INVESTIGATIONS ON THE CRITICAL PARAMETERS INFLUENCING THE PROPERTIES AND FUNCTIONAL PERFORMANCE OF ABLATIVE COMPOSITES

A thesis submitted
in partial fulfillment for the degree of

Doctor of Philosophy

by

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CERTIFICATE

This is to certify that the thesis titled **“Investigations on the critical parameters influencing the properties and functional performance of ablative composites”,** submitted by **Mohan Kumar. L.,** to the Indian Institute of Space Science and Technology, Thiruvananthapuram, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under our supervision. The contents of this thesis, in full or in parts, have not been submitted to any other institute or University for the award of any degree or diploma.

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DECLARATION

I declare that this thesis titled “**Investigations on the critical parameters influencing the properties and functional performance of ablative composites”** submitted in partial fulfilment of the degree of Doctor of Philosophy is a record of original work carried out by me under the supervision of **Dr.Chakravarthy. P.,** and has not formed the basis for the award of any degree, diploma, associateship, fellowship or other titles in this or any other institution or University of higher learning. In keeping with the ethical practice in reporting scientific information, due acknowledgments have been made wherever the findings of others have been cited.

Mohan Kumar. L.
SC14D011

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ABSTRACT

Ablative composites are widely employed as thermal protection systems in the internal surfaces of solid rocket motors, in liquid engine throats and on the external surfaces of reentry space vehicles. These materials are simple, reliable and efficient in handling extreme hostile thermal environments encountered in aerospace applications. They are the best candidate materials for protecting the nozzle structures from the extremely high temperature and high pressure gas flows and the external surfaces of reentry vehicles from frictional heating during reentry into the earth's atmosphere. Carbon and silica are the most common fibres used as reinforcement in combination with phenolic resin for manufacturing the ablative composites used for aerospace applications.

Ablative systems are basically designed based on thermal considerations but the structural properties also play a vital role during the operating conditions. There is a sizeable number of key process variables which are to be carefully selected based on the end product requirements. This study is a series of systematic investigations on the critical factors affecting the properties and functional performance of ablative composites. A detailed literature survey of the raw materials, processing techniques, equipments etc and a survey at different ablative processing laboratories were conducted to understand the different processes and the process variables being followed currently. The raw materials were characterized completely. The important thermostructural properties required for an ablative were identified and the test methods were finalized. The entire spectrum of process variables were enumerated and broadly classified into critical and non critical parameters depending on their likely influence on the final product properties. Then, the chosen parameters were subjected to deeper investigations and the results were analysed. Composite laminates were made using carbon fabric/silica fabric and phenol formaldehyde resin by varying the different parameters selected for the study.

By a systematic study of the ablative materials, processing techniques and characterisation methods, all the raw material and process parameters were tabulated. From this exhaustive list, the most crucial factors affecting the material properties and functional performance of carbon phenolic and silica phenolic ablative composites have been identified. Complete characterization of the reinforcement fibres (carbon and silica) and matrix resin (phenolic) has been completed and the influential parameters have been identified by laminate level studies. Impregnation of the carbon and silica fabric with phenolic resin was done and the critical properties influencing the composite properties were quantified.

Subsequently, ablative composites were processed and the most influential process parameters in each process stage were identified. Processing was done following the standard process in which the chosen variable alone was changed each time and its effect studied. Laminates were subjected to non destructive evaluation techniques of visual inspection, alcohol wipe test and ultrasonic (pulse-echo and through transmission) testing to study the integrity and uniformity. After ensuring that the laminates were free from defects, specimens were fabricated from them as per accepted standards. Evaluation of mechanical and thermal properties was done and the results were tabulated. Apart from density, the crucial mechanical properties like compressive strength, modulus and interlaminar shear strength were studied. Heat of ablation, erosion rate, thermal conductivity and specific heat were the thermal properties evaluated and studied. From the results of the tests, the effect of each variable on the composite properties was quantified and inferences were made accordingly.

Sensitivity studies on the chosen variables to quantify the influence of these variables on the properties and performance of the ablative composites were systematically completed and the results were analysed. The possible effect of other related factors which may have a bearing on the ablative performance were also investigated and suitable inferences were derived.

