacity of such TPS is less against large in plane flight loads and this challenge is encountered through proper design approach to transfer load to vehicle structure. As per design, vehicle configuration and trajectories, the TPS occupies major part of vehicle exterior and contributes for significant proportion of launch weight. During flight, TPS gets exposed to variations in atmospheric conditions & vehicle velocities at different timings as per trajectories design based on mission objectives. The kinetic heating and loads experienced by TPS is primarily function of vehicle configuration (Shape & size) and mission trajectories like space shuttle /long range ballistic missiles TPS experiences different atmospheric conditions during ascent and reentry while space capsules encounter severe conditions only during reentry as shielded by shroud during launch. The design and material selection considerations for TPS are very important to meet functional thermal requirements with light weight.

2.2 Thermal Protection Systems (TPS) Considerations

Thermal protection systems are functionally critical and involves some basic considerations [11] which are summarized as follows:

Thermal Load:

The TPS most fundamental functional requirements includes thermal management on exterior of vehicle. In majority of the cases the governing design factor is aerothermal heating at different instances of flight including most severe conditions during re -entry into earth atmosphere. Based on vehicle design and configurations, the TPS near to propulsion exhaust like rocket nozzle plume, liquid engines exhaust both as reaction control system as well as propulsion is subjected to substantial plume heating. The combustion of propellants generate plume and produces enormous heat after ignition near to nozzles, known as plume heating. In case of cryogenic tanks, TPS is required to function as insulation in order to inhibit heat transfer to avoid formation of liquid oxygen or ice on external surface and also to prevent cryogenic fuel loss like Venture Star. There are some other significant factors for TPS design especially in case of vehicles with mission objectives of spending more time in space are solar heating and heat loss through radiation from exterior to space. The materials play most important role for TPS functional performance and its properties needs to be adequate to sustain high temperature without significant properties degradation.

Flight Loads:

There are various flight loads on vehicle and TPS including lateral aerodynamic pressure loads, in-plane inertial loads, acoustic and dynamic loads. Theses loads depends on vehicle configurations and trajectory requirements and also the location of TPS on vehicles. In case of space shuttle, leading edges on wings & tail, nose shroud faces very high aerodynamic loads. The wind ward side of space capsule experiences very high aerodynamic load however leeward side and other zones loads are very less. The TPS on the read side of vehicle faces considerably high in plane inertial loads than located on front side of vehicle. Propulsion systems are usually source for acoustic and dynamic loads on TPS. TPS must sustain these loads for yielding and buckling modes of failures with adequate margin of safety to meet functional requirements.

Deformation Limits:

TPS is part of vehicle external surface and play very important role for aerodynamic considerations especially outer profile. Thermo-structural loads expected during flight causes deflection on external surface and such deflections needs to be with in specified limits in order to maintain the aerodynamic profile. If there will be any high local deflection in outer surface, will cause local kinetic heating and can lead to failures.

Impact Loads:

Vehicle TPS experiences impact loads mainly during launch, stage separations, rocket motor ignition, re-entry into earth atmosphere and landing. TPS material impact resistance another functionally required property. TPS is required to withstand impact by space debris and other objects.

Chemical Stability:

TPS material should be able to withstand high temperature including during most severe thermal conditions like re- entry and should not undergo oxidation. TPS properties should not be affected due to moisture absorption and other substances during storage and maintenance. TPS material should have good chemical stability to resist such factors.

Maintainability:

Maintenance of TPS during entire life cycle is also desirable. TPS can be periodically inspected and if required there should be scope to repairs for any observations. In case of any requirement, it should be possible to replace and repair the TPS.

TPS Weight:

TPS constitutes considerable area on space vehicles and contributes for good proportion of the launch weight. It is always desirable to design and configure TPS with minimum possible weight. This is usually achieved by optimized design practices considering contradictory requirement and critical selection of materials based on their properties and density.

2.3 Thermal Protection System Approaches

TPS specific functional requirements and design considerations broadly depends on vehicle configuration, various flight parameters based on trajectory requirement. Accordingly, TPS types and their design depends on various deduced inputs like expected heat fluxes with duration, objective and location on vehicle. TPS approaches [13] classification can be done in three types: active, semi-passive, and passive given as follows:

Active TPS:

In active TPS coolant is circulated continuously as heat exchanger to carry away heat and prevent heat transfer in to structure. Due to such requirements, the active TPS needs to be equipped with external system to supply and regulate continuous coolant circulation. Active TPS working mechanisms are based on three concepts: transpiration, film and convective cooling. The transpiration and film cooling are based on fluid circulation along external surface. Vehicle configuration needs to include provision for fluid ejection and flow along surface. Heat generated due to aerodynamic kinetic heating is absorbed by the fluid and it gets evaporated and thus inhibiting heat recession into vehicle. In convective cooling also fluid gets circulated through groves in airframe to carry way heat absorbed due to kinetic heating. This is relatively more feasible and application-oriented concept. In all types of active TPS external setup consists of pump, fluid accumulator is needed for coolant circulation up to vehicle surface. There are some disadvantages of active TPS including more weight addition due to coolant and pump system, difficult maintenance and complexities in design.

Semi-Passive TPS:

Semi-passive TPS concept working is also based on heat transfer through fluid without external pump system for fluid circulation. There are two main semi-passive TPS working mechanisms: heat pipes and ablators. Heat pipes applications are specific when there are high heating localized zones closer to cooler zones. The working mechanism of heat pipes are based on heat absorption by fluid in hot zones, vaporization of fluid, vapor flow to cooler zone followed by condensation after heat exchange to cool structure. The coolant is circulated back to hot zones by capillary action. Ablators working mechanism is very simple in which generated kinetic heat gets absorbed by exposed surface. Ablator after absorbing heat undergoes decomposition, pyrolysis and other chemical changes with char formation and generate gases due to exothermic reactions and prevent heat transfer to vehicle surface. Ablative materials concept for thermal protection were most practical and widely being used like in space capsules Apollo and Soyuz.

Passive TPS:

Passive TPS working mechanism is based on radiation from external surface as any hot object radiates heat to atmosphere. In this case, heat is absorbed by surface material during more heat flux period and gets radiated outside when heat flux reduces. Passive TPS application is limited to very low heat flux conditions. Design is simplest for passive TPS with limited application. There are mainly three types of passive TPS given as follows: heat sink, hot structure and insulated structure:

In heat Sink, major proportion of total heat being exposed to TPS gets absorbed in it. The total heat which can be absorbed depends on material heat capacity, material maximum allowable temperature and TPS initial temperature. When exposed heat is high, the TPS material increases with condition that maximum expected temperature lies below service temperature. This concept was implemented in early long-range missile systems and reae end bodies of re -entry vehicles of Mercury and Gemini. Heat sink approach design being simple is main advantage with limitation of low heat working.

Hot Structure working mechanism is based on increase of exposed TPS surface temperature close to radiation equilibrium temperature. This leads to radiation of major proportion of heat to outside. The temperature of TPS surface at which heat flux ejected out through radiation becomes equal to incoming heat flux is defined as radiation equilibrium temperature. The material for hot structure is very critical for thermal stability and thermo structural properties must withstand extremely high temperatures. The radiation equilibrium temperature is of the order of 2500 F to 3500 F for aerothermal conditions & heat flux of re- entry for missiles and space shuttles like Orbiter.

Insulated Structure working mechanism is based on combined concept of hot structure and heat sink. In such TPS, insulating material layer is configured on external surface and hence beneath structure is fully insulated. Insulation layer inhibits heat recession inside and only fraction of incident heat recedes. As a result, temperature on outer surfaces increases till radiation equilibrium temperature and then starts most of heat radiation outside. The absorbed fraction of incident heat reaches structure and it function as heat sink. Insulation TPS have limitation for load carrying capacity against significant mechanical and insulation material are usually of low density.

The advantages of active TPS approaches include TPS performance for high heat fluxes and considerable duration. However, design of such TPS are complex and involves technical challenges apart from operational difficulties, maintenance issues and increased launch mass. Due to such limitations, such TPS are limited to localized zone of high kinetic heating and find less applications. Passive and semi passive TPS are most widely used for vehicle external surfaces.

2.4 Historical Research Overview of TPS at NASA

NASA has been prime agency since inception in 1958 for research and development of systems and technologies related to manned space flight [12]. The manned flights involved lot of technology challenges and TPS has been one of the foremost critical. TPS evolution at NASA can be manifested through early manned space vehicles: Apollo, Space shuttle Orbiter and X33 Venture Star. The objective of Apollo program (1963 to 1972) was to carry men to moon and return them back to Earth safely. Saturn V rocket was designed with three stage solid propulsion to launch space craft into space with mission objective to reach moon. TPS for Apollo was critical and basic concepts and design were adopted from two prior man space flight namely Mercury (1959 to 1963) and Gemini (1963 to 1966) to develop its TPS [12]. Apollo command module carried crew to moon and after mission completion, it was only component which returned back to earth. The design of this module was done considering ballistic re -entry into earth atmosphere with very high speed of the order 9725 m/s. The re -entry conditions were extremely severe to generate very high aerothermal loads and kinetic heating load carrying on fore end and lower heating on aft end. Ablative TPS was configured for these capsules due to high heat flux. Considering this program requirement, lot of ablating materials were developed, out of which low density AVCOAT 5026-39/HC-GP was selection for this application. The NASA space capsules are shown in figure 2.1(a),(b),(c) and (d).

Figure 2.1(a): Mercury

Figure 2.1(b): Gemini

Figure 2.1(c): Apollo

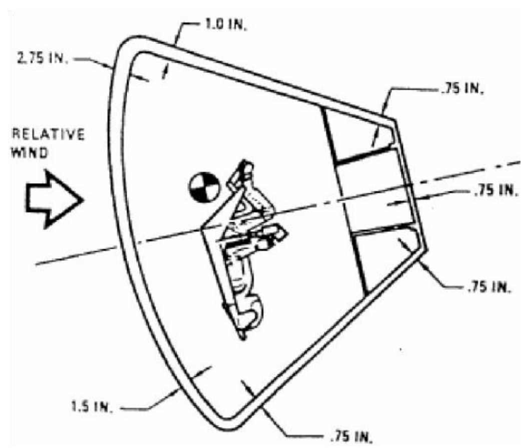

Figure 2.1(d): Apollo ablative thickness

Figure 2.1: Space capsules (Courtesy: NASA Report)

The ablative TPS of Apollo heat shield made up of fiberglass reinforced-nylon-phenolic honeycomb structure [13]. The heat shield structure configuration consists of aluminum honeycomb panel at base as primary load carrying member [12]. The stainless-steel honeycomb substructure was assembled above base panel. By design, to take care of differential thermal deformation a strain isolation system is used between both panels. Design criterion for ablator thickness was considered as maximum allowable temperature at ablator and stainless-steel panel to be 600F. In Apollo mission space capsules were meant for single time use and none of sub systems were used for subsequent mission.

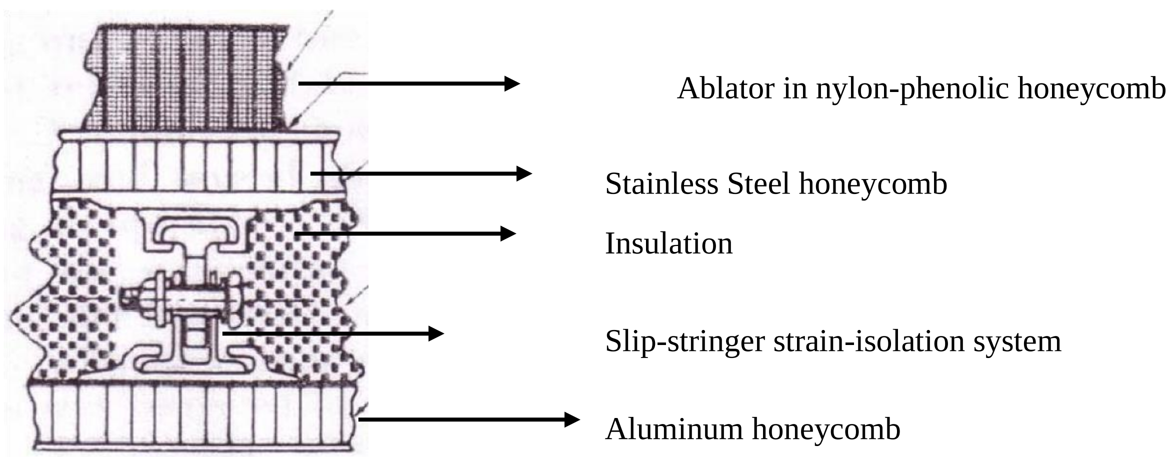

Figure 2.2: Apollo Thermal Protection Structure (Courtesy: NASA Report)

Orbiter manned Space Shuttle development commenced in 1960 with concept of airplane shape with vertical liftoff and horizontal landing Orbiter which was much different than space capsules. The reentry phase was very critical in this case as navigation was like airplane except with very high velocity. The reentry for space capsules were ballistic reentry and duration was short however in case of Orbiter space shuttle reentry trajectory was loner and much higher duration. Space shuttle external profile was also complex in comparison to space capsules. Due to complex aerodynamic profile, high heat flux and longer duration, the total heat input was high and TPS design and materials performance were critical. In this case passive TPS made up of heigh heat resistant ceramic tiles were used for majority of external surface. The first manned orbiter space flight took place in 1981.The various TPS materials used for space shuttle surface include carbon-carbon composites, different types of ceramic tiles and ablative materials based on locations on vehicle[13]. Carbon-carbon composite were used for the zones where heat flux rates were very high like nose cap and leading edges. The considerable exterior of shuttle was configured with ceramic reusable surface insulation tiles which were of two types viz. high and low temperature surface reusable surface insulation. At some zones based on loading condition, fibrous refractory composites having more strength were used as replacement for high temperature reusable surface insulation material. The Orbiter thermal protection details of Orbiter are given in figure 2.3.

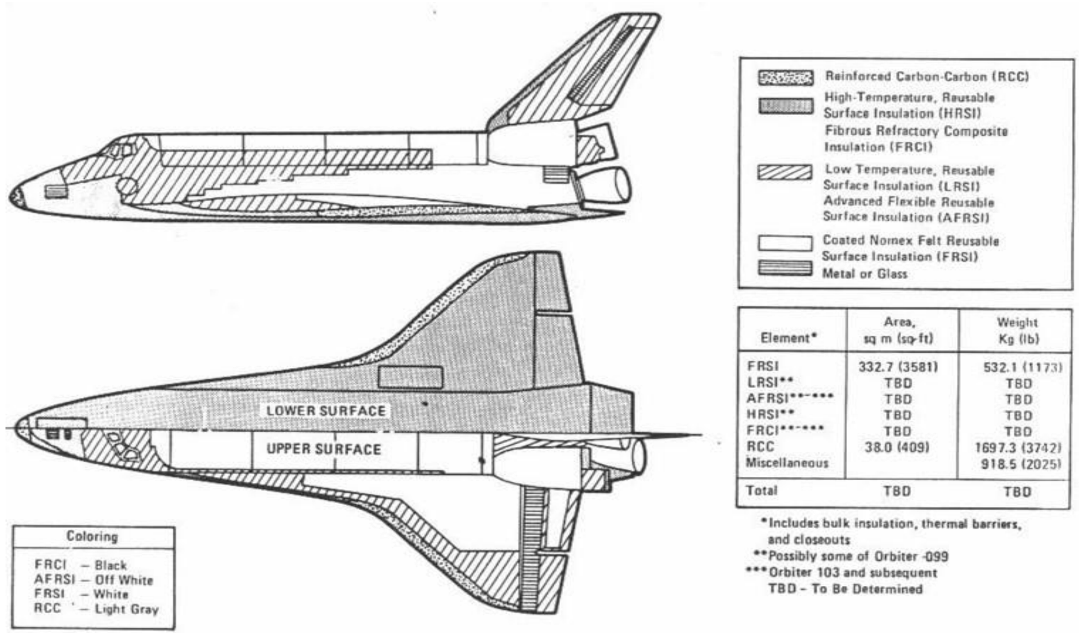

Figure 2.3: Details of Thermal Protection System of Orbiter (Courtesy: NASA Report)

Advanced flexible reusable surface insulation material was developed and were used to replace low temperature reusable surface insulation of leeward side of space shuttle [12]. The ceramic tiles cannot be used as structural load bearing member due to their highly brittle nature, low impact strength and have very low failure strain. In this case, structure frame was designed to withstand mechanical loads. The structural frame was made up of Al alloy and tiles were bonded on load bearing frame. Al alloy have high coefficient of thermal expansion compared to ceramic tiles and if tiles are bonded directly on frame will develop high tensile strains and can lead to crack initiation during thermal exposure. Strain isolation pads having low shear and young's modulus were used at ceramic tiles and structure frame interface to avoid cracking problem [12]. Tiles dimensions were approximately six inch or less and tiles layout were made with gap between tile edges to accommodate Al alloy frame expansion or contraction during thermal exposure. The tiles assembly with metallic structure is shown in figure 2.4.

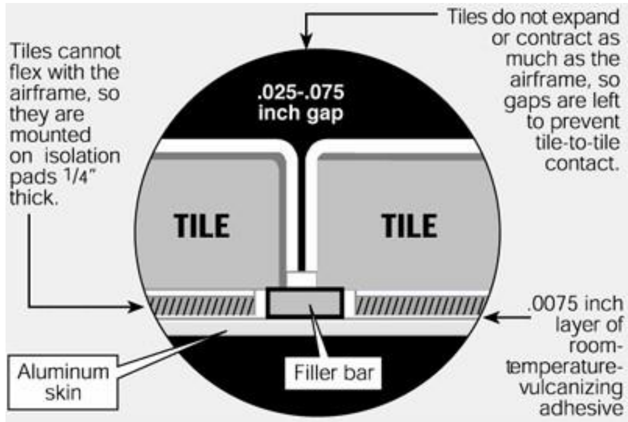

Figure 2.4: Configuration of tile on metallic structure (Courtesy: NASA Report)

Silicon polymer coating were also applied before flight to ensure water proofness. Tiles maintenance between launches was cumbersome and cost intensive. TPS was meeting functional requirements but always used to be prone for damages. All such issues led to very high cost of space shuttle flight besides structure prone for various problems.

The Venture Star reusable launch vehicle program was commenced in 1990. This vehicle was configured with Boeing spike engine and having single stage to orbit concept. The take-off and landing provisions were similar to space shuttle with all fuel tanks or motors were equipped inside vehicle. This concept led to increase of Venture Star size in comparison to space shuttle which in turn caused external surface area to be large for TPS lining. The Venture Star program was called off in 2001 due to enormous delay, technical issues and cost over runs but lot of TPS related technologies were developed. During TPS development of Venture Star, the prime objective was to resolve various technical issues related to ceramic tiles based TPS of Space shuttle and to evolve good design. As per Venture Star configuration layout, internal volume was mainly equipped with cryogenic fuel tanks and concept of almost fully metallic TPS was proposed in 1990. This TPS was configured to get assembled with cryogenic tanks frame structure. This TPS was named as ARMOR which elaborates as adaptable, robust, metallic, operable, and reusable [12]. The ARMOR thermal protection construction details are shown in figure 2.5.

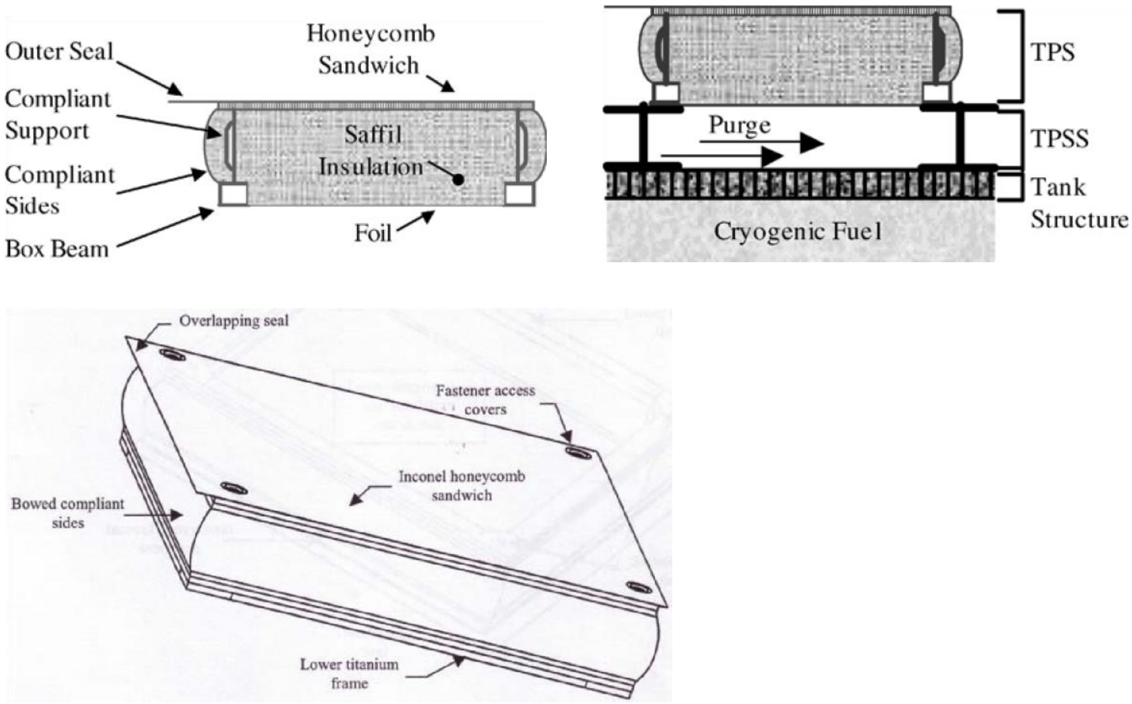

Figure 2.5: Construction details of ARMOR Thermal Protection System

(Courtesy: NASA Report)

ARMOR thermal protection system consists of honeycomb sandwich panel made up of metallic material on top surface and designed to sustain small load due to aerodynamic pressure distribution. Top surface attains high temperature after getting exposed to heat and re-radiate substantial part of transferred heat on TPS. The top honey comb panel was provided with thick insulation layer made up of alumina fiber known as Saffil material. The insulation material was housed using thin metal foils at side and bottom. The sides of such foil were bulged and were inhibiting radiation between panel gaps. To restrict hot gases entry at panel gaps during reentry, the top surface of panel length was more to provide required overlap with adjacent panel for sealing action. At bottom surface titanium frame was used for attaching TPS with basic structure. There were provisions of vent in insulation material for venting out inside pressures through bottom titanium foil. This provision facilitated for aerodynamic load bearing by top honey comb panel surface. As per design, load on top panel was transferred to titanium frame through four brackets. These brackets were designed based on low stiffness for bending stress to allow for required deflection of top surface in order to reduce thermal stresses in panel. ARMOR thermal protection system load bearing capacity is limited for aerodynamic load, in-plane loads and can withstands relatively lesser load due to propulsion, aerodynamics and acoustic. This thermal protection system being metallic is advantageous for impact resistance properties and less prone for damage unlike in case of space shuttle thermal protection system. ARMOR thermal protection system design was based on blend of both hot structures along with insulation concept to meet functional requirements with light weight thermal protection system. This thermal protection system design also functions as heat sink and absorbs proportion of heat due to high heat capacity of used insulation materials. The various metallic based thermal protection system designs options were worked out for reusable launch vehicles prior to ARMOR thermal protection system. One of the main thermal protection systems which got developed and qualified for X33 was based on Inconel honeycomb panel. This thermal protection system configuration consisted of insulation to withstand high temperature inside and at bottom titanium foil was used. Panel was designed with mounting feature to frame structure through bolted joints. The venting provision were also incorporated so that loads due to aerodynamics were sustained by frame structure instead of panel. Later the ARMOR thermal protection system design was also optimized to reduce weight by using superalloy honeycomb. In such design multilayer of flat and dimpled metallic foils were used alternatively which reduced radiated heat towards inside from top surface. In some design options, the multi layered foils were made with gaps to reduce heat transfer. This concept facilitated for heat conduction through long foil and led to low effective thermal conductivity through panel. The manufacturing of multi layered thermal protection system was complex and gap evacuation was further challenging. Even with this much inherent complexities multi-layer thermal protection system found to have twice thermal conductivity than ceramic tiles thermal protection system for space shuttle.

In initial thermal protection system developmental phase, there was deep impact of concepts and design approaches from ballistic missiles. One of the prominent ideas of blunt body shape emerged from missile design which helps major heat to be transferred away due bow shock wave formation. Based on application various thermal protection system are known as leading edge thermal protection system, acreage and inside thermal protection which all broadly can be classified as reusable or ablative. In case of reusable thermal protection system, no material properties get change and with some refurbishment thermal protection system is reused after mission. Ablative thermal protection system application is for high heat flux and aerothermal load, such material undergoes decomposition, pyrolysis, phase change, char formation and material loss due to heat absorption. Concept of ablative thermal protection system with blunt body was very advantageous as due to bow shock wave considerable heat was rejected and reradiated instead fully getting absorbed. Ablative thermal protection system application was adopted in Apollo and Orion missions. In beginning of Apollo program, the most challenging requirement was for thermal protection system to sustain the aerothermal environment during return from lunar orbit. There was also need to protect thermal protection system from meteoroids and debris apart from withstanding vacuum and ultraviolet. Ablative heat shield was configured to meet aerothermal environment during reentry from lunar orbit [13]. This heat shield worked on ablation mechanism and material loss happened which caused it for single use. In case of crew module, the constraint on interface temperature of ablative liner and metallic backup was 600^0F during reentry for design. The ablative material selected for such application was having constituents viz Avcoat 5026-39, epoxy novolac resin and fiberglass honeycomb. The Apollo thermal protection system construction details are shown in figure 2.6.

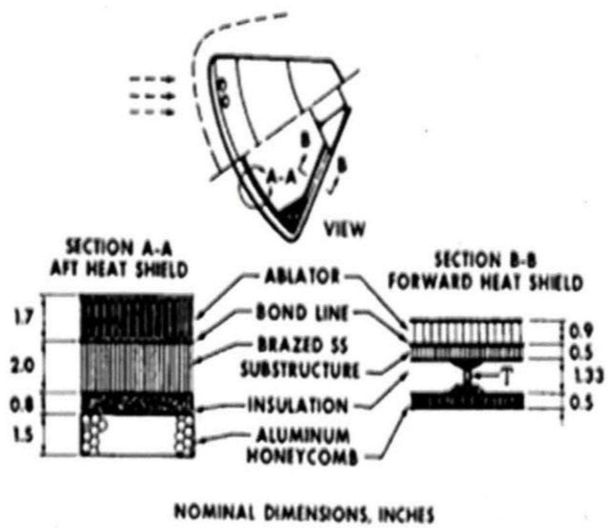

Figure 2.6: Thermal Protection system details of Apollo (Courtesy: NASA Report)

NASA thermal protection system types and mass fraction for historic crewed vehicles are given in following figure 2.7:

	MERCURY	GEMINI	APOLLO	SHUTTLE
DATE No. of flight	10/7/58 - 5/16/63 6 flights	3/23/65 - 11/15/66 10 flights	10/11/69 - 12/19/72 11 flights	4/12/81 – 3/9/11 133 (131) flights
				
AREA	32 FT^2	45 FT^2	365 FT^2	11 895 FT^2
WEIGHT	315 LB	348 LB	1465 LB	18 904 LB
WT/FT^2	10.2	7.5	3.9	1.7
MATERIAL	ABLATOR (FIBERGLASS-REINFORCED LAMINATED PLASTIC)	ABLATOR (DOW CORNING DC 325)	ABLATOR (AVCO 5026-39)	Rigidized silica fibers
DENSITY	114 LB/FT^3	54 LB/FT^3	33 LB/FT^3	9-22 LB/FT^3
USAGE	1 FLIGHT	1 FLIGHT	1 FLIGHT	133 (131) FLIGHTS
Vehicle Weight	**2724 lb**	**4861 lb**	**11500 lb**	**180,000 lb**
TPS Mass Fraction	**11.6%***	**7.16%***	**12.8%**	**10.5%**

* TPS Mass only includes heat shield, and not the metallic backshell

Figure 2.7: Thermal Protection System History (Courtesy: NASA Report)

2.5 Research Papers Summary:

The comprehensive literature review is carried out covering main focus on composite materials, composite material characterization, composite manufacturing processes, solid rocket motor, FRP composite rocket motor case, composite case manufacturing , Thermal protection system, Thermal protection approaches, Thermal protection Types, Thermal protection working mechanism, Ablative thermal protection system, ablation, ablative materials, Resins cure characteristics, Thermogravimetric analysis technique, Dry scanning calorimetry method, composite case hydrostatic pressure test and NDT techniques for composites. The research papers, articles gist which are useful to develop concept and methodologies to carry out present work are given as follows:

Charles W. Bert, Walter S. Hyler (1966) This paper includes details of solid rocket motor elements namely rocket motor case, internal insulation, igniter, propellant grain and nozzle. Motor case is major sub system of solid rocket motor. Material details and various structural failure issues encountered for motor cases are discussed in paper. Solid rocket motor also constitutes part of primary structure for vehicles and needs to sustain for all flight loads apart from internal pressure.

L. H. Caveny, Huntsville (1969) This invention was regarding possible modifications in thermal protection system for missile systems to have effective thermal management during aerothermal conditions. This invention was specifically adapted for missiles with solid rocket motor as propulsion system, so that temperatures on structure could be limited with in allowable limits. This was absolute essential requirement as structural materials properties degrades with increase in temperature beyond limits for missiles to meets its mission objectives. Thermal protection system was functionally catering to keep various interface temperatures with in conducive limits for adhesives and bonding materials.

R.J. Schwighamer (1977) This paper research background was on re-useability requirement of Space shuttle subsystems to achieve low-cost missions. The Space Shuttle configuration consists of Orbiter, an external tank, main engines and two solid rocket boosters. The external tank carries propellant for main engines and two boosters to meet requirement in ascent phase. The external tank is consumed in each flight however Orbiter and solid rocket boosters were reusable. The reusability requirements forced lot of challenges for new material and processes developments This paper includes details of materials, manufacturing processes and space shuttle mission. This paper also described various aspects of material section, control system reliability and various criticalities related to main engines, external tank and solid rocket boosters.

Chase, Michael John (1990) This paper described concept of thermal insulator for rocket motor surface which was configured as sleeve for external surface**.** The sleeve consisted of composite cork on outer side and layer of polymeric composite made up finer having low thermal conductivity. Two basic factors which were critical for temperature point of view were first burning rate of propellants and maximum expected temperature of burning grain inside motor case and second polymeric materials, elastomers and adhesives used for rocket motor casing. This polymeric materials strength degradation typically starts at 100°C.

Howard and D. Trudeau (1990) covered all elements of solid rocket motor along with basic design concepts. The design of three segment metallic rocket motor with bolted joints of flanges, insulation details, propellant are described.

James R. Sides, Oakton, Va. (1994) This paper covers concept of motor case consists of aluminum barrel and composite layer build up around barrel. The basic purpose of this composite overwrap layer is mentioned as protection layer for operators in case of barrel failure due to presence of internal insulation defects during firing. This composite layer was manufactured with fiber reinforcement and resin with low curing temperature. Composite layer was manufactured separately and bonded to barrel. This bonding required surface preparation on barrel surface which had projections also and, on these locations, fiber impregnated with low temperature curable resin was wrapped and cured.

L. Torre et al (1998) This paper described the application of thermogravimetric analysis (TGA) and other thermal analysis techniques for evaluation of ablative composite properties for application as thermal protection system. In this work these techniques were applied to generate various characteristics which were required for simulation studies of space reentry. Specifically modelling of silicone-based composite was done for degradation kinetics using TGA in conjunction with mass spectroscopic analysis. In addition, heat of ablation for silicone-based composites were also calculated through thermal analysis.

Y.H. Andoh , B. Lips (2003) This included development heat transfer model based on energy balance equation for porous plate subjected to high heat fluxes**.** In this study, the important selected parameters were the volumetric heat transfer coefficient, the equivalent thermal conductivity of the material and fluid flow characteristics. The study also included effect of these parameters on each other to arrive at relative comparisons. The results were verified for porous material subjected to heat flux corresponding to 3500 K followed by cooling through refrigerant.

Raffaele Savino et al (2005) This paper covers study on thermal response of Ultra High Temperature Ceramics (UHTC) through CFD analysis and thermal models. Ultra-High Temperature Ceramics (UHTC) were considered as potential thermal protection system for re-usable reentry vehicles. The numerical approach was adopted for such studies. Based on analytical approaches, aerothermal heating effects on sharp vehicle nose was predicted through combined flow and thermal conditions models in TPS. Various approaches were considered for this analysis accounting effects of surface catalysis and laminar-turbulent transition.

Satish Kumar Bapanapalli (2007) This work covers overview of TPS approaches, Thermal protection systems (TPS) are essential feature to protect space craft against severe aerothermal environment due to its very high speed and planetary atmosphere. The concepts of ablative TPS were incorporated in space capsule Apollo and high temperature resistant tiles, blankets on the Space Shuttle Orbiter for thermal protection over load bearing structures. Due to thermal characteristics incompatibility like coefficient of thermal expansion of ablators, tiles and structures, the external surface becomes prone for damages or crack. In present research, Integral Thermal Protection System (ITPS) concept was evolved for space craft external surface to be reasonably robust.

Bernard Laub et al (2008) This paper covers fundamental related to thermal protection system, extreme aerothermal conditions, material**s** and characterization techniques. Entry of high velocity vehicles into planetary environment is most severe thermal condition. This entry aerothermal conditions govern selection of ablative TPS for any mission. There are various contradictory requirements like ablative TPS with high density undergoes less ablation but will have high weight, hence TPS selection is comprehensive and critical. Based on the studies it was concluded that Arc plasma test technique generate test conditions very close to atmospheric entry conditions. Ablative materials were always potential option for thermal protection since beginning phase will be very vulnerable in future.

F. Gori et al (2008) This paper covers transient thermal analysis with FEM code to check adequacy of second stage Vega Solid Rocket Motor (SRM) base thermal protection system. The work has evolved suitable numerical Fortran subroutines for radiation and convection boundary conditions.

Joseph H. Koo et al (2009) This paper covers evaluation of silicone polymer composites using a Simulated Solid Rocket Motor, a Scaled Ducted Launcher, and a Quarter Scaled Launcher subjected to solid rocket exhaust plume. The organic Silicone polymer gets transformed to a ceramic or silica structure when gets subjected to high temperature or flame impingement which adds for excellent thermal stability. This research work was aimed to characterize silicone polymer composites as thermal protection systems for defence applications. This paper includes studies on effect of reinforcement variation for its form and type, type and proportion of fillers on thermal performance of silicone polymer composite materials. The studies included various types of reinforcements like glass, silica, quartz, Nextel, and Nicolan in their different forms such as random continuous-fiber mat, chopped-fiber mat, 2-D fabric, chopped roving, and broad good tapes with different ply angles. The filler proportions were varied for Silica and alumina fillers for testing and evaluation. The characterization for the phenolic-based composite and silicone-based composites were conducted to compare average material mass loss and peak erosion. Thermal protection performance of silicone-based composites was superior to conventional phenolic-based composites.

Joseph H. Koo et al (2010) This paper extended the work of previous studies and carried out evaluation of silicone-based composites by varying more types and forms of reinforcement and proportion of fillers for thermal performance

Xiaoving Zhang (2011) present paper includes description of the temperature distribution on the rocket nozzle ablative liner in excessive high temperature environment through simulations which is very important to assess and predict nozzle performance during motor action time. The approach of coupling simulation of heat transfer and transient temperature of the rocket nozzle liner is adopted.

Peter Gerd Fisch et al (2011) This paper cover concept of designing solid rocket motor with outer casing and separate chamber for combustion. This combustion chamber was housed in outer casing. This configuration facilitated for simplification in attachment of fittings due to combustion chamber being separate component. A new concept of configuration is described, combustion chamber is housed in side outer casing. The combustion chamber is manufactured from polymeric composite materials. The outer casing is designed to withstand all the flight loads apart from internal pressure and material can sustain relatively high temperature than polymeric composite.

Anthony M. Calomino et al (2012) This paper covers various factors for design of TPS and various inherent uncertainties in analysis and material properties. Mission success of any planetary atmospheric entry is critical to design of TPS. In design and analysis of TPS, there are various uncertainties such as Aerothermal conditions prediction, material properties, material response prediction to thermal environment. These uncertainties were managed through conservative design margins which usually results into increased TPS mass. In present work improved modelling techniques were adopted and resulted into reduction in TPS mass.

Lu Haibo, Liu Weiqiang (2013) This paper brings out concept of combining configuration of forward facing cavity and opposing jet as thermal protection system for hypersonic vehicles. In present work combined configuration with hemisphere- cone nose-tip was evaluated numerically in hypersonic free stream conditions. The numerical rests were also validated through experimental results.

Martin Alberto Masuelli (2013) This paper covers brief review of unique and broad prospects of application for FRP composites like, Polymers, Aramids, Composites, Carbon FRP, and Glass-FRP. In case of such materials properties are driven by chemistry aspects which plays significant role in defining their applications. Most with such materials there is always tradeoff between processing aspects and functionality.

Fiore V and Valenza A. (2013) This section covers details related to properties and characteristics of epoxy resins. Epoxy resins are thermosetting resins having very versatile properties which are very conducive for manufacturing processes. The resin mechanical properties are excellent and very suitable for structural applications. The effect of various fillers on epoxy resin properties are also studied.

J. E. Millera et al (2015) This paper describes details of thermal protection systems which were made of porous materials and monolithic. These TPS were majorly configured on the Apollo command module, and also on the next generation of US manned spacecraft, Orion. These TPS protects and insulate spacecraft surface and components against severe aerothermal environment during atmospheric reentry. TPS is also exposed to various possibilities in space like solid particles impacts. This paper also included studies related to impact up to 10 km/s on Avcoat ablator having density of .56 g/cm3 .

Cong Zhang et al (2015) This paper describes various approaches and methods which were used to develop TPS of hydrogen fueled scramjet for cooling of engine. To meet challenging functional requirements of high Mach no scramjet flight for long duration, the combined thermal protection system was developed consisting of active and passive thermal protection systems.

D.D. Jayaseelan et al (2015) this describes about Multi-layered TPS made up of UHTC composites to withstand severe oxidation environment. These TPS were manufactured by co-sintering process. This TPS consisted of three layers: (i) Outer most layer designed to function for heat flux exposure more than 25 MW m^{-2}, (ii) Intermediate layer with specific characteristic to reduce diffusion of O_2 and (iii) bottom layer to have with better performance at high temperatures.

Weijie Li et al (2016) this paper covered modelling approaches for charring composites. The performance of TPS in reentry vehicles under severe aerothermal heating were predicted with nonlinear pyrolysis model. These studies lead to optimization of TPS. The thermal characteristics of charring composites under exposure to aerothermal heating were simulated through computer software.

Zhongmin Deng et al (2016) This paper covers heat transfer analysis for thermal protection system hypersonic aircrafts through various analytical and experimental studies**.** Thermal protection systems (TPS) are most significant for hypersonic aircrafts and performance of TPS depends on temperature field due to aerothermal conditions. Temperature fields involve lot of uncertain factors and therefore in this paper approaches with uncertainty analysis were adopted for reasonable results.

Alvaro Rodriguez et al (2016) TPS design for Space shuttle involved lot of technical challenges to meet critical functional requirements such as insulation, material thermal characteristics and other configuration constrains. The Orbiter's external surfaces were subjected to severe aerothermal environment and required to be reusable low density TPS. There was additional challenge involved due to bonding of Orbiter's thermal protection directly over aluminum skin. The TPS was required for External Tank to maintain, liquid hydrogen, and liquid oxygen apart from catering for required structural integrity through launch and after release from the Orbiter.

M.Rivier et al (2019) The ablative Thermal Protection System (TPS) were designed for Stardust spacecrafts for their atmospheric entry with hypersonic velocity. Phenolic Impregnated Carbon Ablator (PICA) material which were advanced got application in the Stardust mission as TPS. PICA was low density with excellent thermal responses and found lot of aerospace applications. During atmospheric entry under severe thermal conditions, Phenolic undergoes pyrolysis and other complex heat and mass transfer phenomenon and computer program with simulation tools were used for analysis.

Obinna Uyanna, Hamidreza Najafi (2020) In this paper, technology development and evolution for various types of TPS from mid twentieth century to the present time is presented as detailed survey. Thermal Protection System (TPS) is functionally critical and most needed component of space vehicles which protect them against severe aerothermal heating during entry in atmosphere. Paper also covered various types of TPS incorporated for reusable launch vehicles and present status of available TPS technology.

Rachid Hsissou et.al (2021) This paper coves detailed review of polymeric composite materials with thermosetting, thermoplastic and elastomers are matrix materials. The reinforcement for such advanced composite materials includes organic, inorganic having various fillers. The various critical concepts and fundamentals related polymeric composite materials with explicit details of reinforcement and matrix are also covered. The unique composite materials properties like mechanical properties, thermal properties, impact properties, corrosion resistance related to various formulations and constituents of composites explained.

Subramani Devaraju and Muthukaruppan Alagar (2021) Composites based on polymeric matrix are most vital for many critical applications especially aerospace. Due to lot of advantages and composites high performance, manufacturing flexibility and tailored strength properties makes it highly suitable for aerospace applications. Composite materials advancement is leading to replacement of conventional materials from various areas and components. This paper covers various aspects for application of polymeric composites in aerospace with more details on effect of thermoplastic and thermosetting resin on composite properties and their application.

Dermot Brabazon (2021) This article covers comprehensive review of composite materials, various manufacturing processes and properties of polymeric composite materials. The effect of type and form of various reinforcements and matrix materials studied and covered. The detailed review of manufacturing process parameters, obtained properties and characteristics along with criticalities related to applications are covered.

2.6 Gap Analysis

In literature review, considering present research work, the following few gaps are observed:

- Thermal protection system (TPS) is specific field required for launch vehicles, space crafts and long-range ballistic missiles and explicit details of research works are not available for open access
- No specific research work is reported for external thermal protection of composite rocket motor casing
- TPS Types and various approaches are available in broad sense without critical details
- TPS materials reported in literature are of specific grade and make available in particular country
- TPS concepts are available, however materials selection and process development for external ablative thermal protection system for composite rocket motor are not reported

2.7 Summary

In comprehensive literature review, various research papers, review papers, articles and NASA technical reports are studied related to thermal protection systems (TPS), TPS types, TPS approaches, TPS materials, Material testing and characterization, polymeric composite materials and composite manufacturing processes. Based on literature studies for TPS concepts/ approaches, other functional and process related considerations, the ablative thermal protection approach found suitable for protection of external surface of composite rocket motor case against kinetic heating during flight. The literature review got further focused on ablative TPS, ablative TPS working mechanisms, ablative materials, ablative materials testing, resin studies through Thermogravimetric analysis (TGA) and Dry scanning calorimetry (DSC), Filament winding process and hand lay-up process for polymeric composites. The various concepts learned from literature review were helpful to formulate difference studies as research objectives to achieve goal of present work to develop ablative external thermal protection system for composite rocket motor case.

CHAPTER 3

EXPERIMENTAL TESTING OF CARBON EPOXY COMPOSITES

3.1 Introduction

Composite Rocket motor case is made up of polymeric composite materials with Polyacrylonitrile (PAN) based carbon fibre as reinforcement and Epoxy resin as matrix[14]. Carbon fibre is principal load carrying constituent, hence composite mechanical properties depend predominantly on fibre properties. Epoxy resin major role is to act like load transfer medium, to protect fibres and keep them in required orientation. Resin properties such as viscosity, viscosity build up after hardener mixing, gel time and pot life are very critical for wet filament winding process used for manufacturing of composite rocket motor case. Carbon-Epoxy Composite glass transition temperature (Tg) predominantly depends upon epoxy resin cure characteristics and neat resin Tg. Epoxy resin properties, cure characteristics and Carbon-Epoxy glass transition temperature (Tg) are significant parameters to be considered for development of ablative external thermal protection for composite rocket motor case [16].

The experimental mechanical properties testing for Carbon-Epoxy composite is carried out in phased levels i.e Carbon roving level by impregnated tow test as per ASTM D 4018, Carbon-Epoxy flat specimen level from uni-directional laminate specimens as per ASTM D3039 and followed by ring specimens made by filament winding as per ASTM D2290. The correlation of tensile strength of Carbon Roving-Carbon Epoxy Flat specimen- Carbon Epoxy ring specimen is also established based on test results. The ring specimens simulates cylindrical geometry of composite rocket motor case along with wet filament winding process which is used for manufacturing of composite rocket motor cases as well ring specimens. In ring specimen test, the apparent tensile test is measured due presence of bending moment also apart from tensile load during test and tensile modulus measurement is not possible. As per ASTM D2290 test method, a split disc fixture is used for ring specimen tensile testing and at locations of split due to curvature change bending moment also acts. In case of Carbon-Epoxy composite mechanical properties evaluation are specifically relevant to composite case, both flat and ring specimens are tested and correlation also is also drawn based on test results.

The maximum allowable interface temperature between ablative external thermal protection system (ETPS) and composite case is one of the most essential parameters required to be determined. In order to experimentally determine the temperature at which tensile strength degradation happens for Carbon-Epoxy composite, the ring specimens tensile is carried out at different temperature above ambient. The constraint for Carbon-Epoxy composite for maximum allowable temperature is evaluated based on test results. Composite rocket motor case being polymeric composites, the glass transition temperature (Tg) is also important to assess available thermal margin in terms of temperature. The Carbon-Epoxy glass transition temperature (Tg) and Epoxy cure characteristics are also determined by DSC technique. The epoxy resin cure characteristics play important role for ablative external thermal protection resin selection and various process aspects.

In present research work, composite rocket motor case is made up of PAN based carbon roving and epoxy resin[16]. In this regard testing and evaluation for Carbon-Epoxy composite is undertaken with following broad objectives:

- To generate tested mechanical properties for PAN based Carbon fiber, Epoxy Resin, Uni-Directional Laminate and Ring specimen

- To correlate mechanical properties for Carbon fiber-Uni-D laminate – Ring Specimens
- To generate tensile strength values for Ring specimens at elevated temperatures
- To finalize constraint on external thermal protection and Carbon Epoxy interface temperature based on strength degradation
- To determine Glass Transition Temperature (Tg) for neat Epoxy Resin and Carbon -Epoxy composite by DSC

3.2 Mechanical Properties Evaluation

The Instron ultimate tensile machine (UTM) with maximum load capacity of 100KN is used for mechanical properties testing of carbon-epoxy composites. The machine is having capability for tensile and compressive type load application. There various load cells options provided by machine supplier like 10N, 1KN, 10 KN and 100KN. While carrying out the test, load cell is selected based on expected strength of material. There are various fixtures also provided with machine viz. tensile, compressive, flexural and shear properties. The fixture is chosen based on type of test for materials. Strain measurements is carried out through strain gauges or extensometer. On this machine all the tests can be performed as per standards like ASTM, ISO, BS, IS. The load alignment during the test is very important. The cross-head speed during the tests needs to be ensured as per specification for accurate results.

The Instron UTM is shown in following figure 3.1:

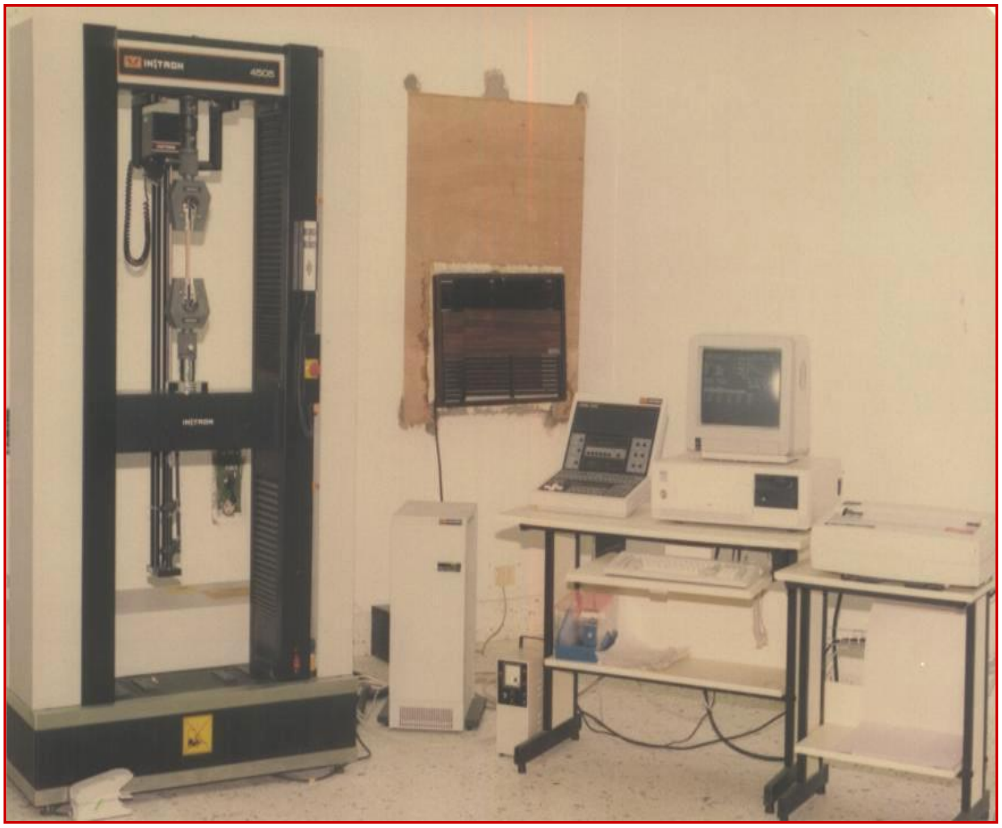

Figure 3.1: Instron UTM

3.2.1 Mechanical Testing of Carbon Roving

The Polyacrylonitrile based Carbon Roving is principal load carrying element of carbon epoxy composite [17]. As per earlier ASTM D 3379 test method, carbon monofilament tensile test used to be recommended. In case of tensile test at carbon monofilament level, separation of monofilament from roving, monofilament handing and mounting in UTM grips are difficult and affects the test results. Due to such practical implications, the tensile failure load variation among carbon monofilaments used to be high and in turn more scattering in tensile strength values. In order to overcome such issues, in present work, impregnated tow test as per ASTM D 4018 is adopted for mechanical properties testing of carbon roving. In this test, specimen preparation is very crucial and is done by impregnating carbon tow with low temperature curable rein with conducive resin mixture viscosity [18].

The specifications of PAN based carbon roving used for present studies are given as follows:

Table 3.1: Polyacrylonitrile Carbon Roving Specifications

Sl No	Test Parameters	Specified Values
1	Tex, g/km	800 for 12 K
2	Density, g/cc	1. 8
3	Diameter of monofilament, µm	7
4	Tensile Strength, Mpa	4 900
	Tensile Modulus, Gpa	230
	% Strain	1.9
5	Sizing Content (% by wt)	1 %
6	Carbon Content (% by Wt)	93

Above specifications are design and quality control parameters and extract of in-house report

Carbon roving spool is shown in following figure 3.2:

Figure 3.2: Carbon Roving

The mechanical properties testing of Carbon fiber is carried out by impregnated tow test method as per ASTM D 4018. This test method is adopted here due to consistent and accurate results of tested properties. This test is done on UTM with extensometer to determine tensile strength and modulus of carbon roving as shown in following figure 3.3:

Figure 3.3: Impregnated tow tensile test on UTM

Glass/epoxy tabs are used for mounting specimens on UTM and cross head speed of 12.7mm/min. Cross section area of impregnated tow specimen is calculated from roving tex and density (tex/density). As per ASTM standard, acceptable failure mode of explosive failure in gauge length is achieved in tests. There are various criticalities involved in preparation and consolidation of resin impregnated tow test specimens given as follows:

- The resin must be compatible with the carbon fiber. In present work, Araldite grade LY556/LY1564 and Hardener grade HY3486 is used for impregnation and consolidation of carbon roving
- Resin system must have double elongation than that of fiber
- The resin must be low temperature curing so that the thermal stress induced in tow during curing are low.