The gap in the understanding of the dependence of the properties and performance of the ablative composites on the raw material properties and process parameters has been narrowed down by this study. The studies on the sensitivity of the most critical raw material and process parameters on the important thermal, physical and mechanical properties of ablative composites, the important factors were completed. Significant gains in terms of cost, process cycle time and inert mass can be achieved by understanding the influence of the critical factors.

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ABBREVIATIONS, SYMBOLS and NOTATIONS

8HS	8 Harness Satin
AIAA	American Institute of Aeronautics and Astronautics
ASTM	American Society for Testing and Materials
AWT	Alcohol Wipe Test
CI	Chang's Index
CM	Compressive Modulus
CMM	Coordinate Measuring Machine
CNF	Carbon Nanofibres
CNT	Carbon Nanotubes
CP	Carbon Phenolic
CRCF	Carbon Reinforced Carbon Fibre
CS	Compressive Strength
CTE	Coefficient of Thermal Expansion
ESA	European Space Agency
FRP	Fibre Reinforced Plastics
HTCF	High Temperature Carbon Fibres
IIST	Indian Institute of Space Science and Technology
ILSS	Inter Laminar Shear Strength
LTCF	Low Temperature Carbon Fibres
MWCNT	Multi Walled Carbon Nanotubes
NASA	National Aeronautics and Space Administration
NDT	Non Destructive Testing
PAN	Polyacrylonitirile
PF	Phenol Formaldehyde resin
PMC	Polymer Matrix Composites

POSS	Polyhedral Oligomeric Silsesquioxane
RT	Room Temperature
RTE	Radiographic Testing and Evaluation
SP	Silica Phenolic
SRM	Solid Rocket Motor
STS	Space Transportation System
SSO	Space Shuttle Orbiter
SWCNT	Single Walled Carbon Nanotubes
TG	Thermogravimetry
TPS	Thermal Protection Systems
UT	Ultrasonic Testing
UTM	Universal Testing Machine
VC	Volatile content
VSSC	Vikram Sarabhai Space Centre
WRC	Wet Resin Content
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
MPa	MegaPascal
m	Mass
gsm	grams per square metre
ppm	parts per million
C	Specific heat
ΔT	Change in temperature
α	Thermal diffusivity
k	Thermal conductivity
ρ	Density
T	Time

Note: The symbols and notations which are not included here are defined in the thesis where they appear.

CHAPTER 1

INTRODUCTION

Composites are materials synthesized from two or more dissimilar constituents having significantly distinct properties. The constituents are heterogeneous at a microscopic level but are homogeneous at the macroscopic level. One of the constituent acts as the reinforcement and the other constituent in which the reinforcement is embedded is the matrix. Composite material is a multi-phase system consisting of matrix material and reinforcing material. Matrix material is a continuous phase, and it can be metal matrix composite materials, inorganic nonmetallic matrix composite materials or polymer matrix composites. Reinforcing material is a dispersed phase, usually in the form of fibres or particulates. Polymer matrix composite material is the one that uses an organic polymer as the matrix and usually a fibre such as silica, quartz, carbon or graphite as the reinforcement. Strength and modulus of fibres are normally higher than those of the matrix material. This makes fibres the main load bearing component. The reinforcement is generally a fibre, possessing high specific strength and high specific stiffness. It contributes the desired mechanical properties to the composites. However, there must be a matrix material with good adhesion properties to firmly bond the fibres together. The matrix material also helps to uniformly distribute the applied load, protects the reinforcements from the environment and transfer load to the fibres. The composite generally exhibits characteristics superior to those of the constituents taking advantage of the synergy. Composites can be tailor made to suit any property requirement and for this very reason, composites are favourite candidates for various advanced applications. A judicious selection of reinforcement, matrix and composition will result in the formation of composites with specific properties. In addition, some properties of composite materials mainly depend on the characteristics of the matrix material. As a result, in composite materials, the performance of fibre, matrix and the interface between them directly have a significant impact on the performance of composite materials [1-3]. Many conventional materials have been gradually replaced over a period of time with composites mainly due to their exotic properties of light weight, high specific strength and high performance. To realize the full potential of a composite material, an appropriate processing technique coupled with optimum processing parameters should be ensured. This is the real challenge for composites seeking to replace the conventional proven materials like metals in high performance sectors like aerospace, atomic energy, automobile sector and defense [4-6].