- The individual filaments must be well collimated in the impregnated tow.

The impregnated tow test specimens are made by impregnation of carbon roving with Araldite resin (Grade: LY556) and hardener HY 3486 and impregnated tow is cured at 90^0C.The impregnated tow test specimens are shown in following figure 3.4:

Figure 3.4: Impregnated tow specimens

Tensile Test results:

Impregnated tow test is carried out for ten specimens, the tensile test results are given as follows:

Table 3.2: Carbon Impregnated Tow Tensile Strength

S. No	Test properties	Test Results
1	Tensile Strength (MPa)	4895, 4905,4915,4908,4910, 4902,4898,4910, 4907, 4915 Average: 4906
2	Tensile Modulus (GPa)	230, 228, 230, 232, 225, 235, 227, 234, 232, 230 Average: 230

The failure modes for impregnated carbon tow are fibre breakage which is as expected. The test result of tensile strength vs strain for one specimen and failure modes are shown in figures 3.5 and 3.5 respectively given as follows:

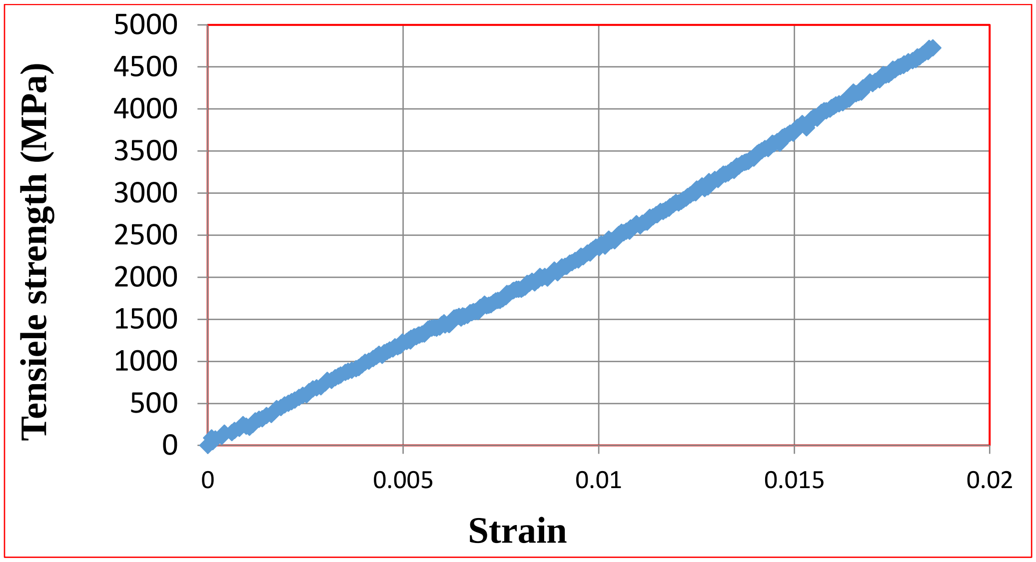

Figure 3.5: Tensile Strength vs Strain

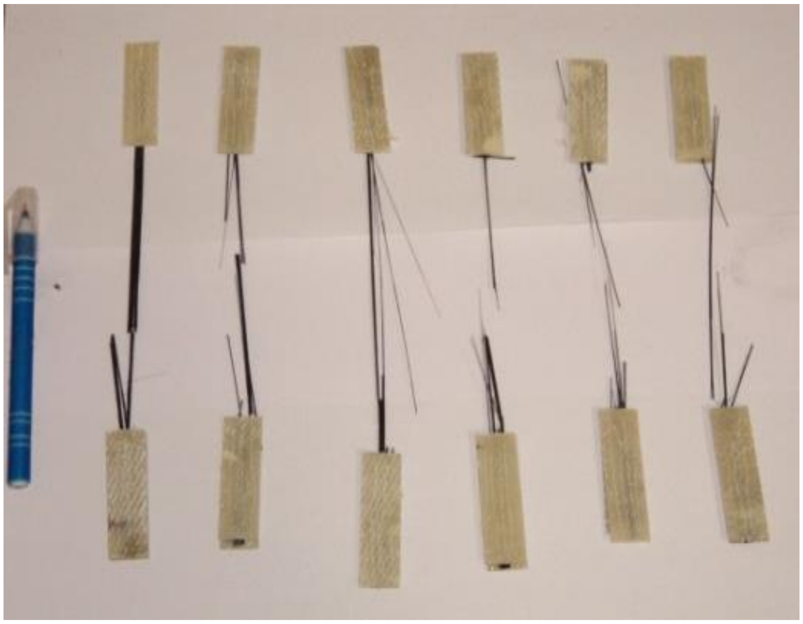

Figure 3.6: Failure modes of impregnated tow specimens

3.2.2 Mechanical Testing of Carbon-Epoxy Flat Specimens

Mechanical Testing is carried out on longitudinal and transverse specimens made from Uni-directional Carbon Epoxy Laminate as per ASTM D 3039 for evaluation of Tensile strength, Tensile modulus, Poison's ratio and Ultimate failure strain at ambient temperature. In present study test results for mechanical properties of longitudinal flat specimens are of more interest however from laminate transverse flat specimens are also prepared and tested for mechanical properties [19]. In case of transverse specimens testing, obtained tensile strength is mainly contributed by epoxy resin as fiber direction is perpendicular to load application direction. In present mechanical testing plan, fifteen longitudinal specimens and ten transverse specimens are tested. The mechanical test set up including Instron mounted with specimen and data acquisition system is shown in following figure 3.7.

Figure 3.7: Mechanical Test Set Up (Instron with specimen & Data acquisition system)

Physical properties viz fiber volume fraction and composite density are also determined which are important parameters for various correlation for composite characteristics and properties apart from design aspects. The measured value of volume fraction is very significant for design and analysis aspects and also is good basis for composite processes correlation and consistency. Density values also indicates curing aspects, constituents proportion and achieved mass.

Manufacturing of Uni-Directional Laminate and flat Specimens

Carbon Epoxy Uni-directional laminates are manufactured by wet filament winding process on flat plate mandrel by maintaining proper fiber tension and resin mix viscosity in resin bath [20]. Resin and hardener are mixed in ratio of 100: 27. In present work this manufacturing process is chosen as it simulates the actual process which is being followed for manufacturing of composite rocket motor case. The rectangular mandrel which is used to wind laminate is shown as follows.

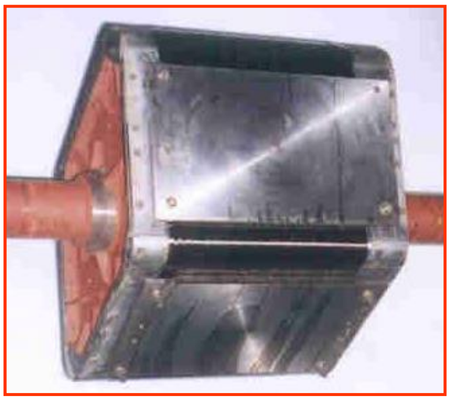

Figure 3.8 (a) Rectangular Mandrel

Figure 3.8 (b) Filament winding

Figure 3.8: Manufacturing of CE Uni-directional laminate by filament winding process

Once filament winding gets completed, the laminate is cured in an oven having accurate temperature control [21]. The flat mandrel is placed inside the oven on metal stands. The following cure cycle is followed:

- ✓ Temperature of the oven raised from room temperature to 120°C with heating rate of 2 to 4°C per minute
- ✓ Temperature held at 120°C ±5°C for 3 hours.
- ✓ Temperature of the oven raised from 120°C to 160°C with heating rate of 2 to 4°C per minute.
- ✓ Temperature held at 160°C ±5°C for 4 hours
- ✓ Switch off the oven and allow the component to cool naturally.
- ✓ Oven door got opened and mandrel is removed when temperature falls below 40°C.

Specimen Preparation:

As per the required dimensions, flat specimens are marked on laminate in longitudinal direction i.e in direction of carbon fiber. Similarly on other laminates flat specimens are marked in transverse direction[22]. Flat specimens in longitudinal and transverse directions are machined from identified laminates through diamond wheel cutting machine. The dimensions of longitudinal and transverse specimens are maintained as per ASTM D 3039 given in figures 3.9 and 3.10. The uni-directional flat Carbon-Epoxy composite specimens are shown in figure 3.11. The Carbon-Epoxy E flat specimens bonded with strain gauges and tabs at ends are shown in figure 3.12.

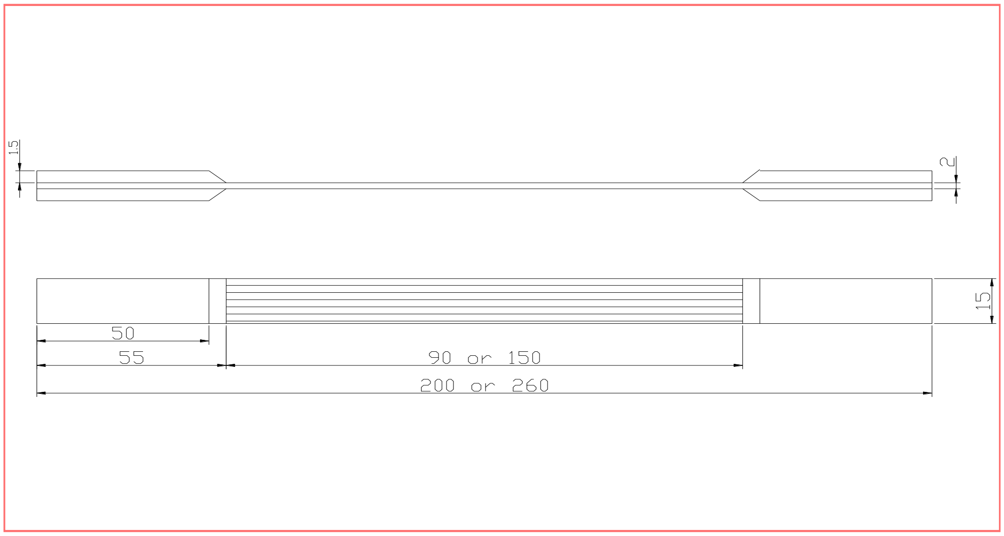

Figure 3.9: Longitudinal Flat Tensile Test Specimen (ASTM D 3039)

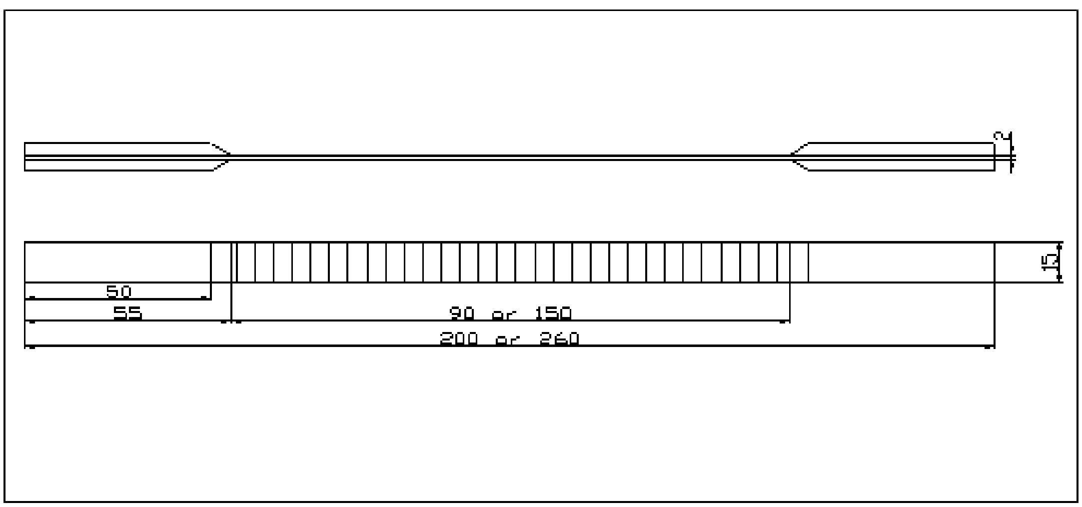

Figure 3.10: Transverse Flat Tensile Test Specimen (ASTM D 3039)

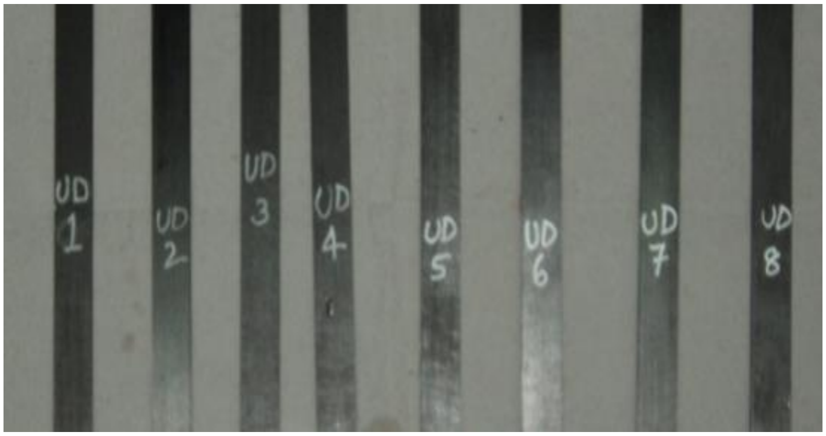

Figure 3.11: Uni-Directional Tensile test Flat specimens

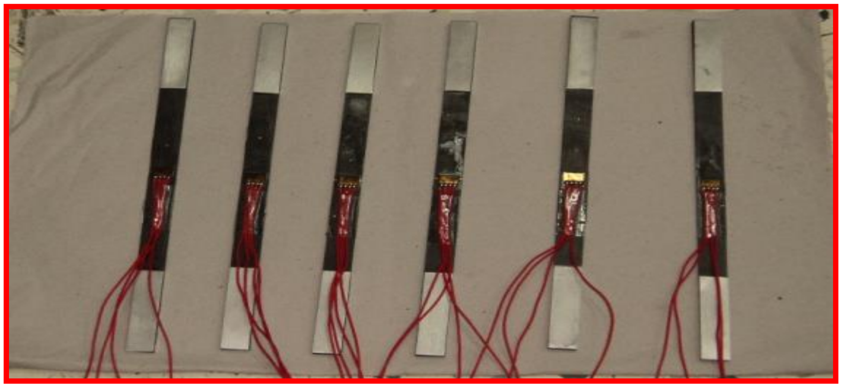

Figure 3.12: Tensile test Flat specimens with strain gauges and tabs

Once specimens are prepared, the visual inspection and dimensional inspections were carried out for all specimens before testing.

Mechanical Test Results:

Mechanical testing for Carbon-Epoxy flat specimens is carried out as per ASTM D3039. The mechanical test results for Carbon-Epoxy composite flat longitudinal and transverse specimens are given in following sections.

Test Results of Longitudinal Specimens:

The strains are measured in both longitudinal as well transverse direction on flat specimens while carrying out tensile test for longitudinal specimens (load applied in fiber direction). The both direction strains values are required for major poision's ratio evaluation. The stress- strain plot obtained in tensile testing for one longitudinal CE flat specimen is given as follows in figure 3.13:

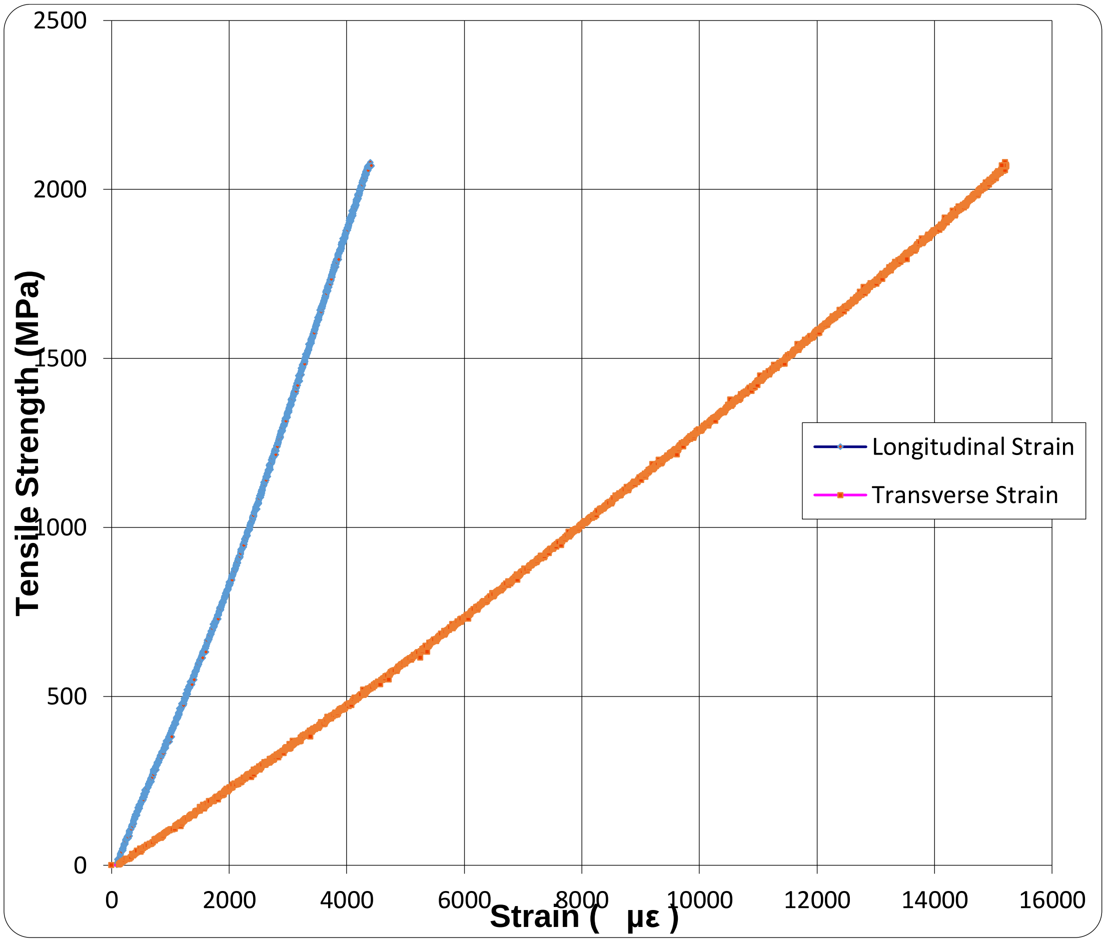

Figure 3.13: Tensile strength – Strain plot for CE flat longitudinal specimen

The mechanical test results for all the 15 specimens are given in following table 3.3:

Table 3.3: Mechanical Test Results of Longitudinal CE Flat specimens

Specimen No.	Ultimate Tensile Strength σ_{11}, (MPa)	Tensile Modulus E_{11}(GPa)	Poisson Ratio ν_{12}	Ultimate Failure Strain (με)	Failure Mode as per ASTMD3039
01	2242	132	0.29	15751	Splitting
02	2050	133	0.29	15960	Splitting
03	2080	133	0.29	15891	Splitting
04	2258	132	0.32	16010	XGM
05	2028	134	0.32	16150	Splitting
06	2280	128	0.30	16819	XGM
07	2260	123	0.32	15290	XGM
08	2265	129	0.28	16767	XGM
09	2358	128	0.28	15917	XGM
10	2213	124	0.29	16760	XGM
11	2293	125	0.29	16848	XGM
12	2238	124	0.30	16530	XGM
13	2198	123	0.28	16845	XGM
14	2242	121	0.28	15345	XGM
15	2300	124	0.29	16757	XGM
Average	**2220**	**128**	**0.29**	**16243**	

‘XGM’ is tensile failure mode described by three-part failure mode as per ASTM D 3039 defined as follows: Failure Type (‘X’ means explosive failure), Failure Area (‘G’ means gauge length), Failure location (‘M’ means middle of gauge length).

The observed failure modes of longitudinal Carbon-Epoxy flat specimens after tensile testing is shown in following figure 3.14:

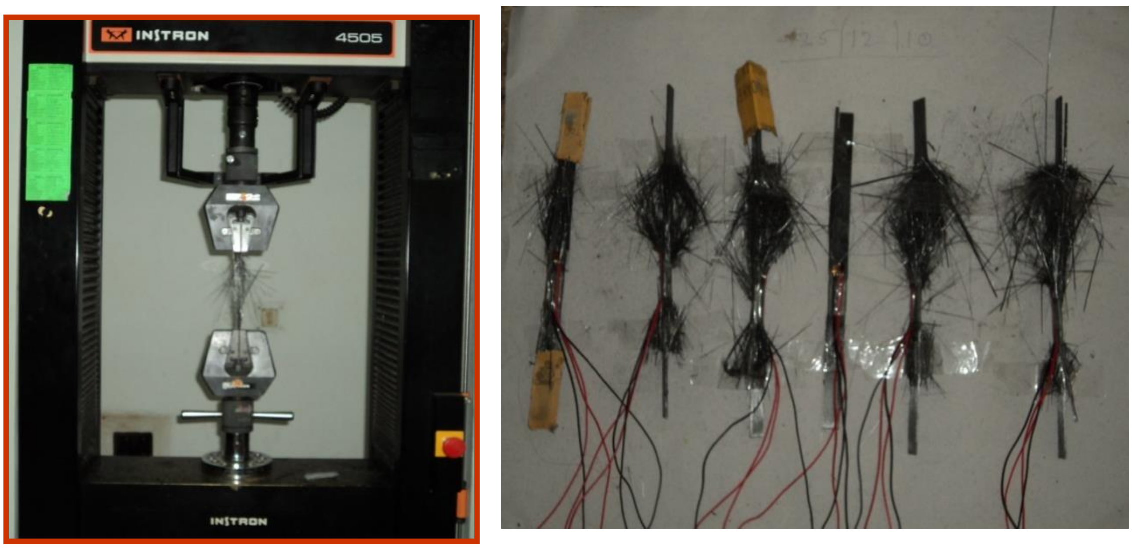

Figure 3.14: CE longitudinal flat specimens after tensile test

Test Results of Transverse Specimens:

The stress- strain plot obtained in tensile testing for one transverse Carbon-Epoxy flat specimen is given as follows in figure 3.15:

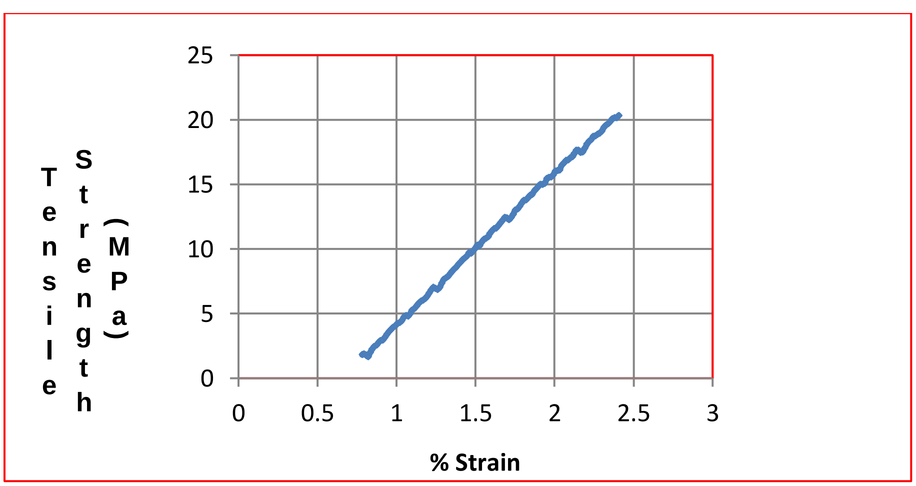

Figure 3.15: Tensile Strength – Strain plot for CE transverse flat specimen

The mechanical Test results for all ten CE transverse specimens are given in following table 3.4:

Table 3.4: Mechanical Test Results of Transverse Carbon-Epoxy Flat specimens

Specimen No.	**UTS σ_{22}, (MPa)**	**Modulus, E_{22} (GPa)**	**Failure Mode** **As per ASTMD3039**
01	16.6	9.40	LGB
02	15.70	8.70	LGT
03	17.0	8.50	LGM
04	15.40	8.28	LGB
05	15.70	8.0	LGB
06	15.50	8.63	LGB
07	15.80	8.52	LGB
08	16.30	9.50	LGT
09	17.50	9.30	LGM
10	17.70	9.20	LGM
Average	18.40	9.0	

The observed failure modes of transverse Carbon-Epoxy flat specimens after tensile testing are shown in following figure 3.16:

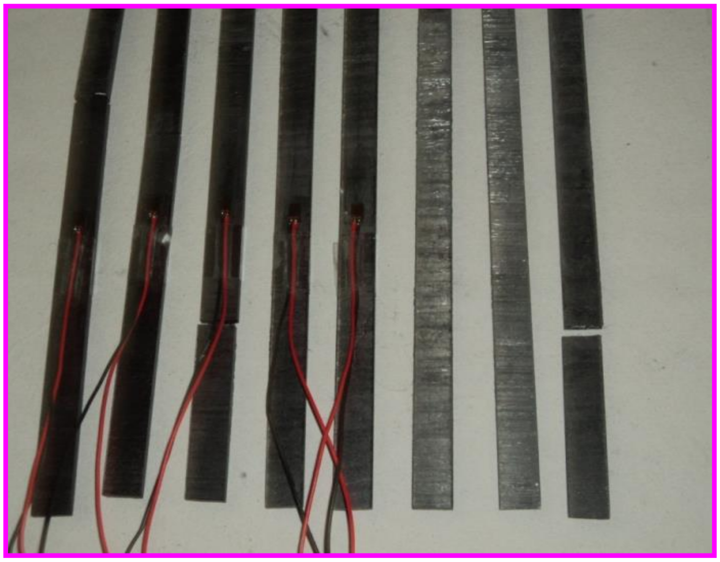

Figure 3.16: CE transverse flat specimens after tensile test

The summary of test results for mechanical properties and physical properties of arbon-Epoxy flat specimens are given in following table 3.5.

Table 3.5: Summary of test results for CE mechanical and Physical Properties

Sl.NO	**PROPERTY**	**ASTM No**	**No. of Specimens**	**Average Value**
1.0	**MECHANICAL PROPERTIES**			
1.1	Longitudinal Tensile Strength (MPa)	D3039	15	2220
1.2	Longitudinal Tensile Modulus (GPa)			128
1.3	Major Poison's ratio, υ_{12}			0.29
1.4	Transverse Tensile Strength (MPa)		10	18.5
1.5	Transverse Tensile Modulus (GPa)			9.5

2.0	**PHYSICAL PROPERTIES**			
2.1	Fiber volume fraction, V_f (%)	D3171	3	60
2.2	Density (ρ), g/cc	D792	3	1.54

3.2.3 Testing of Carbon-Epoxy Ring Specimens at Ambient Temperature

The Carbon Epoxy filament wound ring specimens which are specifically applicable for pressure vessels are tested as per ASTM D 2290 at ambient temperature. In this test specimen is loaded through split disc test fixture which facilitates for alignment during loading. During test as bending moment is also imposed an apparent tensile strength is determined instead of true tensile strength. The apparent tensile strength is less than actual tensile strength but ring specimens closely simulates composite pressure vessels and test results are highly useful for various correlation[23]. Evaluation of tensile modulus is not possible in this test. Split disc fixture design is done in such a way that it reduces the bending moment. This test is highly significant for various aspects of composite pressure vessels.

Manufacturing of Carbon-Epoxy composite Ring and Specimens

Manufacturing of composite ring is carried out with wet filament winding process similar to Uni-Directional laminate through cylindrical mandrel instead of flat one [22]. Once filament winding gets completed the mandrel is kept inside oven for curing as the same curing cycle mentioned in case of Uni-Directional laminate. Manufacturing is shown in following figure 3.17:

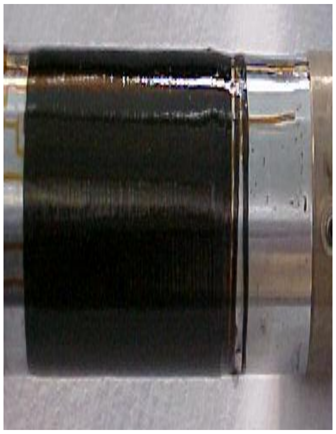

Fig 3.17 (a) Ring Winding Fig 3.17 (b) Machining Fig 3.17 (c) Ring Specimen

Figure 3.17: Manufacturing of Ring by filament winding process & Specimen

The Ring specimen dimensions are maintained as per ASTM D 2290 given as follows In figure 3.18

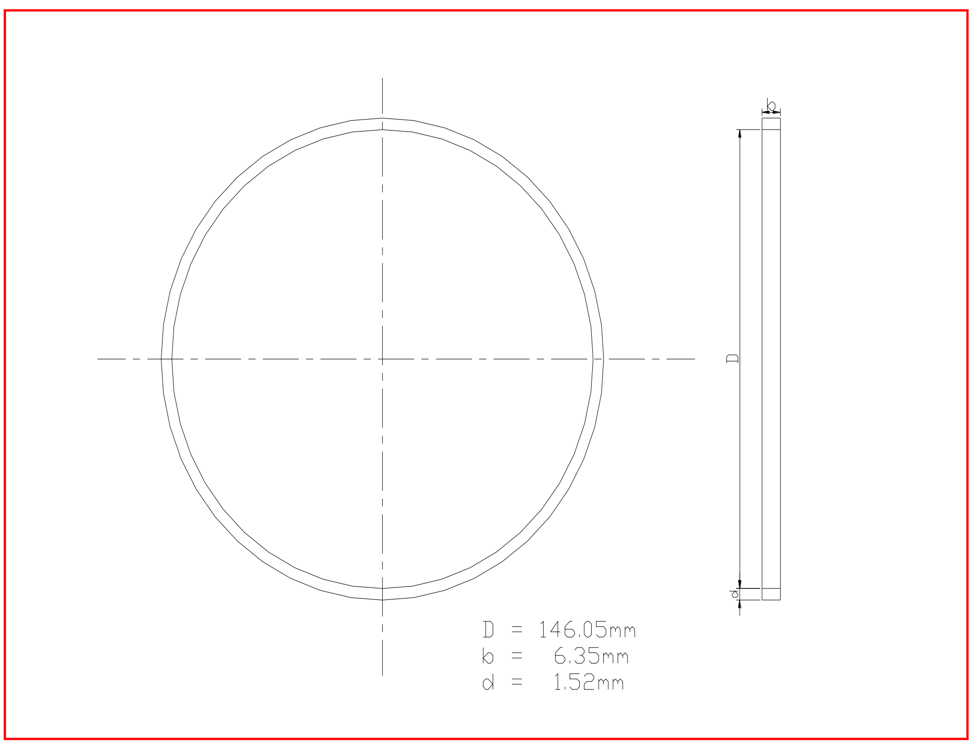

Figure 3.18: Ring Specimen (ASTM D 2290)

Tensile Test Results of Carbon-Epoxy Ring Specimens:

The tensile test of CE ring specimens is carried out as per ASTM D 2290, using split disc fixture on Instron UTM shown in following figure 3.19:

Figure 3.19: Carbon-Epoxy ring specimen testing using split disc fixture

The tensile strength and displacement plot result for one CE ring specimen test is given as follows in figure 3.20:

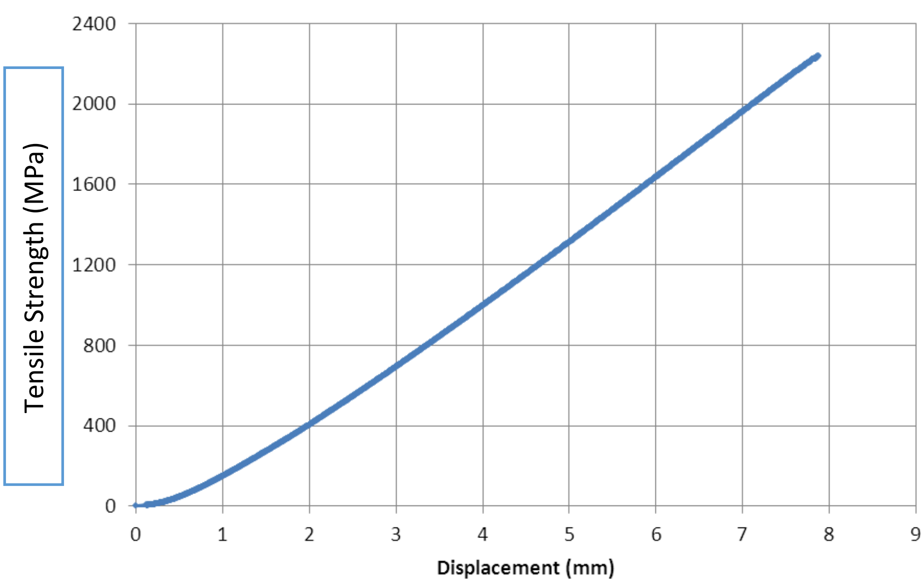

Figure 3.20: Tensile strength and displacement plot for Ring specimen

In present experimental evaluation ten Carbon-Epoxy ring specimens are prepared and tested for apparent tensile strength. The test results are given in following table 3.6:

Table 3.6: Carbon-Epoxy Ring Specimens Tensile test results at ambient temperature

Ring Specimens	Tensile Strength (MPa)
1	1913
2	2116
3	2089
4	1888
5	2178
6	1865
7	2057
8	1784
9	2228
10	1935
Average	2005

The Carbon-Epoxy ring specimens observed failure modes are delamination and circumferential splitting as shown in following figure 3.21:

Figure 3.21: CE ring specimens after test

3.2.4 Testing of Carbon-Epoxy Ring Specimens at high temperature

The Carbon Epoxy filament wound ring specimens are tested as per ASTM D 2290 at above ambient temperatures. The prime objective of this test is to experimentally determine the temperature at which tensile strength degradation starts for Carbon-Epoxy composite. In this test five specimens are tested at each temperature. Test is carried out from ambient temperature up to 130^{0}C. The test setup for ring specimens at higher temperature is shown in following figure 3.22:

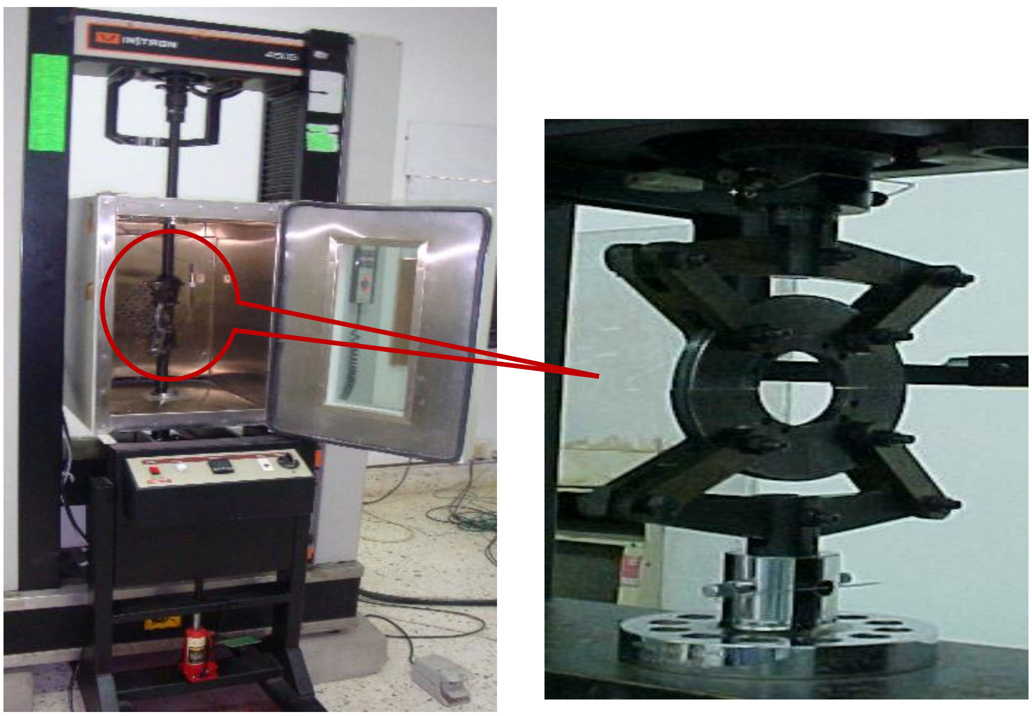

Figure 3.22: Instron UTM with furnace (test set up)

Tensile Test Results of Carbon-Epoxy Ring Specimens at high temperature:

The test results for tensile strength at each temperature for all five specimens are given as follows in table 3.7:

Table 3.7: Carbon-Epoxy Ring Specimens Tensile test results at higher temperatures

Temperature	Tensile Strength (MPa)		Average Tensile Strength (MPa)	% Drop in Tensile Strength
Ambient	Specimen 1	2000	1947	-------
	Specimen 2	1920		
	Specimen 3	1936		
	Specimen 4	2041		
	Specimen 5	1841		
100^0C	Specimen 1	1881	1863	4.31
	Specimen 2	1826		
	Specimen 3	1888		
	Specimen 4	1871		
	Specimen 5	1847		
110^0C	Specimen 1	1871	1798	7.6
	Specimen 2	1779		
	Specimen 3	1804		
	Specimen 4	1790		
	Specimen 5	1747		
120^0C	Specimen 1	1650	1648	15.3
	Specimen 2	1612		
	Specimen 3	1712		
	Specimen 4	1643		
	Specimen 5	1624		
130^0C	Specimen 1	1570	1545	20.6
	Specimen 2	1456		
	Specimen 3	1570		
	Specimen 4	1552		
	Specimen 5	1576		

The Tensile strength and temperature plot for one set of specimens are given as follows in figure 3.23:

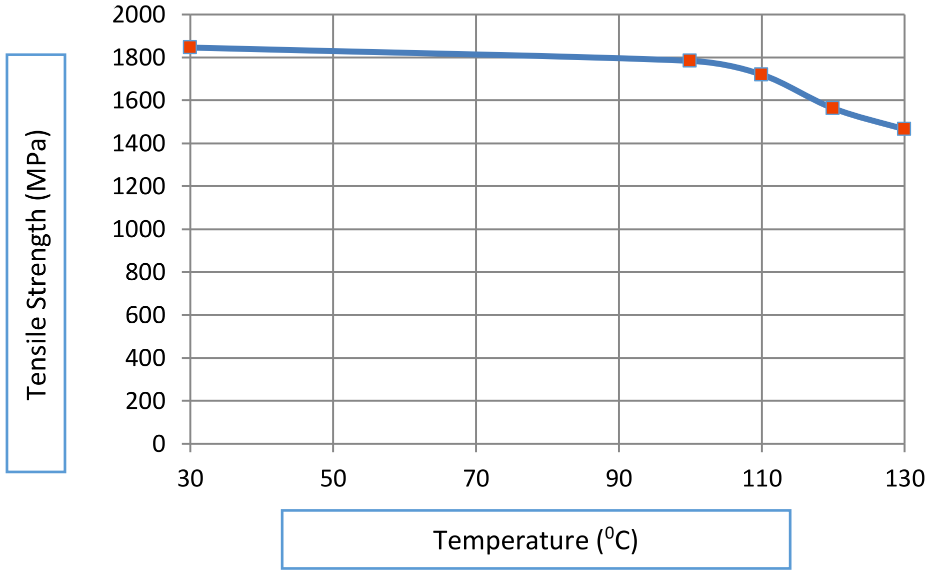

Figure 3.23: CE Ring specimen Tensile strength and Temperature plot

3.3 Determination of Glass Transition Temperature (Tg)

In present study the Glass transition temperature for CE composite is determined with Dry scanning Calorimetry (DSC) technique as per ASTM E 1256. Differential Scanning Calorimetry, or DSC, is a thermal test method in which change in heat capacity of material is monitored and recorded with respect to temperature. In this technique, specimen of measured mass is subjected to heating or cooling and change in heat flow is recorded which in turn is correlated with change in heat capacity [21]. This allows the detection of transitions such as melts, glass transitions, phase changes, and curing. The DSC test set up is shown in following figure 3.24:

Figure 3.24: DSC Test Set Up

Test Results:

The heat flow in Carbon-Epoxy specimen is plotted against temperature during DSC run and from curve is seen that at 161.16 ^{0}C heat is liberated out and the temperature is identified as glass transition temperature. The measured Glass transition temperature for Carbon-Epoxy sample is 161.16^{0} C. DSC run plot for heat flow and temperature for Carbon-Epoxy sample is given below in figure 3.25:

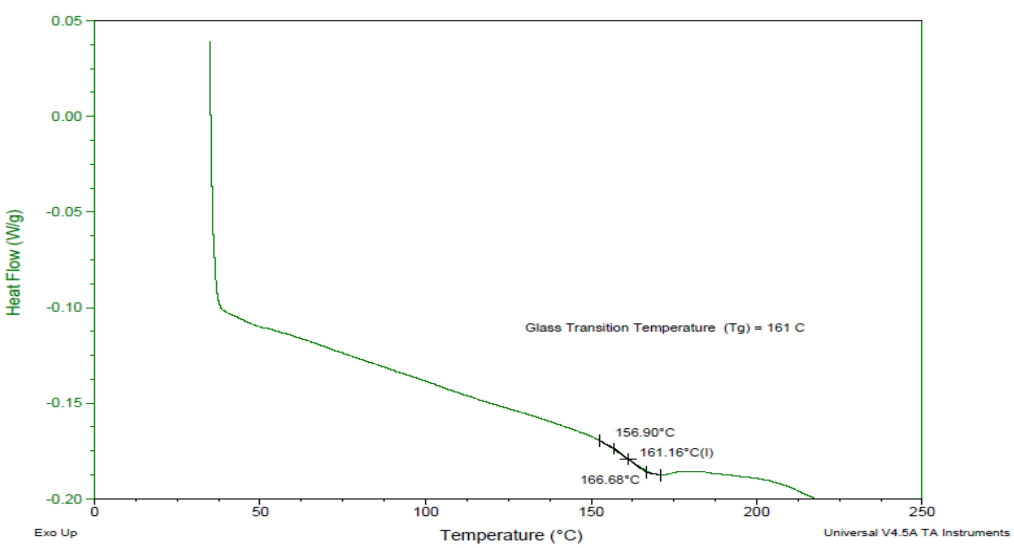

Figure 3.25: Heat flow and temperature plot through DSC

3.4 Summary

The mechanical properties test results of Carbon roving impregnated tow test, Carbon-Epoxy flat specimens prepared from uni-directional laminates, ring specimens are generated and summarized as follows in table 3.8:

Table 3.8: Correlation of Tensile strength (carbon roving- CE flat specimen- Ring specimen)

Test stage	**Tensile Strength (Mpa)**	**Tensile Modulus (Gpa)**
Carbon Roving (Impregnated Tow Test)	4906	230
CE composite (Flat Specimens from laminate)	2220	128
CE Ring Specimens (Filament Wound)	2005	Not applicable as per ASTM

The correlation of tensile strength test results for Carbon roving- Carbon Epoxy flat specimens- Carbon Epoxy ring specimens is established for chosen materials. The decreasing trend of tensile strength from Carbon roving- Carbon Epoxy flat specimens- Carbon Epoxy ring specimens is as expected, and corresponds to fiber volume fraction and process effects. The mechanical properties generated above are used for design and analysis of carbon epoxy structure however filament wound rings simulate closely with composite rocket motor casing in terms of process and fiber orientations particularly in hoop direction. The tensile strength obtained through ring specimen is apparent tensile strength as in testing bending moment also exists though effect is minimized through split disc test fixture. The correlation and comparative analysis of test results from flat specimens and ring specimens provides basis to effectively exploit merits of both namely mechanical properties test results used as design inputs and apparent tensile strength for process and application. In case of filament wound composite structure like rocket motor case ring specimens closely simulates real condition and important.

The experimental data for tensile strength with respect to temperature is also generated to establish the constraint on external surface temperature of composite rocket motor case for design aspects of composite rocket motor case and thermal protection system.Carbon-Epoxy Ring specimens simulate closely with this requirement and tested for temperatures above the ambient in to generate data for tensile strength with respect to temperature. Test results shows, that tensile strength degradation starts at 100^0C from 1947 Mpa at ambient to 1863 MPa, and hence same is considered as maximum allowable temperature for CE layer. In case of polymeric composites apart from strength degradation temperature, the glass transition temperature is also important. The glass transition temperature of Carbon Epoxy composite is also determined by DSC technique which is 161^0C. The test results for strength degradation temperature and glass transition temperature for carbon Epoxy composite provides basis to design structural layer considering kinetic heating effect and also design of thermal protection system.

CHAPTER 4

EXPERIMENTAL STUDIES OF RESINS FOR ABLATIVE THERMAL PROTECTION SYSTEM

4.1 Introduction

The composite rocket motor case operational requirement is only there in powered phase of missile which is during ascent of trajectory and aero thermal conditions are not that severe like re- entry or protection against impingement of rocket motor exhaust[26]. Performance of ablative thermal protection system on composite rocket motor case external surface predominantly depends on resin thermal characteristics and stability considering such operational needs. Resin thermal characteristics and properties play the most vital role for ablative thermal protection systems performance. The aim of present studies is to finalize the resin for the ablative external thermal protection layer of composite rocket motor case based on the following considerations:

- Thermal Characteristics (Thermal stability, Char yield, and decomposition temperatures)
- Manufacturing process requirements (In-situ layup over Carbon-Epoxy structural layer, Curing characteristics [21] & Tg of Epoxy resin)

The ablative thermal protection system (TPS) for composite rocket motor case (CRMC) external surface is specific application in which resin thermal stability and char yield after thermal exposure are most significant. Resin char yield also affects insulating performance of ablative TPS [28]. The scope of present studies is limited to ablative TPS resins only considering specific application. In the present studies, Phenolic Resin and Silicone Resin are chosen for experimental thermal stability evaluation as both are very good candidate materials for ablative TPS. Resin thermal characteristics[8] are very significant for ablation to meet functional requirements of ablative TPS. Thermal conductivity for Glass-Phenolic and Glass- Silicone composites [29] are also experimentally determined for comparison in present studies. Ablative TPS for CRMC performance is very crucial as insulative layer hence thermal conductivity evaluation is highly relevant and included.

The details and properties of Phenolic and Silicone resins are given as follows:

Phenolic Resin:

Phenolic resins consist of chain of polymers and these are synthesized by chemical reaction and polymerization of phenolic monomers with aldehyde chemicals. Phenolic resin is polymerized phenol by substituting formaldehyde on the phenol's aromatic ring via a condensation reaction [28]. The selection of suitable reaction parameter results in optimum molecular weight distribution and residual monomer content necessary for maximum efficiency based on application. Depending on the pH of the catalyst, these monomers react to form one of two general resin types: Novolac Phenolic and Resol Phenolic Resins. In present study Resol Phenolic Resin is considered. A basic (alkaline) catalyst and, usually but not necessarily, a molar excess of formaldehyde is used to make resol resins. The synthesis of phenolic resin chemical reactions is carried out in two stages. In first stage, phenol reacts with methylene glycol and methylol phenol is formed and in second stage Methylol phenol reacts with itself to form a longer chain methylol phenolic. In Resol resin chemistry most vital mechanism is chemistry of this resin which means when an excess of formaldehyde is taken there will be adequate number of active groups of methylol and dibenzyl ether to complete the polymerization and resin is cured without requirement of cure agent. Phenolic resins consist of a chain of polymers and these are synthesized by chemical reaction and polymerization of phenolic monomers with aldehyde chemicals[9]. Phenolic resin is condensation polymerized in which formaldehyde is substituted on the phenol's aromatic ring. The various reaction conditions are chosen to obtain optimum dispersion of molecular weight and required fraction of residual monomer based on application[10]. In the present study, Resol Phenolic Resin is considered. The Specifications for Resole Phenolic resin (Make: IVP Ltd, Tarapur, India, Grade: Resole IVA REZ ISRO) which is considered in the present work are given as follows in Table 4.1:

Table 4.1: Specification of Phenolic Resin

Sl. No	Parameter/Property	Specification
1	Viscosity of Resin at 30°C	100 -150
2	Specific Gravity at 30°C	1.12 -1.16
3	Point of Trouble, ml (Resin is diluted with AR grade of Ethyl alcohol to get specific gravity of diluted resin is 0.860)	8 -12 ml of H2O (Per 10 ml diluted resin)
4	Solid Resin content (% Weight)	60- 65
5	Volatile content (% Weight)	32 -38
6	Free Phenol Content (Max %) (Bromination Method)	6
7	Free Formaldehyde (Max %) (Hydroxyl Amine HCl method)	3

Silicone Resin:

Silicone resins are synthesized of silicon-oxygen lattice having some fraction of the SiO4/2 or R-SiO3/2 elements, where R signifies any alkyl or aryl groups generally methyl or phenyl. Silicone resins possess greater resistance to thermal degradation in comparison to organic resins which have their carbon-carbon as prime element[30]. The high thermal stability against thermal exposure of these resins is attributed to excellent bond strength between silicon and oxygen.

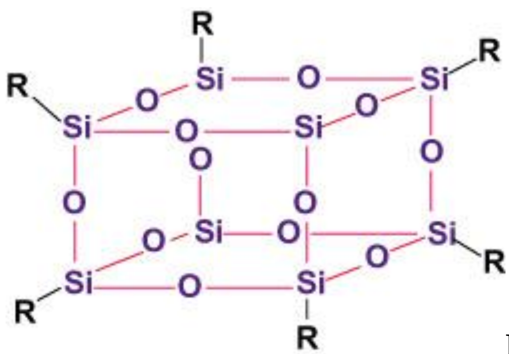

Figure 4.1: Silicone Structure

Further condensation occurs to form three-dimensional siloxane lattices as shown in Fig 4.1. The silicone resins are highly versatile and exhibits excellent compatibility with many other polymers. These features facilitate for synthesis of silicone resins having flexible properties namely curing characteristics, mechanical & thermal properties and adhesion properties to suit specific applications. The most vital characteristic of silicone resins is its excellent thermal stability. These resins possess excellent thermal stability at 200 to 250^{0}C during continuous heat flux exposure and even up to 600^{0}C for shorter period of heat exposures. Their excellent oxidation resistance and superb mechanical properties make them ideally suited for critical application[13-14].

In the present work Silicone solid flake resin is chosen which contains 100 percent silicone and silanol functional resin. This resin for application is made as a solution with a 60% Toluene solution. Technical Specifications of Silicone flake Resin (Make: Dow Corning Corporation, USA, Grade RSN 0249) is given as follows in table 4.2:

Table 4.2: Specifications of Silicone Resin

S. No.	Parameter/ Property	Specification
Silicone Solid Flake resin		
1	Non-Volatile Content (% by weight)	98 (Minimum)
2	Specific gravity at 25°C	1.33-1.43
3	Hydroxyl content, (mg KOH/g)	5.5-6.5
4	Melt Viscosity at 150°C, cP	212-258
5	Balance Shelf life on receipt at ASL	24 months
As 60 % Toluene Solution		
6	Solid Resin content (% by weight)	58-62
7	Volatile content (% by weight)	38-42
8	Specific gravity at 30°C	1.05-1.15
9	Solution Viscosity at 30°C, cP	30-110

4.2 Test Methods for Resins Studies

The following two techniques are used for resins characterization for functional requirements.

Thermal Gravimetric Analysis (TGA):

Thermal gravimetric analysis is a test method which involves recording of material specimen mass with respect to temperature or time under condition of specified temperature program with controlled ambient conditions. The TGA method works on the principle that whenever any material is heated its weight increases or decreases. The instrument used was make TA Instruments with Model Q-500.

Figure 4.2: TGA Test Set Up

Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimetry (DSC), is a test method based on thermal analysis which monitors and records the change in heat capacity of a material by varying temperature. In this technique, a specimen of measured mass is subjected to heating or cooling and the change in heat capacity is recorded and correlated as variation in the heat flow. The change in heat flow gives a basis for identifying critical materials transformations like melting, glass transitions, phase changes, and curing/polymerization. The instrument used was make TA instruments with model no Q200.

Figure 4.3: DSC Test Set Up

4.3 Samples Preparation

Samples for neat Phenolic resin to carry out TGA and DSC were prepared by taking two gram of resin into a plate and same was heated to 70^0C for duration of one hour to allow volatiles to get evaporated. The curing of resin was carried out in oven with following curing cycle: Increasing temperature to 90°C with dwell period of one hour, increasing temperature to 120°C and keep dwell period for two hours, increase temperature to 150° C with dwell time of one hour and increase temperature to 170°C with dwell time of two hour finally reduce he temperature to ambient. Similarly for Silicone resin also two gram of resin was taken into a plate and sample was heat to 90^0C for one hour to allow volatiles to get evaporated. Later resin sample curing was carried out in oven through curing cycle given as follows: Oven temperature increased to 105°C with dwell time one hour, temperature increased to 120°C with dwell time one hour, temperature increased to140° C with dwell time four hour followed by cooling to ambient. To carryout TGA and DSC runs, 10 mg cured specimens were taken for both Phenolic and Silicone Resins.

The samples for Glass Phenolic and glass Silicone composites thermal conductivity testing were prepared from their laminates. Ten glass fabric layers of 300x300 x0.35 mm size were cut for each laminate type and fabric layers were impregnated with phenolic and Silicone resins. The plies were laid as specified on metallic mould by manual lay-up process. After lay-up, the vacuum bagging was prepared and curing carried out in autoclave. The curing cycle followed for Glass Phenolic were at temperature 90°C with soak time one hour with steps of 120°C for soaking of two hours, increasing to 150° C with soak time one hour and 170°C with soak time two hour with autoclave pressure & vacuum of five bar and one torr respectively. Curing cycle followed for Glass Silicone was at 105°C for 1h with further temperature steps of 120°C with soaking of one hour, 140° C with soaking of four hour with five bar pressure and one torr vacuum. Specimens of size 80mmx 80mm x 4mm were cut from respective laminates.

4.4 Experimental Evaluation of Resin Systems

The experimental works were conceived to test and evaluate the thermal stability and char yield due to pyrolysis of Phenolic and Silicone resins through TGA and DSC. The thermal conductivity for Glass Phenolic and Glass Silicone are also tested to generate data. The cure characteristics and glass transition temperature (Tg) of Epoxy resin in composite rocket motor case structural layer are also tested through DSC. This will generate basic characteristics of ablative TPS resin and Epoxy resin of the structural layer for thermal stability and curing parameters for design considerations, processing, and available thermal margins.

TGA for Phenolic Resin and Silicone were carried out. The weight of the samples is measured as a function of temperature under purging of nitrogen gas. The plots between weight as a percentage of initial weight and derivative weight percentage and temperature are obtained and shown in Figure 4.4 & 4.5 respectively:

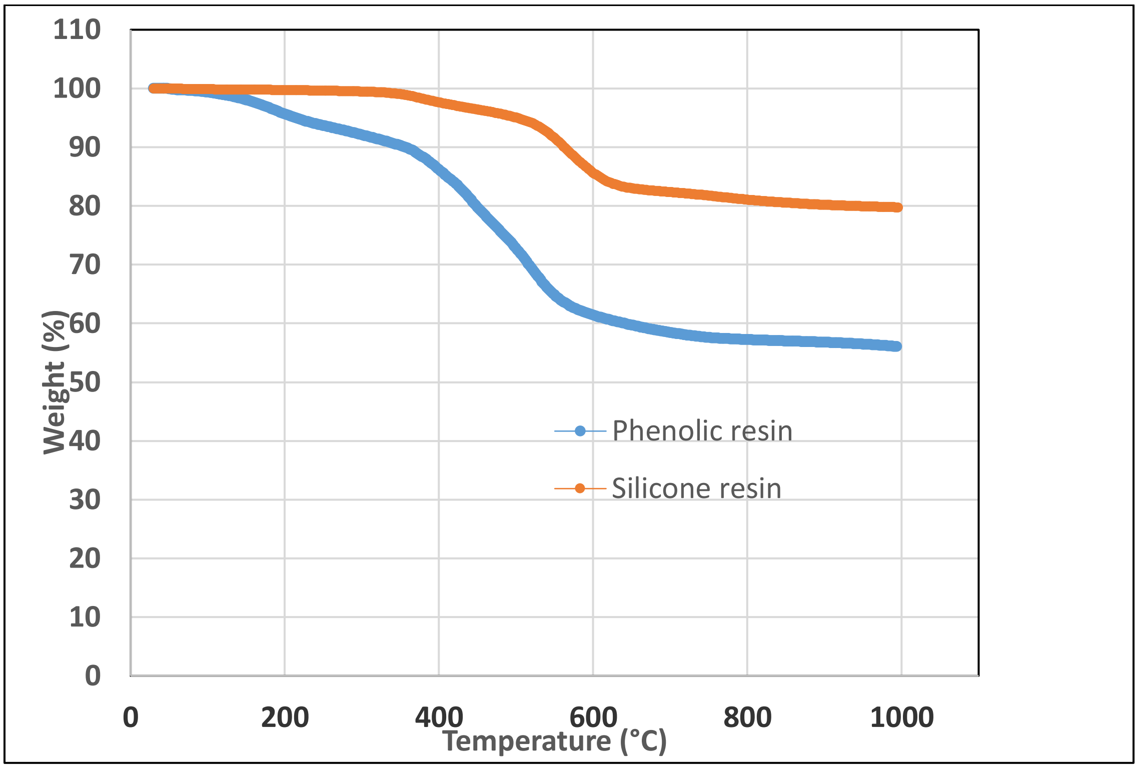

Figure 4.4: TGA curve for Phenolic & Silicone Resin

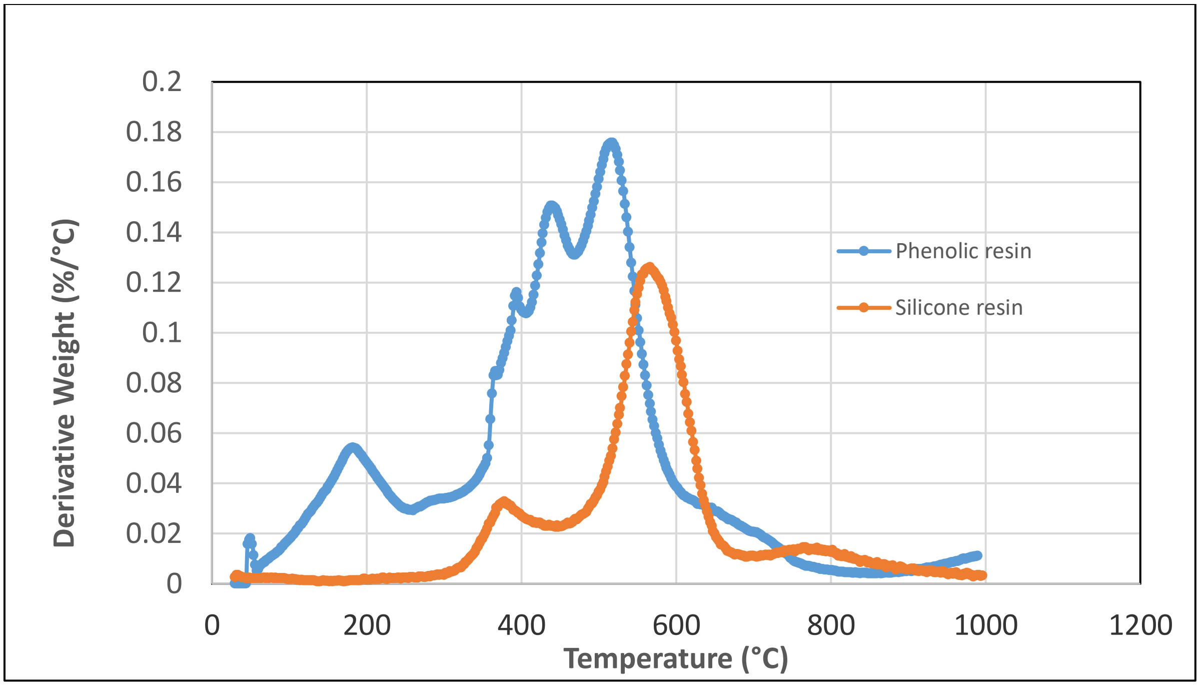

Fig 4.5: DTG Curve for Phenolic & Silicone Resin

DSC for Phenolic and Silicone resins were carried out. Phenolic and Silicone Resin samples were taken and cured for specimens preparation to for DSC analysis and graphs between Heat flow vs temperature were obtained. The plots are given in figure 4.6.

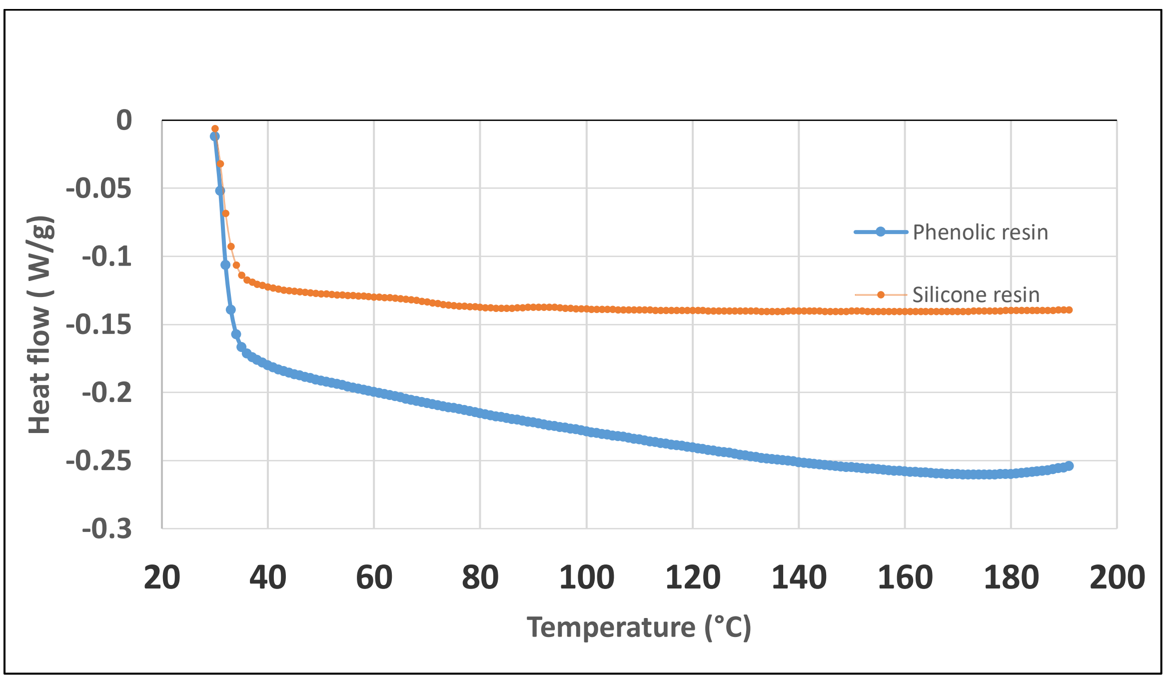

Figure 4.6: DSC Plots for Phenolic & Silicone Resin

The evaluation of thermal conductivity of Glass Phenolic and Glass silicone composite samples were carried out by test method as specified in ISO 22007-2. Two samples were taken for each composite having approximate size of 80mmx 80mm x 4mm for tests. The sensor was inserted between specimens and sensor fulfills two functional needs namely as heat source and thermometer. The sensor was subjected to electrical heating with recording of its temperature with time. The increase of sensor temperature will depend on thermal conductivity and diffusivity of the specimen material. Based on this principle, the thermal conductivity of both composites was calculated and results are as follows in table 4.3:

Table 4.3: Thermal Conductivity Results

Temperature (°C)	**Thermal Conductivity of Glass/ Phenolic Composite**	**Thermal Conductivity of Glass/ Silicone Composite**
25	0.26	0.28
100	0.29	0.31
200	0.31	0.32
300	0.32	0.34

DSC was carried out for Epoxy resin to evaluate thermal stability and cure characteristics which provided basis for design and process considerations for TPS over CE structural layer of composite case. The DSC run was given to evaluate glass transition temperature (Tg) and cure characteristics and plots for same are given as follows in Figure 4.7 & 4.8 respectively.

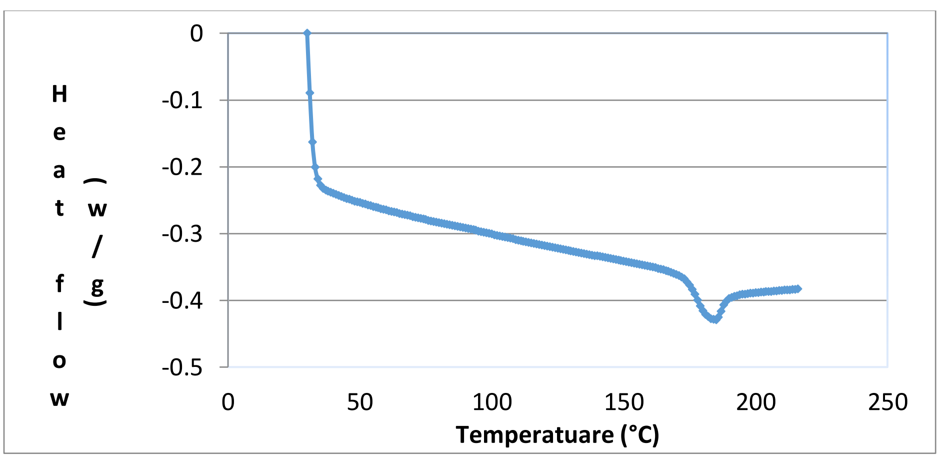

Figure 4.7: Epoxy Glass Transition Temperature (Tg)

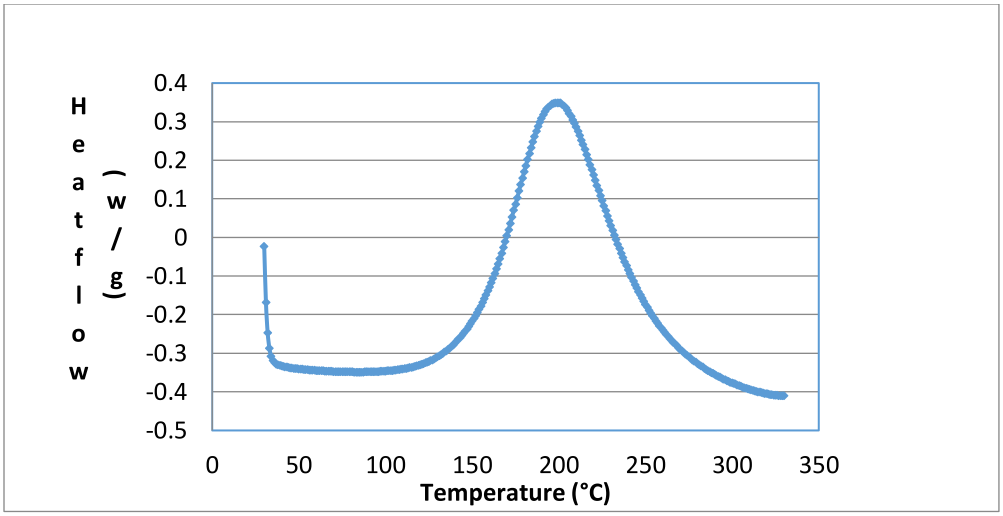

Figure 4.8: Epoxy Cure Characteristics

4.5 Test Results

TGA for Phenolic resin and Silicone resin is carried out to evaluate thermal stability i.e resin initial decomposition temperature and char yield (residual weight after final decomposition) of resins. The thermal stability of Phenolic and Silicone resin is compared based on their initial decomposition temperature, temperature at 10% weight loss and residual weight char yield) of resin after final decomposition at 1000^0C. DTG curves indicate mass loss rate depending on an increase in temperature. DTG curve shows peak for differential weight loss for silicone resin is at higher temperature with lower magnitudes than Phenolic resin. These parameters are true basis for functional requirements of thermal protection system for composite case external surface.

- The Initial Decomposition temperature for Phenolic Resin is 190^0C and 10% weight loss is at 350 ºC. The char yield i.e residual weight of resin after final decomposition is 55 %.
- The Initial Decomposition temperature for Silicon Resin is 370^0C and 10% weight loss is at 590 ºC. The residual weight (char yield) of resin after final decomposition is 79.82 %.

` In the DSC run, no exotherms are observed which confirms that specimens were fully cured. Thermal stability is much better for silicone resin in comparison to Phenolic resin based on above plots.

The Epoxy resin DSC test results for Glass transition temperature and cure characteristics provides basis to compare with TPS resin characteristics. These are required for thermal margins and to decide various processing aspects including curing parameters. The Initial Decomposition temperature for Epoxy Resin is 250^0C & 10% weight loss at 375 ºC. The other cure characteristics results are as follows:

- Glass transition temperature (Tg) is 161.58 ^{0}C
- Cure initiation Temperature is 93^oC
- Cure Onset Temperature is 140^oC
- Cure Peak Temperature is 195^oC
- Cure Completion Temperature is 295^oC

Thermal Conductivity Test results for Glass Phenolic and Glass Silicone samples shows that both are almost same.

4.6 Summary

Resin thermal characteristics and properties play the most vital role for ablative Thermal protection systems performance. In this regard, TGA and DSC test results for Phenolic resin and Silicone resin are evaluated and compared. The TGA plots for Phenolic Resin and Silicone Resin are compared and summary of TGA characteristics for both Resins are given as follows in Table 4.4:

Table 4.4: TGA Characteristics for Resins

Resin	**Initial Decomposition Temperature (^{0}C)**	**Temperature at 10 % weight loss of sample (^{0}C)**	**Char Yield after final decomposition (%)**
Phenolic	190	350	55
Silicone	370	590	79

The test results of present studies on Phenolic and Silicone Resins determines that Silicone resin is better for ablative thermal protection application based on thermal stability characteristics namely initial decomposition temperature, temperature at ten percent weight loss, and residual weight (Char yield) after final decomposition. These parameters are directly related to TPS resin driven functional requirements. Thermal conductivity of Glass Phenolic and Glass Silicone composites was also measured and found similar.

The DSC studies on Epoxy resin are carried to assess the margins and generate temperature constraints as input for the design of an ablative thermal protection system for a composite rocket motor case which is made up of Epoxy resin. Test results of DSC for Epoxy resin i.e glass transition temperature (Tg), Initial decomposition temperature, and temperature at ten percent weight loss also confirm availability of thermal stability margins for Silicone resin in ablative thermal protection system.

Experimental TGA & DSC studies for Phenolic Resin, Silicone, and Epoxy resin as a part of structural composite concludes Silicone Resin as a suitable one for ablative thermal protection layer for Carbon Epoxy structural layer. Present studies also provide design inputs, temperature constraints, and curing parameters that are useful for configuring thermal protection for Carbon-Epoxy composite rocket motor case.

CHAPTER 5

EXPERIMENTAL STUDIES FOR THERMAL PROTECTION SYSTEM

5.1 Introduction

In case of launch vehicles and long-range ballistic missiles, solid rocket motors as propulsion stages are integrated with vehicles and also function as primary structure to with stand various flight and other loads. The stages get separated after respective motor action time is completed based on the mission objectives and trajectory design. All the stages of solid rocket motors are operationally required only during powered phase (ascent) of trajectory and hence external ablative thermal protection for composite rocket motor case also needed for same periods[26]. When missiles lift off and accelerates through atmosphere and kinetic heating due to aerodynamics causes external surface being subjected to heat flux for stage duration based on trajectory design and missile configuration. The experimental studies for thermal protection system are formulated in two phases namely phase-I and phase-II given as follows:

- Phase-I: Experiment studies on thermal protection system (TPS) samples by thermal test
- Phase-II: Experimental studies on missile sub scale model with external ablative thermal protection layer

5.2 Experimental Studies on Thermal Protection System (TPS) Samples

The present studies are conceived and formulated to simulate this scenario in the form of thermal test on thermal protection system (TPS) samples to generate critical data like TPS material & layer, ablative layer condition, interface temperature of external thermal protection system and composite case. To carry out present studies, one of the expected heat flux vs time profiles based on simulated trajectory design is selected [31]. TPS samples in present studies are manufactured by choosing silicone resin as matrix based on studies carried out as one of the research objectives in previous chapter and varying reinforcement materials and layers. External ablative thermal protection system (ETPS) layer needs to integral with composite case and various process, configuration related aspects, are also considered for types and form of reinforcement. ETPS layer mass and functionally needed insulation properties are also considered for planning TPS samples. The samples are manufactured with substrate material of caron-epoxy (CE) simulating composite rocket motor case structural layer material and thickness over which TPS layers are build and cured as per different samples plan.

Thermal test setup including instrumentation requirements like thermocouples, heat flux gauges and data acquisition system are designed and configured to meet studies objectives. Insulation for set up other than samples are also planned and realized. IR lamps are considered as heat source for thermal test to generate required heat flux profile for samples testing. Generation of required heat flux profile is established for the test set up (IR lamp and Sample distance) based on various test trials. In actual test setup, the generated heat flux prolife is measured by heat flux gauges for verification before actual test on samples.

The objective and scope of experimental studies on TPS samples by thermal test includes, finalization of reinforcement material, thickness and layer configuration for composite case external ablative TPS based on following considerations:

- Heat flux profile chosen from one of simulated flight trajectory
- External thermal protection layer and composite case interface temperature constraint of maximum 100 ^{0}C experimentally evaluated in present work

- Silicone Resin is chosen as matrix material for all samples based on experimental studies in present work
- Candidate materials for reinforment are chosen based on: in house lab experience/ data, functional & process aspects, material availability

General external thermal protection system configuration on composite rocket motor case integrated in missile system is shown in following Figure 5.1:

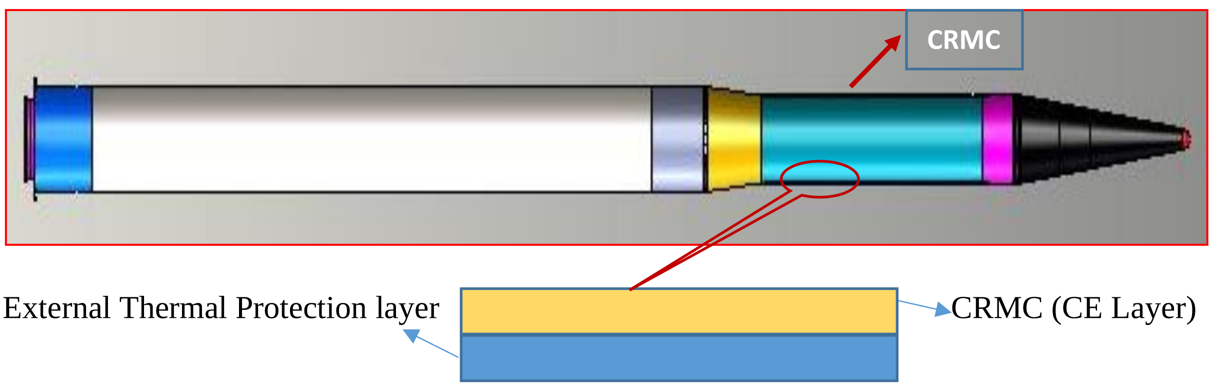

Figure 5.1: Missile System with composite case and thermal protection layer

5.2.1 Laminate Manufacturing and Sample Preparation

Laminates are manufactured with Carbon Epoxy (CE) material by filament winding using rectangular mandrel as per required thickness of 7.0mm. Carbon roving and epoxy resin used here for substrate layer are of same specifications which is being used for manufacturing of composite case mentioned in other studies. Curing is also carried out in oven following the same curing cycle as that of composite rocket motor case. The following materials were selected for thermal protection layer:

- Silicon based PC10
- Carbon Panox /Silicone
- E-Glass/ Silicone
- Kevlar/ Silicone

The above materials are chosen based on their properties suitable for present application, in house experiences in various other applications and availability with required quality. PC 10 is silicone polymer-based compound which is having good heat resistant properties. This compound is cured at room temperature. Application of this compound is simple and conducive on substrate material by spraying, brushing and putty blade. Carbon Panox felt is made from crimped Panox fibers by advanced needle machine. Panox is an oxidized polyacrylonitrile (PAN) fiber which possess characteristics that it does not burn, melt, soften or drip. Thermal stabilization of PAN is carried out at 300^0C to produce Panox fiber. This process enables to produce oxidized textile fiber with carbon content of 62%. Oxidized PAN fiber is used in wide variety of applications like fire retardant and thermal protection due to its special properties. Besides high thermal stability, Panox offers high chemical resistance, very good insulating properties and excellent thermal stability. As a result, felt containing Panox fibers offers high thermal stability, excellent fire and heat protection. They also have good insulating properties due to low thermal conductivity. Carbon panox is porous and exhibits excellent thermal stability and insulation with very less weight which is foremost advantageous to develop TPS having less weight. E glass and Kevlar roving are having good insulating properties and highly conducive for wet filament winding with silicone resin impregnation. The TPS materials and thicknesses based on various test trials are considered for preparation of sample types and plan. As per sample types requirements, TPS layer thickness using respective reinforcement is built over substrate CE material and cured as per silicone resin curing cycle of maximum temperature of 140^0C for four hours except PC 10 sample which is room temperature cured. The details of all types of prepared samples for thermal tests are given as follows:

SAMPLE 1 (S1): Bare Sample with thickness of structural layer (thickness :7.0 mm)

SAMPLE 2 (S2): Coated with Silicon based PC-10 (Thickness: 0.5 mm)

SAMPLE 3 (S3): One layer carbon Panox / Silicone Resin (Thickness:0.6 mm)

SAMPLE 4 (S4): Two-layer carbon Panox / Silicone Resin (Thickness:1.2 mm)

SAMPLE 5 (S5): One inner layer (thickness 0.6 mm) Carbon Panox / Silicone Resin & one outer layer of E-Glass/Silicone (thickness 0.7mm)

To measure temperature at ETP layer and CE layer interface, 'K' type thermocouples are also bonded at interface. In samples type 4 and type 5 (S4 & S5), the additional thermocouples are bonded at 2mm, 4mm and 6mm from bottom face to measure the temperature gradient with in composite case structural layer. The photos of samples are shown in following figures 5.2:

(a)Bare CE sample (S1) (b) Sample S2 & S3 on two faces (C) Sample S4 &S5

Figure 5.2 Thermal Protection System (TPS) samples

5.2.2 Thermal Test Methodology

Thermal tests for TPS samples are carried out with IR heating lamps as heat source. The heat flux profile for test is taken from one of simulated flight trajectory shown in following figure 5.3:

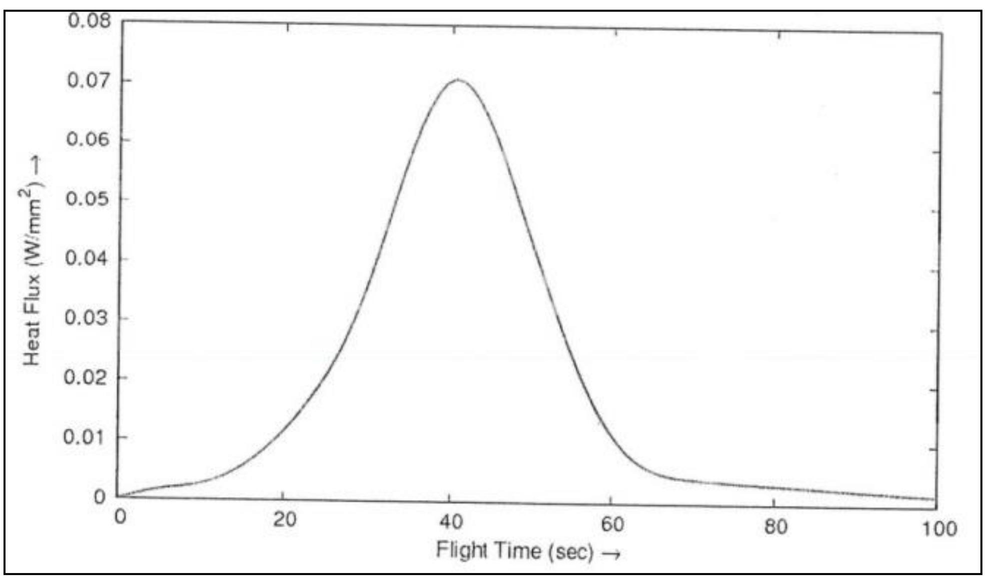

Figure 5.3: Heat Flux Profile

Thermal test setup is worked considering test criticalities and instrumentation requirements of temperature measurements by thermocouples and heat flux by heat flux gauges. Thermal test set up includes samples holder, fixture for mounting of IR lamps with adequate insulation for fixture protection. Data acquisition system is used to acquire and log temperature and heat flux data. Thermal test set up schematic is shown in following figure 5.4:

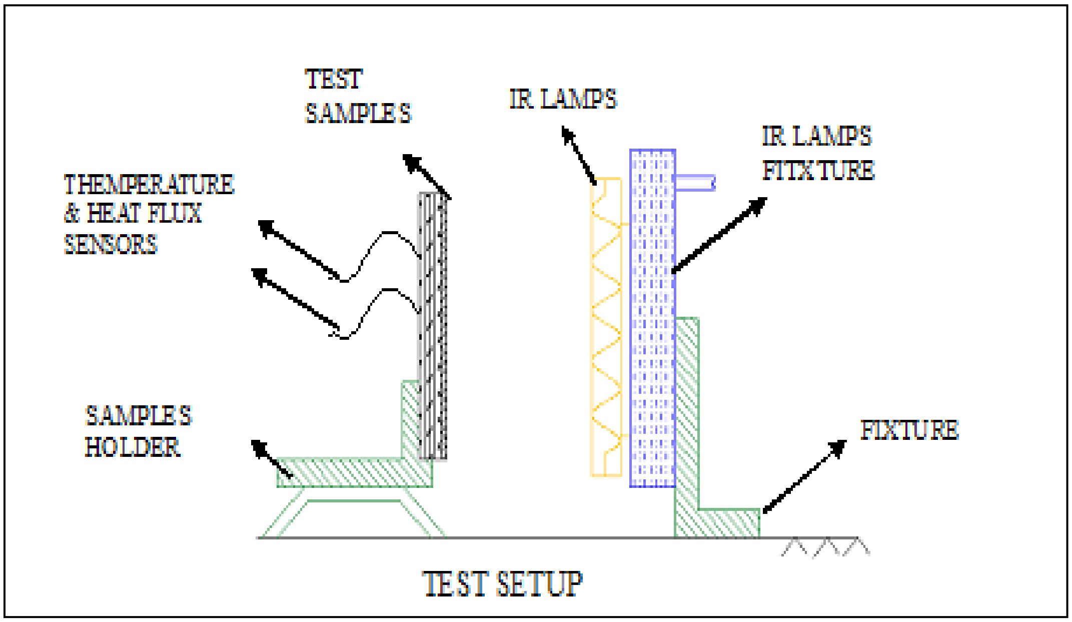

Figure 5.4: Thermal Test Setup

One of the most significant prerequisites for thermal test is to establish and validate heat flux profile achieved in test setup with respect to required heat flux profile to get accurate test results. This is carried out through heating trials using actual thermal test set up with selected IR lamps. During heating trials, distance between heat source and samples are also adjusted and heat flux gauges are used for achieved heat flux measurements. Test set up is finalized and achieved heat flux profile in actual test set up is closely matching with required profile. The validation results for achieved and required heat flux profile are shown in following figure 5.5:

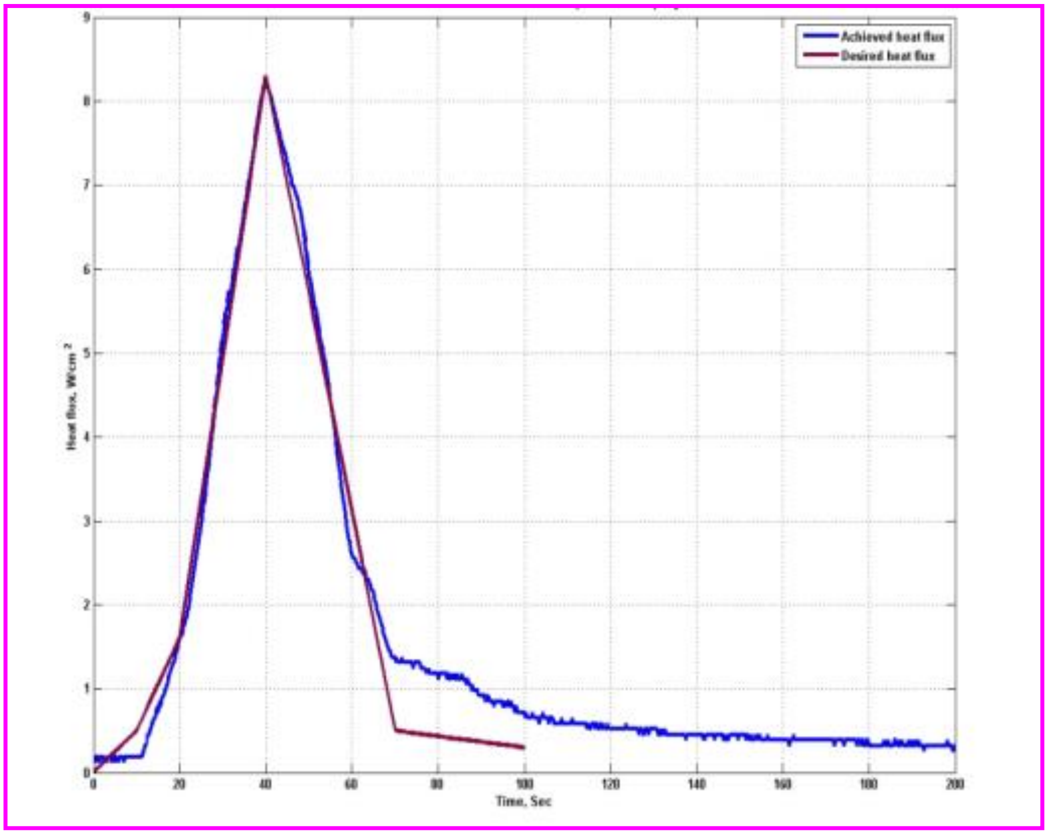

Figure 5.5: Achieved and required heat flux profiles

The actual samples are mounted on test set up and all cables are connected from sensors to data acquisition system as shown in following figure 5.6:

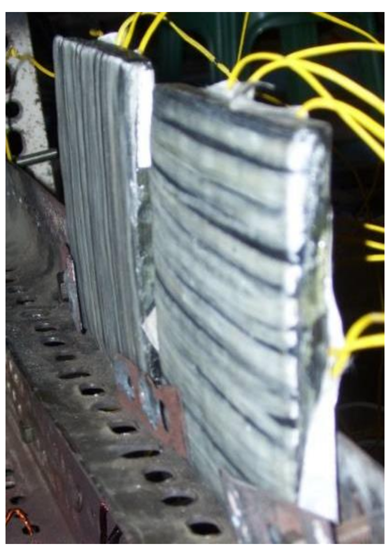

Figure 5.6: Samples on Thermal Test Set Up

5.2.3 Thermal Test Results

Temperature data for each sample thermocouple is acquired in data acquisition system and data is plotted with respect to time along with heat flux profile. The thermal test results for all samples are shown in following figures 5.7, 5.8 and 5.9:

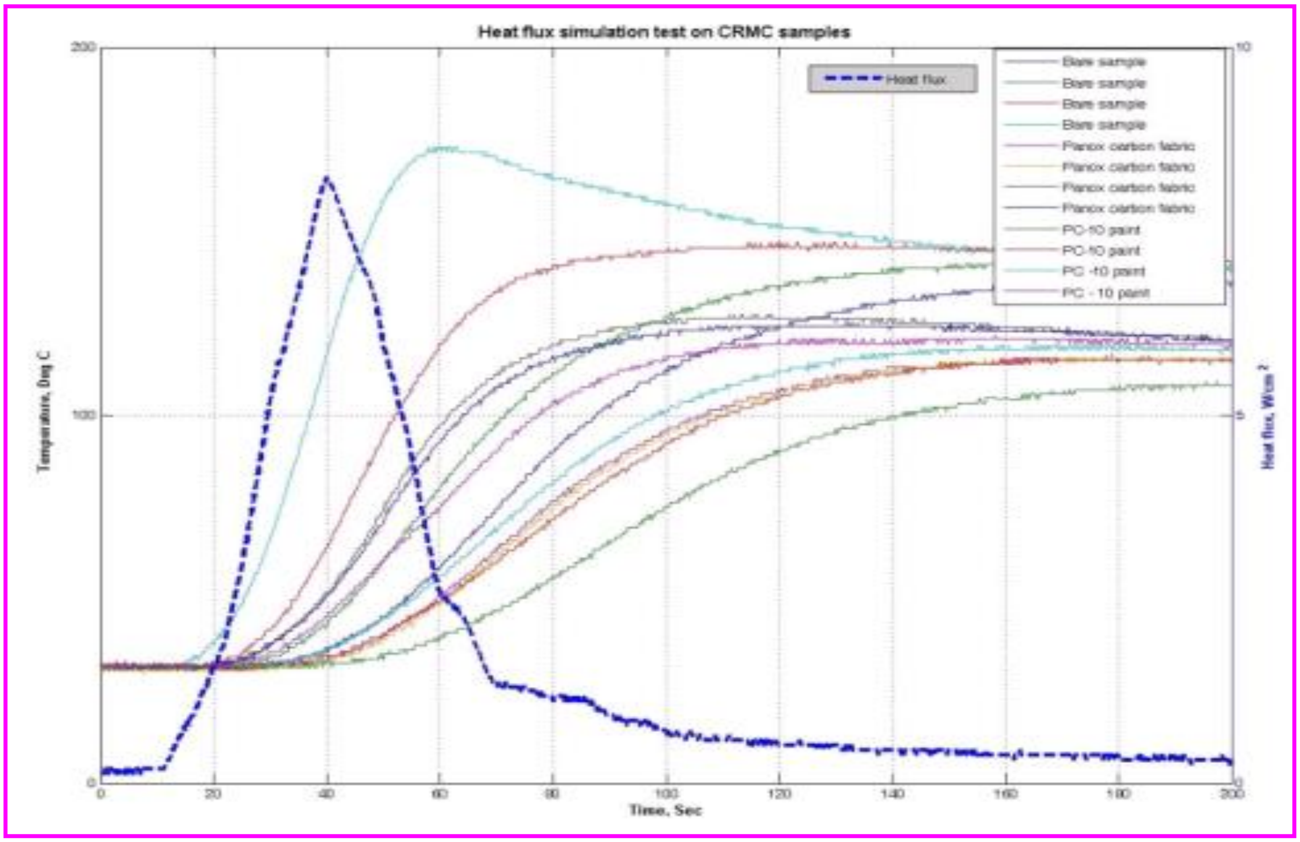

Figure 5.7: Temperature at TPS and CE interface for Samples 1,2 and 3

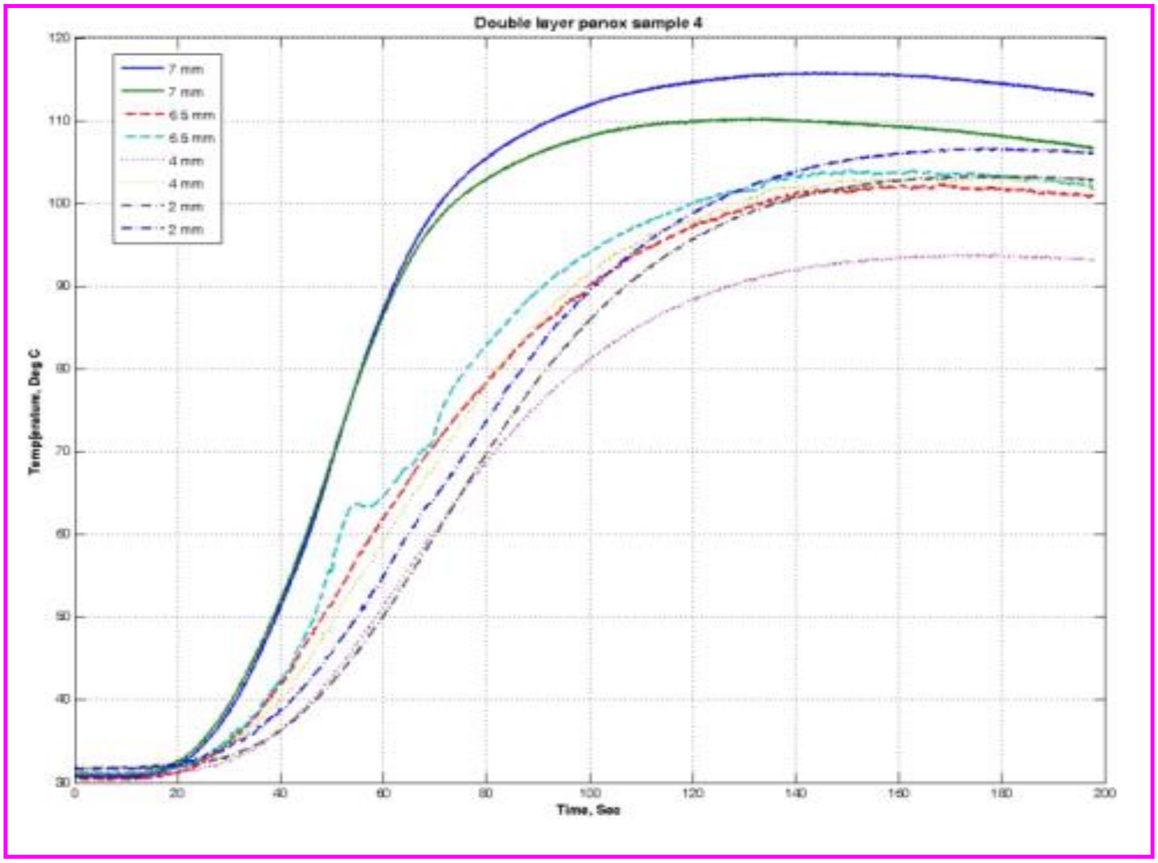

Figure 5.8: Temperature at TPS and CE interface and different depths for sample4

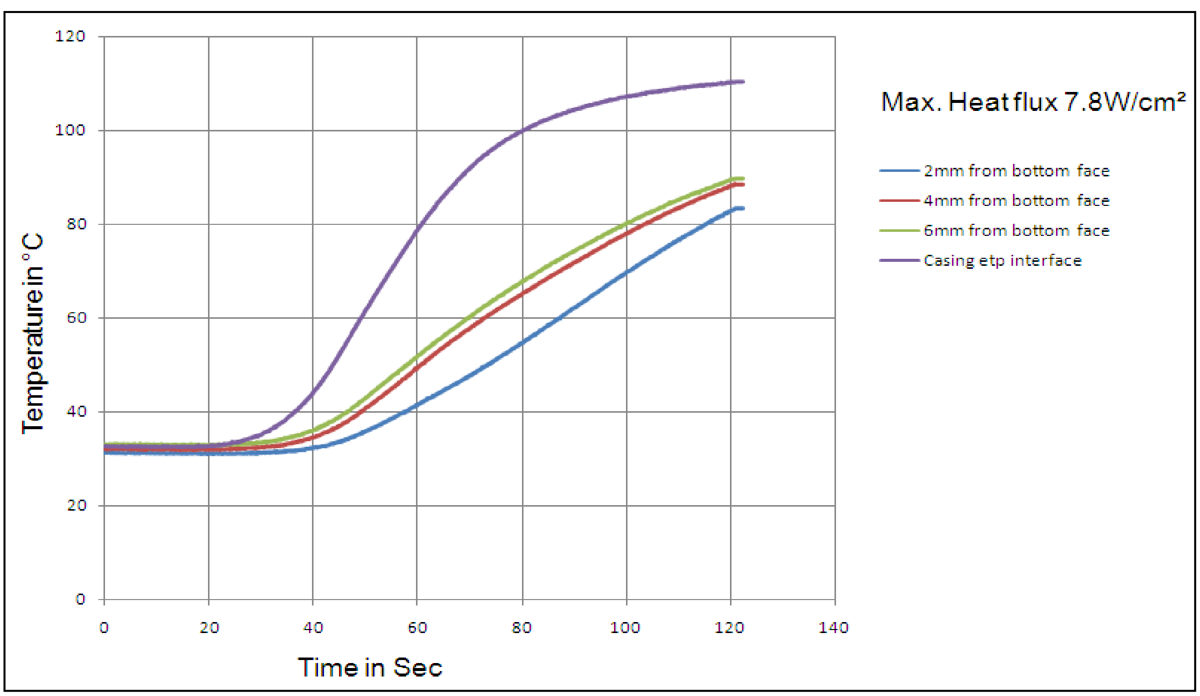

Figure 5.9: Temperature at TPS and CE interface and different depths for sample 5

The measured temperatures at interface of external thermal protection (ETP) layer and CE layer at 95 second for all samples are given in following table 5.1:

Table 5.1: Interface (TPS-CE) temperature for samples

Samples	**Temperature (^{0}C)**
Sample-1	180
Sample-2	120
Sample-3	120
Sample-4	110
Sample-5	100

The above test results are analyzed considering heat flux profile for simulated missile trajectory and flight time for rocket motor of 95 seconds.

5.3 Experimental Studies on Missile Sub Scale Model with Ablative External Thermal Protection Layer

The long-range ballistic missiles and launch vehicles configurations usually consists of multiple propulsion stages based on solid rocket motors. As per trajectory design and mission objectives, the stages get successively separated through various separation mechanisms. The instant of lift off until stage (solid rocket motor) gets separated is the operational phase of composite rocket motor case including its ablative external thermal protection system (ETPS). During this phase, the external ablative thermal protection layer on composite case is subjected to kinetic heating and flow conditions due to aerodynamics. The present studies are conceived and formulated to simulate heating and flow conditions due to aerodynamics of actual flight environment on ground test on to vehicle. Missile metallic sub scale (20:1) model is manufactured in order to simulate actual configuration and geometry to carry out present studies. Missile sub scale model is made with dimensions considering the required Carbon-Epoxy layer thickness at composite rocket motor case location. Carbon-Epoxy actual material has been used for composite case are wet filament wound over metallic subscale model of required thickness at identified composite case zone. After completion of filament winding of all layers, curing is carried out in oven as per Carbon-Epoxy specified curing cycle. On the cured Carbon-Epoxy substrate material, the external ablative thermal protection layer as finalized in previous chapter studies are built over followed by curing of thermal protection layer as per silicone curing cycle. This scheme of manufacturing missile sub scale model is planned to establish processes of both external thermal protection layers built up over Carbon-Epoxy substrate at sub scale level. Missile sub scale model manufactured with present scheme is able to simulate the exact external thermal protection layer configuration over composite rocket motor case along with all process aspects and materials like actual case. Wind tunnel is chosen to simulate required flow conditions due to aerodynamics.

Present experimental studies are carried out with objective to assess integrity of external thermal protection layer with composite case (CE layer) under shear load and flow conditions. These shear load and flow conditions will be encountered in flight due to aerodynamics on outer surface of external thermal protection layer on composite rocket motor case.

5.3.1 Testing Methodology

Testing methodology is evolved based on various functional conditions considered as requirements and objectives. Testing methodology is given as follows in figure 5.10:

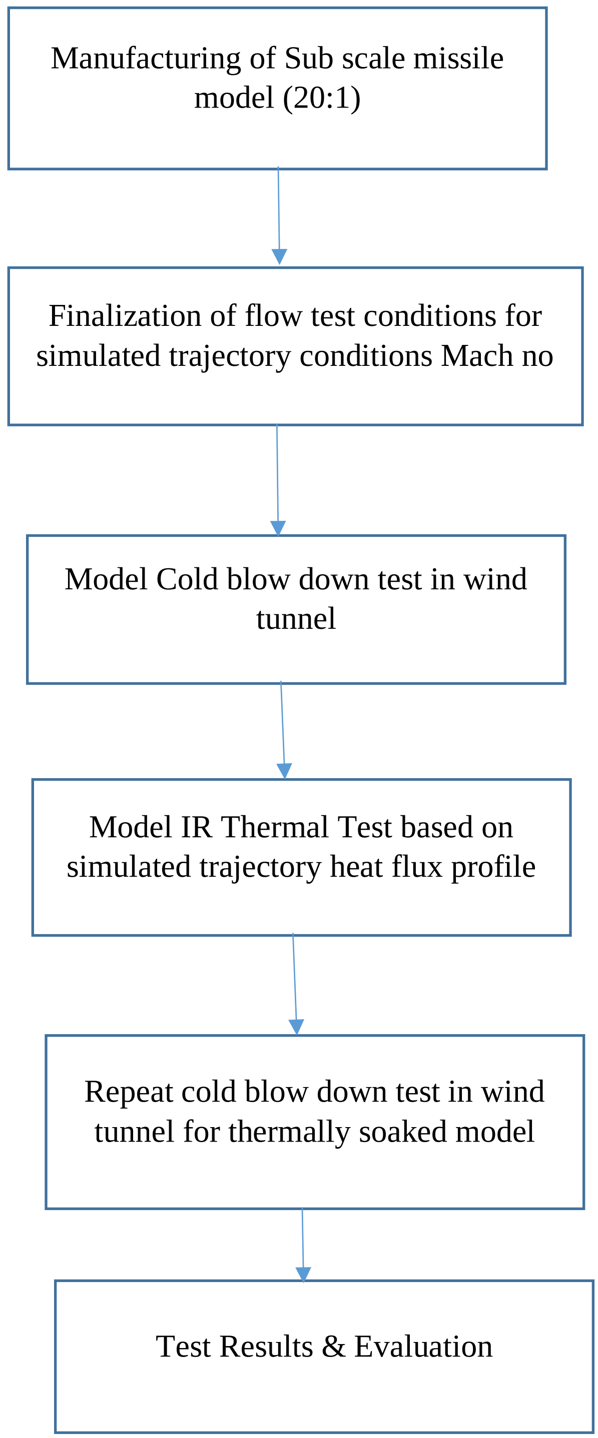

Figure 5.10: Test Methodology

5.3.2 Manufacturing of Missile Sub Scale Model

Missile sub scale metallic model is made with 20:1 scale as per requirement. The metallic sub scale model dimensions are configured in such a way to accommodate Carbon-Epoxy layer (7 mm) and external thermal protection layer (1.3 mm) over composite rocket motor case location. The Carbon -Epoxy layer of required thickness of 7 mm is filament wound and cured. After curing, inner layer of external thermal protection system made up of Panox/ silicone resin of 0.6 mm is hand lay-up followed by winding of outer glass/ silicone resin layer of 0.7mm as outer layer. Curing of external thermal protection layer is carried out as per finalized cure cycle and model is ready for tests. The sub scale missile model is shown in following figure 5.11:

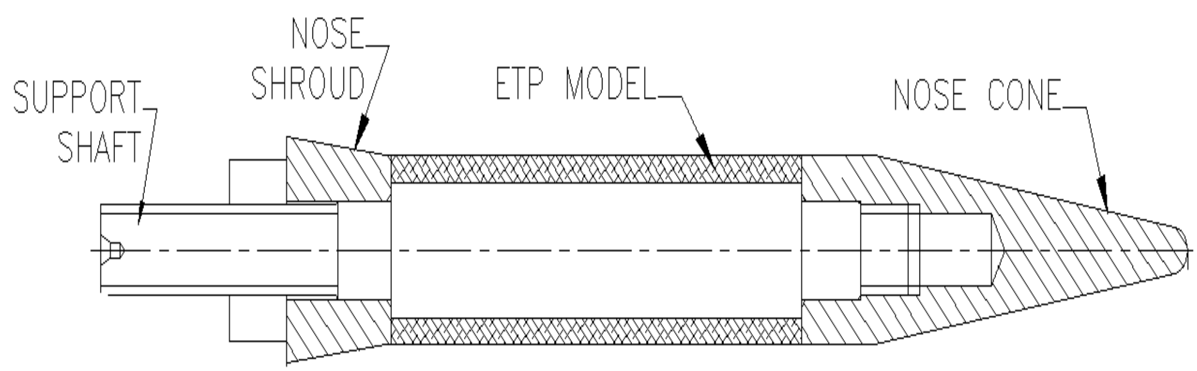

Figure 5.11: Missile Sub Scale Model

Model is subjected to Radiographic and ultrasonic test to assess presence of any defect with in external thermal protection layer and at interface of this layer and Carbon-Epoxy layer. In Radiographic test and ultrasonic test, no defects are observed.

5.3.3 Testing and Evaluation

Wind tunnel is selected to simulate shear and flow conditions for external thermal protection layer over Carbon-Epoxy layer in sub scale missile model. The conditions for wind tunnel test are considered based on simulated flight trajectory requirements of 3.5 Mach for 60 seconds. Model was mounted in front of wind tunnel and sheal under flow cold test is conducted at 3.5 Mach for 60 secs. The model in wind tunnel is shown in following figure 5.12:

Figure 5.12: Missile Model in Wind Tunnel

Once wind tunnel test is over, visual inspection, radiographic test and ultrasonic test is carried on model to assess any defect with in external thermal protection layer and at interface of this layer and CE layer. The Ultrasonic test was carried out with pulse echo technique and no recordable indications were observed. In case of radiographic test minor density variations were observed which were classified as resin rich zones and without any delamination. External thermal protection layer integrity with Carbon-Epoxy layer found intact in cold shear under flow test.

The same model is subjected to thermal test with IR heating to study effect of thermal soaking on external thermal protection layer and also to measure interface temperature (TPS/CE layer) at subscale model level. Applied Heat flux profile is same as used in thermal test of TPS samples mentioned in earlier studies. Heat flux profile is given in following figure 5.13

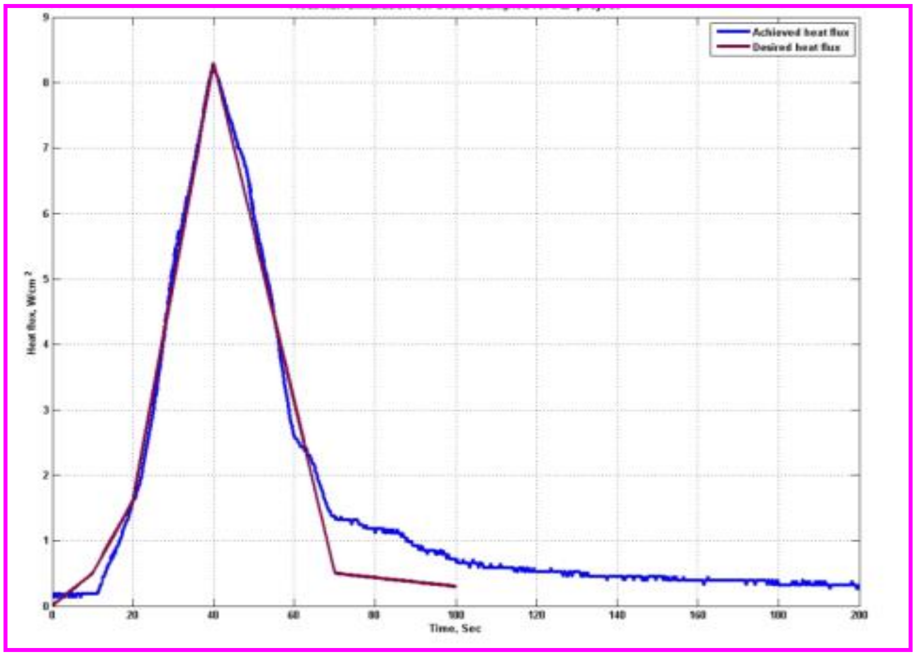

Figure 5.13: Heat flux profile (Expected and achieved in set up)

Thermal test for model is carried out with IR heating inside a cylindrical chamber fixture. On the circumferential periphery of fixture inner surface IR heaters were mounted. The insulation is also applied on the inner surface of fixture. In test setup, through IR lamps heat flux profile is generated and same is verified through heat flux gauge measurement and found closely matching before actual test. Thermocouples are connected through cables to data acquisition system. The thermal test for model with IR heating is shown in following figure 5.14:

Figure 5.14: Thermal Test for Model

Model thermal test is carried out as per given heat flux profile from simulated missile trajectory and measured interface temperature at external thermal protection layer and Carbon-Epoxy layer is 100^0C.

Visual inspection and Radiographic test are repeated on model to assess any deterioration at external thermal protection and CE layer interface after completion of model thermal test. No deterioration is observed at interface and external thermal protection layer is found integral with CE layer. Evaluation by visual inspection and radiographic test after thermal test confirmed and validated external thermal protection layer condition and integrity with CE after heat soaking. External thermal protection layer performance and integrity is verified and confirmed through this test. External thermal protection layer condition after thermal test is shown in following figure 5.15:

Figure 5.15: External Thermal Protection Layer after Thermal Test

Thermally soaked model is subjected to wind tunnel test once again for simulated flow conditions to study effect on external thermal protection layer already soaked for total heat input. Thermally soaked model in wind tunnel is shown in following figure 5.16:

Figure 5.16: Thermally Soaked Model with Wind Tunnel

The thermally soaked thermal protection layer is found intact after wind tunnel test under cold flow conditions and integrity of this layer is verified for thermal and flow conditions to meet functional requirements.

5.4 Summary

The present experimental studies on TPS samples are carried out and all intended objectives are achieved. Thermal test results showed that measured temperature at ETP layer and CE interface is meeting requirement for sample-5. ETP layer for sample -5 consists of one inner layer (thickness 0.6 mm) Carbon Panox / Silicone Resin & one outer layer of E-Glass/Silicone (thickness 0.7mm). The outer layer of E-glass/ silicone is ideally suited for TPS process especially filament winding, which will provide excellent consolidation of inner layer and integrity with CRMC structural layer.

The ablative external thermal protection system (ETPS) for CRMC is configured with two layers given as follows:

- ❖ Inner layer having porous filler with less density and facilitates for reduced heat transfer towards inside

  (One layer of Caron Panox & Silicon Resin having thickness of 0.6 mm)

- ❖ Outer layer having fiber with Low thermal conductivity (Insulating) and suitable for filament winding

  (One Layer of E-Glass & Silicon Resin having thickness of 0.7 mm)

Missile sub scale model with actual Carbon-Epoxy layer (simulating composite rocket motor case) and finalized external ablative thermal protection layer (inner and outer layer) is manufactured. Test results of studies carried out above namely cold flow test for shear in wind tunnel for 3.5 Mach, 60 secs on virgin external thermal protection layer model confirmed and validated integrity of this protection layer. Thermal test on the model is also carried for required heat flux profile with temperature measurement at external thermal protection and Carbon-Epoxy layer interface. Evaluation after thermal test through visual inspection and radiography verified external thermal protection layer in good condition and integrity with Carbon-Epoxy layer. The measured interface temperature of 100^0C proved required performance of external thermal protection layer on composite rocket motor case. After thermal test, the heat-soaked model is subjected to repeat cold flow test in wind tunnel test for evaluation. After repeat wind tunnel test, thermally soaked thermal protection layer is found intact with no deterioration of integrity at

Carbon-Epoxy interface. Present studies confirmed integrity of external ablative thermal protection layer with Carbon-Epoxy layer (Composite rocket motor case) to meet actual functional requirements during flight.

CHAPTER 6

PROCESS DEVELOPMENT OF EXTERNAL ABLATIVE THERMAL PROTECTION SYSTEM

6.1 Introduction

Composite rocket motor case (CRMC) is made up of Polyacrylonitrile (PAN) based carbon roving and epoxy resin which polymeric composite material. Composite rocket motor case is manufactured by wet filament winding process. In case of wet filament winding, there are following main requirements like equipment, tools and winding program.:

- Five axes CNC filament winding machine with resin bath, fiber creel stand, fiber tensioning mechanism, payout eye attachments.
- Filament winding program based on design requirements for hoop and helical circuits
- Mandrel with required geometry and attachment features for end metallic polar bosses, skirts bonding fixtures

The required hoop and helical layers are wound as per winding program, however on both side domes (Igniter and nozzle end) of composite case doilies are prepared and hand layup is done as per required ply sequence. To prepare doilies, drum filament winding is also parallely done and based on specific layer, using template segment is cut to carry out hand lay-up. The curing is carried in oven having temperature controller, associated instruments and data logging system. Mandrel gets extracted and for composite rocket motor case, dimensional inspection, NDT (Visual, ultrasonic test, radiography) is carried out for acceptance. Development of external ablative thermal protection layer process over composite case external surface is carried out considering its configuration, materials, manufacturing process and functional requirement especially interface integrity for motor action time. Ablative external protection layer consists of two layers as finalized in earlier studies of present work. The manufacturing processes are selected as hand lay up for inner layer and filament winding for outer layer based on layers materials (type and form) and integrity requirements with composite rocket motor case[33]. In case of polymeric composites, curing is very crucial for resin cross linking and consolidation which depends on resin cure characteristics. Ablative external thermal protection layer is silicone resin based however composite case layer is based on Epoxy resin. Cure characteristic of silicone resin are also evaluated to analyze thermal margins with rest to epoxy resin (characterized in earlier study in present work) and finalize curing cycle of external thermal protection layer.

The multilayer thermal protection was considered to meet two basic requirements one for low density porous material in inner layer and second for reinforcement material with low thermal conductivity in roving form conducive for filament winding in outer layer. The Configuration of ablative external thermal protection layer for composite rocket motor case was evolved based on following:

- Test results of TPS samples thermal tests mentioned in earlier studies as part of present research objective
- Materials & Manufacturing process of FRP structural layer compatibility
- Application based various functional requirements

The details of finalized ablative external thermal protection multilayer are as follows:

- Inner layer having porous filler with less density and facilitates for reduced heat transfer towards inside i.e. One layer of Caron Panox & Silicon Resin having thickness of 0.6 mm.

- Outer layer having fiber with Low thermal conductivity (Insulating) and suitable for filament winding i.e., layer of E-Glass & Silicon Resin having thickness of 0.7 mm.

6.2 Materials for Ablative External Thermal Protection Layer

Ablative thermal protection consists of two layers. The reinforcements in inner and outer layers are Panox felt fabric and E-glass respectively. The matrix material is Silicon resin for both inner and outer layers. The material description is given as follows:

Panox Felt Fabric:

Panox felt is made from crimped Panox fibers by advanced needle machine. Panox is an oxidized polyacronitrile (PAN) fiber which possess characteristics that it does not burn, melt, soften or drip. Thermal stabilization of PAN is carried out at 300^0C to produce Panox fiber. This process enables to produce oxidized textile fiber with carbon content of 62%. Oxidized PAN fiber is used in wide variety of applications like fire retardant and thermal protection due to its special properties. Besides high thermal stability, Panox offers high chemical resistance, very good insulating properties and excellent thermal stability. As a result, felt containing Panox fibers offers high thermal stability, excellent fire and heat protection. They also have good insulating properties due to low thermal conductivity. The properties of Panox fiber of felt considered in present work is given in following Table 6.1:

Table 6.1: Material Properties of Panox Crimped Staple Fibers

S.No	Properties (units)	Specifications
1	Linear density (dtex/den)	1.7/1.5
2	Fiber density (gm/cm^3)	1.39
3	Moisture content (%)	10
4	Elongation at break (%)	22
5	Tensile strength (MPa)	220
6	Tenacity (cN/tex)	1.58
7	Finish content (%)	0.9
8	Fiber length (mm)	63
9	Nominal crimp count (per cm)	6
10	Sizing Type	Antistatic

The felt made from Panox fiber has limited oxygen index more than 40% and it can be used continuously in a very wide temperature range from -196℃ to 360℃.It has no decomposing or melting at 600℃. The Panox felt main characteristics are as follows:

- Excellent flame retardant properties
- Excellent Heat Insulation properties
- No Melt Drip properties
- Excellent high temperature resistance

Silicone Resin:

In present work Silicone solid flake resin is chosen which contains 100 percent silicone and silanol functional resin. This resin for application is made as solution with 60% Toluene solution. Technical Specifications of Silicone flake Resin is given as follows in table 6.2:

Table 6.2: Specifications of Silicone Resin

S. No.	Parameter/ Property	Specification
Silicone Solid Flake resin		
1	Non-Volatile Content (% by weight)	98 (Minimum)
2	Specific gravity at 25°C	1.33-1.43
3	Hydroxyl content, (mg KOH/g)	5.5-6.5
4	Melt Viscosity at 150°C, cP	212-258
As 60 % Toluene Solution		
6	Solid Resin content (% by weight)	58-62
7	Volatile content (% by weight)	38-42
8	Specific gravity at 30°C	1.05-1.15
9	Solution Viscosity at 30°C, cP	30-110

E-Glass Roving

The material properties of E-Glass Roving are given in Table 6.3 as follows:

Table 6.3: Properties of E-Glass Roving

S.No	Properties (units)	Specifications
1	Tex (Gram/Km)	1200 Nominal
2	Dry Roving tensile breaking load (N)	200 Nominal
3	Specific gravity	2.5-2.6
4	Winding	External/Internal unwound

6.3 Ablative External Thermal Protection System Manufacturing Process

The external ablative thermal protection system manufacturing processes needs to decided based on stating raw material, stages of composite manufacturing processes, selection criterion for process and various other functional, substrate materials aspects. The brief on approach for external ablative thermal protection system process selection is given in following sections.

6.3.1 Stages of Composite Manufacturing Process

The composite manufacturing process for polymeric composites with thermosetting resin as matrix basically involves four stages namely impregnation, lay-up, consolidation, and solidification.

Impregnation:

This is preliminary stage, in which reinforcement and matrix are mixed with each other to form a ply also known as lamina. This mechanism of mixing basically depends on type and form of reinforcement as well as component fabrication process. For instance, prepregs used for various lay-up processes are made through impregnation plan under controlled conditions, roving from creel stand moves through resin bath and gets impregnated just before mandrel in wet winding process, fabric layers get wetted with resin by brush or using rollers for adequate impregnation by using measured resin quantity per square meter of fabric to get consistent resin volume fraction in wet hand lay-up process. Impregnation process ensures proper wetting of fibres surface through conducive resin flow. Impetration process basically depends on resin parameters mainly viscosity, surface tension, and capillary action.

Lay-up:

In this stage, the laminae/ plies are staked or placed in sequence, orientation and location as per requirement. Based on component design, the required component thickness is built by staking various impregnated layers of fibre and resin in defined sequence. In case of filament winding, the fibre orientation, distribution and thickness are achieved through relative motion of mandrel cross head through CNC winding program. In a wet hand lay-up process the impregnated fabric and resin sector is built manually on mould as per required thickness. In this phase of fabrication step basic objective is to achieve specified reinforcement orientation, location as per design.

Composites being anisotropic, the performance of composite structures or components depends heavily on transformation of design requirements like fiber orientation and ply sequence into process/product.

Consolidation:

In this phase, the compaction is achieved between lamina or plies during lay-up. The basic objective is to remove any entrapped air between plies during process. This step is very significant in manufacturing composite components with minimum defects and sound quality. Consolidation is achieved in different ways depending on process, for example, in filament winding by maintaining good fiber tension from creel stand to mandrel, during pre -preg tape winding on machine, compaction rolled against mandrel used and during hand wet lay-up rollers are used after each layer. The improper consolidation leads to more void content and resin lean zones.

Solidification:

Solidification is last phase of composite processing. The solidification process depends on resin characteristics. In case of polymeric composites based on thermosetting resin, the solidification time depends on resin formulation and their cure characteristics. In case of thermoset resin, crosslinking of polymers take place during curing and for polymerization advancement heat is also supplied. During curing process, depending on resins, vacuum and pressure simultaneous or one of them are applied in autoclave. Auto clave is a pressure vessel in which pressure, heating and vacuum provision is available.

6.3.2 Selection of Manufacturing Process:

It is always a challenging task to select a most appropriate manufacturing process due to various factors and variety of choices available for raw materials and processing techniques. Most fundamentally, selection of process depends on the application requirements[34]. The selection of process depends on various factors such as production rate, manufacturing cost, design requirements, component configuration (size and shape).

Design Requirements:

The basic design requirements like strength and stiffness are also very important factors for selection of reinforcement form and type which in turn affects manufacturing technique selection.

The composite manufacturing processes are mostly selected based on type and form of starting raw materials depending on design requirements as starting raw material affects component properties. The mechanical properties (strength and modulus) of the composite parts depends on reinforcements like type of fiber, fiber length, fiber directions, and fiber volume fraction. For instance, composite component made from continuous fiber possess higher strength and stiffness than composites of chopped fibers.

Component configuration:

Component configuration includes size, shape or overall geometry of the product. The size of component is very important criterion for composite process selection for example, closed moldings are suitable for small to medium size parts whereas for large size components open molding is preferred. Component shape also play vital role in composite manufacturing process selection for instance, the manufacturing of tubes, pipes, pressure vessels, cylindrical shape is suitable through filament winding process. Similarly, for manufacturing of components having uniform rectangular and circular cross sections, pultrusion is most suitable process

Production Rate:

Demand for production rate for components are different depending on their application and needs. For instance, the automobile sector requires high production rate due the huge demand where as any product in aerospace sector is required in less volume hence production need is drastically less. There are composite manufacturing processes some are conducive for low volume and some for high volume production for example hand -layup and wet lay-up are suitable for low production whereas compression and injection molding processes cater for high volume production. Considering such variation in demand rate of products, suitable manufacturing technique needs to be selected based on requirement.

Cost:

Cost depends on various elements like machinery & equipment, processing tools, manpower cost, raw materials, manufacturing cycle time and integration time. By virtue of composite manufacturing processes, some are conducive for low-cost parts where as some are high cost. The requirement of production volume is very significant factor for component cost.

The present work is for composite rocket motor case which is in the field of aerospace hence design requirements and component configuration (size and shape) are governing factors for process selection. Based on these critical factors including starting raw materials and various functional and substrate layer requirements, the wet hand -up is selected for inner layer and filament winding is selected for outer layer of external ablative thermal protection system manufacturing.

6.3.3 Basics of Selected Processes

The basic steps along with involved criticalities of selected manufacturing processes, wet hand lay-up and filament winding for inner and outer layer of ablative external ablative thermal protection system respectively are summarized as follows:

Wet Lay-Up Process:

The wet lay-up process is versatile and dominantly being used for fabrication composite components since early days to present era. This composite manufacturing technique is process dominant and labour intensive. This process allows lot of flexibility in terms of layers orientation, different types of reinforcement layers, volume fraction during component manufacturing. In this process, liquid resin viscosity is checked and required weight is taken before application on reinforcement. Roller is used for proper impregnation of fabric with resin. Subsequent layers with required quantity of resin impregnation are placed until specified thickness is achieved. After every layer is placed, the roller is applied to achieve good compaction. In this process, layers are stacked manually, hence process is known as hand lay -up. The process is very simple and does not require equipment and widely used for manufacturing of prototypes, manufacturing of test coupons for composite testing and also suitable for simple to complex shapes. The size of component and resin formulation defines manufacturing cycle time. Quality control during in process is very crucial in this case due to process intensiveness to achieve good quality product. After lay-up gets completed, the curing is the next step. The curing process depends on resin being used and accordingly curing is defined for example, for high temperature curable resin, oven or autoclave is used and if during curing volatiles evolution is expected, the vacuum bagging also is needed to apply required vacuum and also pressure application for proper solidification. The wet lay-up process includes following broad steps during process:

- ✓ As per components requirements if lay-up is done on mould, degreasing of mould followed by application of release agent of film. Sometimes due to difference in reinforcement materials in layers, lay-up needs to be carried out on in suite to previous layer after surface preparation.
- ✓ Based on need for good surface finish, if gel coat is needed then it should be applied and allowed to get hardened before actual lay-up starts.
- ✓ Preparation and identification of various templates needed to cut reinforcement based on component shape and size to cover different zones
- ✓ Placement of reinforcement layer on mould followed by resin application for impregnation. Based on product and resin system in some cases fabric is impregnated with resin on table and then impregnated fabric is directly put on mould.
- ✓ Hand rollers are used to spread resin uniformly and removal of entrapped air between layers.
- ✓ As per component thickness requirement, subsequent layer build up continues following above step until required thickness is achieved.
- ✓ Once lay-up gets completed, curing is carried out based on resin system requirements and curing cycle

Filament Winding Process:

Filament winding is a process in which mandrel is used as tool to replicate component inner geometry and fiber impregnated with resin are wound in specified orientation over rotating mandrel. To carry out filament winding, CNC winding program is used which synchronizes all five axes motion in machine to lay the impregnated fiver at desired angle. This process is most commonly used for manufacturing of tubular components, pressure vessels, pipes, rocket motor casings, and rocket launch tubes. The starting materials for this process are continuous roving and thermoset resin having optimum viscosity. Rovings spools are usually kept on creel stand and resin bath is placed on carriage unit before mandrel, roving passes through resin bath and gets wound on mandrel. The proper impregnation of roving with resin is very essential to manufacture component with desired properties. The proper impregnation of roving and resin is achieved through: maintaining constant roving tension, provision of guided pins in roving path, provision of doctor blade at resin bath. Once winding gets completed as per requirement, components is subjected to curing as per specified curing cycle. After curing mandrel is extracted, component is inspected for acceptance.

The major process steps for wet filament winding are given as follows:

- ✓ Identification of roving spools and mounting on creels.
- ✓ Based on number of spools required for winding, rovings are taken from each spool passing through guided pin up to pay out eye.
- ✓ Thermoset resin is mostly used which are two component system namely resin and hardener. Resin and hardener are mixed in specified ratio in separate container and then transferred into resin bath.
- ✓ Mandrel is prepared and loaded on to filament winding machine. Release film are applied on mandrel surface.
- ✓ The starting point is marked on mandrel and roving impregnated with resin is taken manually from payout eye and placed at this point. The required fiber tension is maintained through tensioning device.
- ✓ The tested winding program is loaded on CNC controller of winding machine, through this program synchronized motion between mandrel, carriage and payout eye is generated to wind roving as per design requirements up to full laminate thickness.
- ✓ The roving bandwidth after being delivered on mandrel is verified at starting and winding progresses based on program circuits to build the total thickness.
- ✓ After winding gets completed, to achieve good surface finish Teflon coated bleeder or tape is rolled onto top layer.
- ✓ The mandrel along with wound component is subjected to curing as per resin system and it curing cycle. In most of the cases curing is needed at elevated temperature in oven.
- ✓ Once curing gets completed, mandrel is extracted and component NDT, dimensional and load tests are conducted based on requirements for acceptance.

6.3.4 Manufacturing of External Ablative Thermal Protection System

The selection of processes for composite manufacturing depends on type & form of reinforcement materials and application requirements. The primary considerations for process development of ablative thermal protection system for composite rocket motor case external surface are given as follows:

- Ablative thermal protection layer needs to be integral with composite case during operation
- Ablative thermal protection [15] multilayer configuration

- Reinforcement materials for inner layer as Panox felt and E –glass roving for outer layer and Silicone resin for both layers
- Composite Case curing temperature and its glass transition temperature (Tg)

Based on above considerations, the various processes for inner and outer layers of ablative thermal protection [26] were tried and finalized.

Inner layer

The inner layer is made up of Panox felt as reinforcement and matrix as silicone resin. The manual wet lay-up process was adopted for this layer. The casing was marked into four segments depending on casing dimensions and Panox felt fabric width and length for hand lay-up process. The various process steps are described as follows:

- Identification of Silicone resin & Panox felt lot meeting specifications.
- Surface preparation of external surface of composite case which involves roughening of surface by coarse emery under rotation on filament winding machine followed by cleaning it with LR grade acetone.
- Preparation of Silicone resin and application on carbon-Epoxy structural layer of composite case
- Preparation and identification of templates for cutting of Panox felt as per plan depending on casing marked segments.
- Weighment of silicone resin as per quantity based on required resin volume fraction per square meter of Panox felt for each segment
- Table top impregnation of Panox felt with weighed quantity of silicone resin using brush
- Cutting of impregnated Panox felt using identified templates based on ply location/zone
- Hand lay-up of impregnated Panox felt over composite rocket motor case as per planned sequence to cover external cylindrical surface segment wise

The Impregnation of Panox fabric and wet hand lay-up is shown in following figures 6.1 and 6.2.

Figure 6.1: Impregnation of Panox Fabric and Silicone Resin

Figure 6.2: Hand lay -up of Impregnated Panox Fabric

Outer Layer

The outer layer is made up of E-glass roving and silicone resin. The outer layer winding is carried out over inner layer in in-suite mode and in green condition. The various process steps are given as follows:

- Assembly of fixtures with composite case with inner layer
- Loading of composite case with fixtures on CNC filament winding machine
- Loading of identified Hoop winding program
- Identification of lots for E Glass roving and silicone resin

- Mounting of E-glass roving spools on creel
- Preparation of silicone resin, viscosity measurement and charging into resin bath
- Filament winding of E-glass roving as per program to complete two layers

The E-glass/ silicone resin filament winding is shown in following figure 6.3:

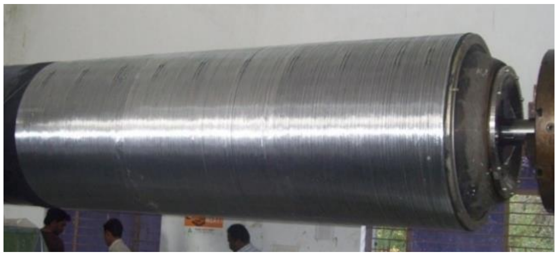

Figure 6.3: E-glass -Silicone Resin Filament Winding

Curing

Curing is carried out for polymerization of silicone resin for cross linking and consolidation. Ablative thermal protection layer becomes integral to composite case structural layer. The curing cycle for ETP layer is finalized based on cure characteristics test results of silicone resin given as follows:

- Cure initiation Temperature = 75°C
- Cure Onset Temperature = 110°C
- Cure Peak Temperature = 160°C
- Cure Completion Temperature = 230°C

Curing cycle for ablative ETPS is finalized as 140°C for four hours based on studies carried out for cure characteristics of Epoxy resin (in earlier studies in present research work) and Silicone resin. Curing is carried out in autoclave. The auto clave internal pressure was raised at 0.2 bar/minute up to 4 bar before heating switch on. The various steps for curing are described as follows:

- Preparation of vacuum bags for external and internal surface of composite case
- Vacuum leak for vacuum bags
- Loading of article into autoclave
- Connection of vacuum lines and all sensors

- Curing as per specified cycle for maximum temperature of 140^{0}C for four hours
- Removal of article from autoclave after 24 hours
- Removal of vacuum bags

The vacuum bagging preparation and curing in autoclave is shown in following figure 6.4:

Figure 6.4: Vacuum Bagging and Curing in Autoclave

The process flow chart of external thermal protection layer on composite case is given in following figure 6.5:

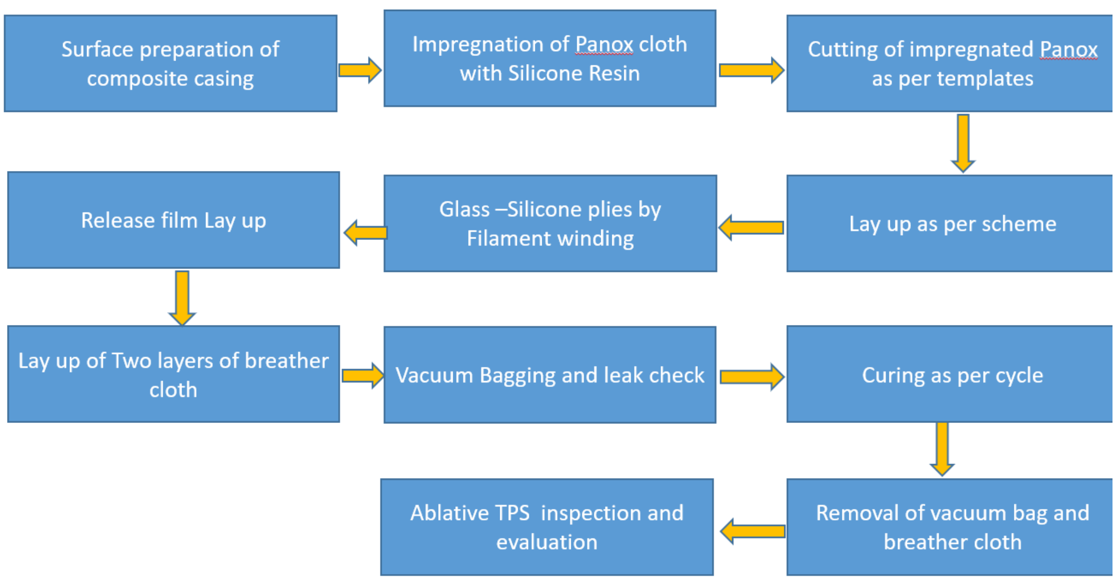

Figure 6.5: Process Flow Chart for External Thermal Protection Layer

6.4 Process Qualification Testing and Results

The evolved processes for two layers of ablative thermal protection system [13] got implemented on external surface of polymeric composite rocket motor case. In present studies, the various testing and evaluation which were formulated as a part of developed process qualification to assess structural integrity and quality of ablative thermal protection layer are described are follows:

Hardness test

The harness test of ablative thermal protection layer was determined using Durometer Hardness (Shore D) as per ASTM D2240. The test involves measurement of penetration of indenter into the material under specified conditions of force and time. In this test, the instrument is placed on surface with its position parallel to surface and indenter is then pressed into the material. The Shore D hardness is read on instrument dial. This hardness test was carried out randomly on various positions to cover entire surface of composite case. The measured Shore D harness values were 82 – 90 against specification of Minimum 75. This harness test is gross test and fair indication of quality of ablative thermal protection layup, integrity and cure consolidation. This test is specified as quality control parameter.

Ultrasonic test

The composite rocket motor case with external thermal protection layer was subjected to dry scan ultrasonic test using through transmission technique. The dry scan technique works upon redirected sound energy rather than simple reflected energy. The main advantage of such technique is to eliminate the need of coupling medium as ultrasonic energy is coupled between probes and material by special plastic pads. In this technique, two probes were used one for transmission and other as receiver of ultrasonic waves. The transmitter and receiver probes need to be aligned with each other across the object. The test parameters for probe frequency and diameter are 0.5 MHz and 10mm respectively. The low frequency is chosen based on trials for better penetration of ultrasonic energy. The in-situ calibration of probe was carried out by tuning the system to obtain optimum beat pattern between 7 to 10 cycles on cathode ray tube screen (CRT). The defects assessments were carried out based on analysis of changes in amplitude and displacement of the beat pattern during actual ultrasonic test on article.

In present case before ultrasonic testing, the grids marking was carried out on composite case with points at 100mm interval in axial direction starting from igniter end side to nozzle end and circumferentially divided into sixteen sectors.

Ultrasonic test through transmission technique requires determination of nominal dB point on article. The nominal dB point was determined by scanning the article randomly at several points and gain values were recorded at which signal amplitude crossed 90% of CRT height for majority of probed points. These recorded points were correlated with thickness variations of article as per configuration and nominal dB points were determined for different thickness zones. These nominal dB points were used as set dB value for respective article thickness zones while carrying out ultrasonic test on article. The test results (as per grids) of ultrasonic test for article were graded as per following grading criterion given in table 6.4 based on set dB and additional dB required for amplitude amplification to cross 90% of full-scale height (FSH) on CRT.

Table 6.4: Ultrasonic Test Grading Criterion

Received Signal Level (% of FSH on CRT)	**Grade**	**Amplification (Set dB + additional dB so that amplitude to cross 90% of FSH**	**Mapping criterion**
Greater than 90%	A	Set dB	Acceptable
50 to 90 %	B	Set dB + 6 dB	Acceptable
25 to 50 %	C	Set dB + 12 dB	Zones to be correlated with Radiographic test (RT)
10 to 25 %	D	Set dB + 20 dB	Debond/ Delamination
Less than 10%	Total Signal loss (TSL)	No further increase in dB	Debond/ Delamination

Ultrasonic test was carried out on composite rocket motor case with external thermal protection layer as per marked grid 560 points to cover full cylindrical portion. The grade A were recorded for 470 points and grade B for balanced 90 points with no grade C & D points. The assessment of integrity between thermal protection layer and structural layer found as excellent and acceptable.

Radiographic Test

The X-Ray radiography was carried out for article to assess the internal defects in external thermal protection (TPS) layer and also delamination at interface with composite rocket motor case structural layer. Radiography was carried out through tangential shots at eight sectors (45^0) of circumference to cover full length of composite rocket motor case. All the zones namely external thermal protection layer and interfaces with composite case structural layer were covered. The films were developed and interpreted with no inherent defects and delamination at interface. There were minor low-density observations which were interpreted as resin rich zones. These zones were also correlated with ultrasonic test results and confirmed as resin rich which were acceptable and functionally non critical.

Hydrostatic Pressure test

Composite rocket motor case with external thermal protection layer was subjected to internal pressure test to qualify the integrity of thermal protection layer with composite case structural layer. The strain gauges were bonded at four stations of rocket motor case along the length in cylindrical portion. At each station, four equispaced locations were identified along circumference for bonding of T-channels of strain gauges. The radial dilations were also measured through LVDTs at two stations on cylindrical portion of case. At each station two LVDTs were placed diametrically opposite locations for measurement. The internal pressure test was conducted up to working pressure of rocket motor case. The hydrostatic pressure test set up, measured values of strain and deflections are given in following figures 6.6, 6.7 & 6.8:

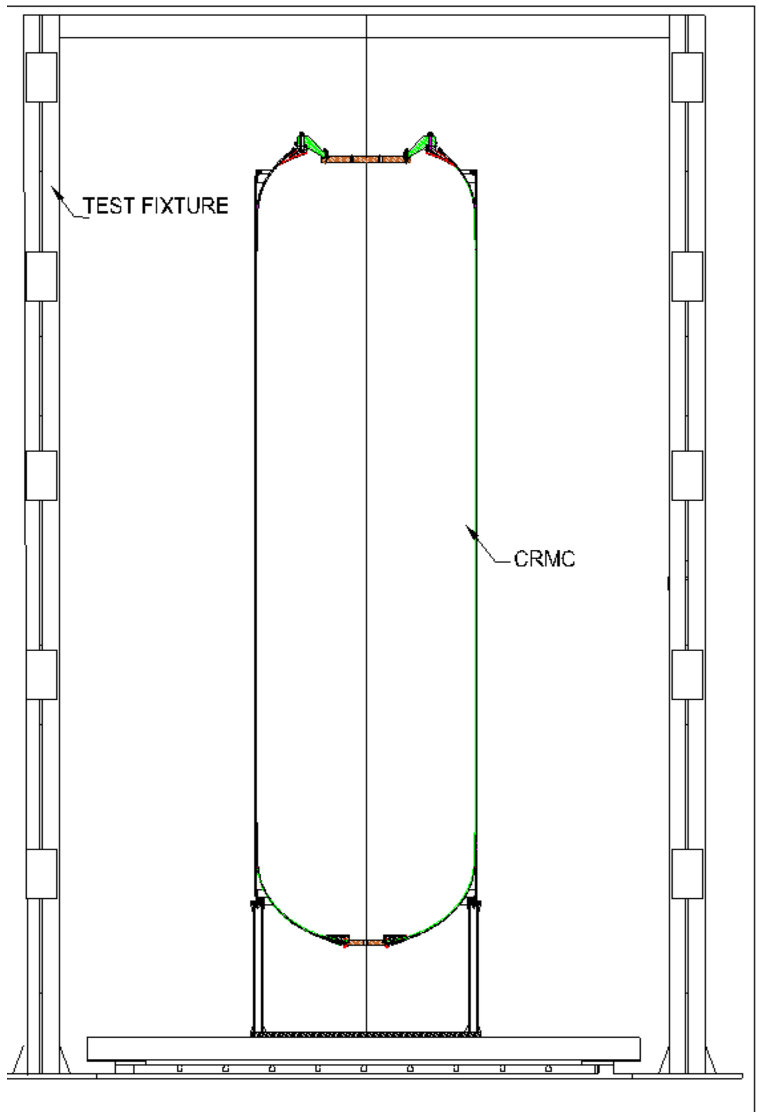

Figure 6.6: Composite Rocket Motor Case (with TPS) Pressure Test

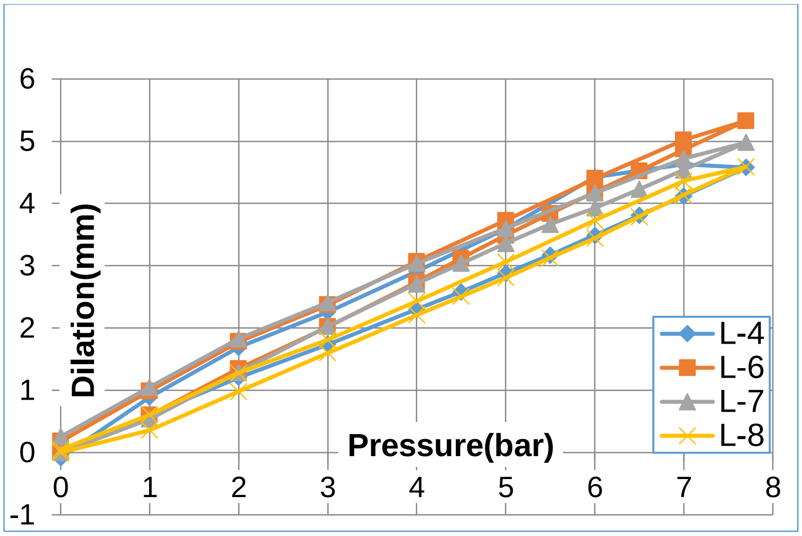

Figure 6.7: Dilation on Cylinder vs Pressure

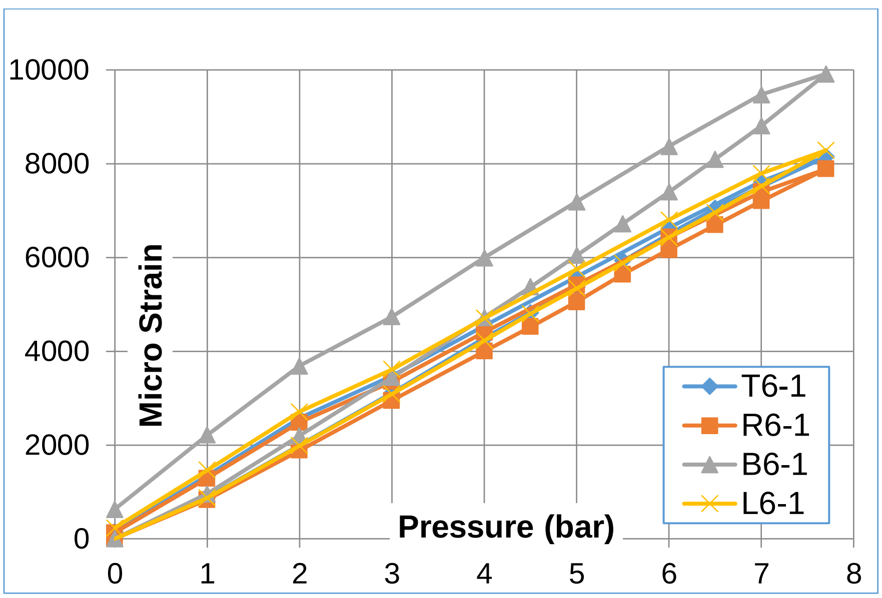

Figure 6.8: Strain on Cylinder vs Pressure

The Radiographic test and Ultrasonic test were repeated after pressure and test results confirmed the integrity of thermal protection layer and structural layer.

6.5 Summary:

The process for multilayer ablative thermal protection for external surface of composite rocket motor case was evolved considering various critical requirements & considerations through process trials. The processes for inner and outer layers of thermal protection were finalized as hand lay-up and filament winding respectively. The curing characteristics for silicone resin were studied through TGA and DSC runs and curing cycle for thermal protection layer was finalized even considering Tg and cure characteristics of Epoxy resin of structural layer. Curing was carried out up to maximum temperature of 140^0C for 4 hours in autoclave with vacuum and 4 bar internal pressure. The composite case with external thermal protection was subjected to hardness test, ultrasonic test, radiographic test, hydrostatic pressure test followed by repeat Ultrasonic & radiography. The ultrasonic and radiographic test results before and after hydrostatic pressure test were compared and analysed and no changes were observed. This assessment confirmed the integrity of external thermal protection layer with composite case structural layer even after being casing subjected to internal pressure. The hydrostatic pressure test simulated the rocket motor operational requirements in terms of internal pressure load. The results of various listed tests were analysed and multilayer thermal protection system manufacturing process got qualified and developed for external surface of polymeric composite rocket motor case.

CHAPTER 7

CONCLUSIONS AND FUTURE SCOPE OF WORK

7.1 Conclusions

The present research work is carried with aim to develop ablative external thermal protection system or composite rocket motor case. To complete this development, various studies were conceptualized, formulated and carried out in form of major four research objectives: Testing and evaluation of Carbon-Epoxy composites, Experimental studies on resins for ablative thermal protection system, Thermal experimental studies for thermal protection system and, Process development of ablative external thermal protection layer over composite rocket motor case. The research objectives were formulated in phased manner starting from generation of mechanical properties for Carbon-Epoxy structural layer at ambient and elevated temperature, ablative layer resin selection through evaluation of thermal characteristics of resins, TPS samples and sub scale model level thermal tests and finally process development of multilayer thermal protection system. These carried out research studies along with major conclusions are presented below:

(i) Composite rocket motor case in present research work is made up of Carbon-Epoxy (CE). This research objective studies included experimental testing and evaluation of mechanical properties for Carbon roving, Carbon Epoxy flat specimens and Carbon Epoxy ring specimens. Carbon-Epoxy tensile testing for ring specimens is carried out at elevated temperature to experimentally determine temperature at which strength degradation starts. Determination of Glass transition temperature (Tg) and Cure characteristics of epoxy resin through Dry Scanning Calorimetry (DSC) is also carried out. The various works accomplished under this research objective are summarized as follows:

- Manufacturing of Impregnated Carbon tow test specimens
- Manufacturing of carbon epoxy unidirectional laminate and preparation of longitudinal and transverse tensile test specimens
- Manufacturing of carbon epoxy filament wound ring and preparation ring specimen
- Mechanical testing of Carbon roving, CE Flat specimens, Filament wound CE Ring specimens
- CE Ring specimen tensile strength testing at elevated temperature
- CE composite and Epoxy Resin testing for Tg and Cure Characteristics

The mechanical properties are experimentally determined for PAN based Carbon fiber, CE Uni-Directional laminate and CE ring specimens to establish correlation. The test results are: Carbon fiber (TS 4906 MPa & TM 230 GPa), Flat CE specimen (TS 2220 MPa & TM 128 GPa), CE Ring Specimens (TS 2005 MPa). The tensile strength for ring specimens is experimentally evaluated at different temperatures up to 130^0C. Allowable interface temperature for ETP and CE interface is determined based on CE tensile strength degradation result as 100°C.The Glass Transition Temperature (Tg) for neat Epoxy Resin and CE composite are determined by DSC as 160°C. The major outcome of these studies includes evaluation of tensile strength degradation temperature and glass transition temperature of carbon epoxy structural layer which are vital parameters for thermal protection layer configuration.

(ii) Resins are very critical for ablative thermal protection system performance to meet functional requirements. The resin system thermal stability and characteristics play major role for ablation working mechanism of thermal protection system. In this research objective, the experimental thermal stability studies of resin systems for ablative thermal protection system were carried out through Thermogravimetric analysis (TGA) and Dry Scanning Calorimetry (DSC) techniques. The Phenolic and Silicones resins were selected for studies. Thermal conductivity of glass-phenolic and glass-silicone were also tested on specimens. The major carried out works in this research objective are given as follows:

- Specimens preparation for Phenolic resin and Silicone resin
- Thermogravimetric analysis (TGA) studies on both Resins for thermal stability characteristics
- Dry Scanning Calorimetry (DSC) studies for both resin specimens
- Manufacturing of glass-phenolic and glass-silicone specimens
- Thermal conductivity test for glass-phenolic and glass-silicone specimens

Silicone resin is better for ablative thermal protection application based on thermal stability characteristics: initial decomposition temperature (375°C), temperature at 10% weight loss (590°C), residual weight (Char yield of 79 %) after final decomposition. Epoxy Resin DSC test results confirmed sufficient thermal stability margins for silicone resin. The measured values of thermal conductivity for glass-phenolic and glass silicone specimens are almost same. The major outcome of present studies is selection of silicone resin for ablative thermal protection layer based on its better thermal stability and results are adequate to meet functional requirements.

(iii) This research objective is carried out for experimental studies of thermal protection layers on carbon epoxy substrate layer of specified thickness (same as composite rocket motor case thickness) on samples through thermal test. The present thermal tests were carried for selected heat flux profile of one of the simulated trajectories. In first phase, samples of different types are made by varying reinforcement material and thickness to measure the interface temperature of thermal protection layer and carbon epoxy layer. The condition of thermal protection layer is also assessed after thermal test. The thermal protection layer material, layer details and thickness were finalized based on thermal test results. In second phase, testing and evaluation for thermal protection layer integrity on carbon epoxy layer was carried under flow and shear to simulate flight conditions. To carry out these studies, missile sub scale metallic model was manufactured with identified zone for composite rocket motor case. At identified zone, winding of carbon epoxy layer was carried out as per required thickness followed by curing. Ablative thermal protection both layers namely inner layer with hand lay-up and outer layer through filament winding process were also built. Missile sub scale virgin model with thermal protection layer on carbon epoxy layer is subjected to flow under shear in wind tunnel test to assess its integrity. The model was subsequently subjected to thermal test for same heat flux profile as sample level test to measure interface temperature (thermal protection layer and carbon epoxy layer interface) and assess thermal protection layer condition. Thermally soaked model was again subjected to wind tunnel test to verify integrity of thermal protection layer with carbon epoxy layer after thermal soaking. These followings major works were carried under these studies:

- Evolution of test methodology
- Manufacturing of thermal test set up
- Testing and validation of heat flux profile in test set up
- Manufacturing of thermal protection samples of five types
- Samples thermal testing through IR lamp, temperature and heat flux measurement
- Manufacturing of Subscale missile model with CE and ETP layer
- Clod blow down test to simulate flow and shear in wind tunnel for virgin model
- IR thermal test on model and post thermal soaking wind tunnel test

Studies on TPS samples are conducted by IR thermal test and ablative external thermal protection system on composite rocket motor case was finalized based on thermal test results as two layers (Inner layer: 0.6mm Panox /silicone and Outer layer 0.7mm Glass/ silicone) for heat flux of 7.8 W/mm2.

In wind tunnel test, experiment was conducted for simulated flow conditions of 3.5 Mach for 60 seconds duration on missile sub scale model and integrity of external thermal protection layer with composite rocket motor case (CE layer) found intact.

Thermal test results with IR heating for required heat flux profile on missile sub scale model confirmed interface temperature of 100^{0}C and external thermal protection layer integrity after heat soaking. Thermally soaked model was subjected to repeat wind tunnel test and results confirmed condition and integrity of external thermal protection system with composite case. The achievement of present studies includes finalization of thermal protection layer configuration and reinforcement material and also verification of thermal protection layer integrity with structural layer at sub scale model.

(iv) The external ablative thermal protection layer on composite rocket motor case got finalized based on previous experimental studies in present research work. External ablative thermal protection layer consists of two layers i.e inner layer made up of panox fabric -silicone resin and outer layer is made up of glass-silicone. This research objective was formulated to develop process for both layers of external ablative thermal protection layer considering type, form of raw material and various functional, composite case configuration related considerations. The ablative thermal protection layers are built over composite rocket motor case and curing carried out as per finalized curing cycle. Ultrasonic and radiography test are carried out to assess thermal protection layer and its integrity with composite case. Composite case with external ablative thermal protection layer is subjected to internal hydrostatic pressure test to simulate real operational requirement to verify and validate developed process. This research objective involved following major accomplished work:

- Process selection for both layers of thermal protection system
- Evolution of wet hand lay -up scheme on cylindrical and domes of composite case
- Preparation of templates to cut impregnated panox felt (fabric)
- Wet hand lay up for inner layer as per plan
- Filament winding of outer layer with glass roving and silicone resin
- Curing as per finalised Curing cycle
- Testing and inspection of thermal protection layer
- Process validation through hydrostatic pressure test to assess integrity between external ablative thermal protection layer and composite case

The process development for external thermal protection layer over filament wound composite rocket motor case was completed through process trials and studies. The hand lay-up process for inner layer (0.6 mm thick Panox/ silicone) is adopted and outer layer (0.7 mm thick glass/silicone) is through wet filament winding process.

The NDT techniques (Ultrasonic test and Radiographic test) were applied to assess presence of any defects within external thermal protection layer and at interface with composite case.

Ultrasonic test and Radiography results showed no defects with in external thermal protection layer and at interface with composite rocket motor case.

To assess external thermal protection layer integrity for most critical operational requirement of rocket motor internal pressure, the composite rocket motor case with ablative external thermal protection layer was subjected to hydrostatic pressure test up to 7.7 MPa (motor working pressure for simulated trajectory). Test results confirmed integrity of ablative external thermal protection layer on composite rocket motor case for internal pressure.

The ablative external thermal protection system with two layers (inner layer: Panox/ silicone porous and outer layer: glass/silicone) was developed for composite rocket moto case made up of carbon epoxy material. The final goal to develop external thermal protection system for composite rocket motor is achieved.

7.2 Future Scope of Work

The present research work can be extended for future scope of studies under following broad frame work:

- Ablation model can be developed through material characterization and evaluation of other related parameters
- Ablation model can be used for design predictions
- Thermal protection system constitutes for considerable mass and always there is aim to reduce weight by selection of low-density materials, characterization of such materials to generate various properties test results
- Composite manufacturing process depend on starting reinforcement materials and based on low density materials, various studies for process related aspects and refinement of process parameters can be formulated

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PUBLICATIONS ON RESEARCH WORK

INTERNATIONAL JOURNALS (SCI)

1. Paper (SCI) in IJAAA (International Journal of Aviation, Aeronautics & Aerospace, USA): “Experimental Evaluation of Strength Degradation Temperature for Carbon Epoxy Filament Wound Composite” International *Journal of Aviation, Aeronautics, and Aerospace, 7*(4). https://commons.erau.edu/ijaaa/vol7/iss4/8

2. Paper (SCI) in Defence Science Journal (India): “Experimental studies of polymeric resins for ablative thermal protection system”, *Defence Science Journal*, *71*(2), 289-295. https://doi.org/10.14429/dsj.71.16252