The main advantage of composites is the superior specific strength and stiffness which helps in realizing light weight structures for aerospace applications. Composites are energy efficient since they are light weight and most composites are synthesized at ambient or slightly above ambient temperatures. Directional properties can be tailored into fibre reinforced composites as it is possible to align the reinforcement fibres in the preferred orientations during manufacturing. In making artificial composite materials, the potential for controlled anisotropy offers considerable scope for integration between the processes of material specification and component design with complex shapes. Since only the polymer matrix is exposed to the operating environment, composites generally have better weather resistance and corrosion resistance. With the attractive advantages of composites, there coexist a few disadvantages also. They are much more expensive than conventional materials and hence are suitable only for high performance applications like aerospace where cost is not the primary criteria. Since composites are made of entirely different materials, chances of defects at the interface are high. This necessitates immense care and diligence during processing [1-5].

In the arena of aerospace and related technologies, high performance coupled with very high efficiency and reliability is the most important requisite. Hence it is essential for the designers to select the high performance materials for the components used in such missions. At the same time, weight considerations are equally important as heavier materials like metals and alloys cannot be used extensively. Reduction in inert mass to the maximum extent is essential to increase the useable payload mass for space missions. The candidate materials for components used for space missions of launch vehicles and spacecrafts should necessarily have the required strength and stiffness properties along with the lowest possible mass. In many missions, these materials have to perform satisfactorily at extreme environments like high temperatures, high pressures, low temperatures, corrosive environments, vacuum conditions and radiative sources in space without significant deformation in shape or deterioration in properties. In addition, they should obviously be light in weight to reduce inert mass and at the same time should have the required structural and thermal properties. So a new material development is always an advantageous factor in space science and technology. Since meeting the conflicting property requirements using a single material was becoming impossible, combination of materials seemed to be the alternative. Hence composites became an undisputed candidate for space applications. In composites, it was possible to achieve properties much superior to those of their constituents by proper synthesis using the optimum process parameters and process conditions [7].

Polymer matrix composites (PMC) or fibre-reinforced plastics (FRP) are used extensively for various strategic applications in the aerospace sector. It uses a polymeric resin as the matrix and a fibre such as carbon, glass or aramid as the reinforcement. High strength and stiffness, ease of moulding complex shapes, high environmental resistance coupled with low densities make the resultant composite superior to metals for many applications. Ablative composites are a class of PMCs which find applications in thermal protection systems of aerospace structures including reentry vehicle external surfaces, solid propellant rocket motor nozzle internal surfaces, liquid propellant engine throat inserts and control thrusters for rockets.

1.1 Overview of ablative composites and applications

Solid propellant rocket motors are used in many satellite launch vehicles as boosters and lower stage motors. A solid rocket motor invariably consists of a motor case filled with solid propellant, an igniter for igniting the propellant and a convergent divergent nozzle. The igniter fires the propellant which burns at a predetermined burn rate generating large quantities of exhaust hot gases which flow through the nozzle. The chemical energy of the propellant is converted into heat energy which in turn gets converted into kinetic energy while expanding through the convergent divergent nozzle. The exhaust gases are of very high temperature and hence the nozzles should have adequate thermal protection on their interior surfaces to prevent their degradation during operation. The design of the nozzle involves designing the aerodynamic internal contour, thermal design for the thickness of the nozzle lining material and structural design to take care of the mechanical loads during the firing of the motor [8]. The internal contour and the dimensions have to remain stable or should erode at a known rate to ensure predictable and acceptable motor behaviour. To ensure these pre requisites, high performance ablative composite materials are to be processed and used in the internal surfaces of the nozzles of solid rocket motors, hot gas flow paths of control thrusters, reentry module external surfaces and throat inserts of liquid propellant rocket engines and can also be applied on the surfaces where the components are exposed to higher heat flux.

Any rocket motor using chemical propulsion uses the conversion of gases of combustion at high temperatures and high pressures traveling at relatively low speeds into a flow with a high momentum, using a nozzle. The internal energy gets converted into kinetic energy thus cooling the product gases as they pass through the nozzle, but even then the gas temperature at the nozzle throat can still be as high as 3500 K. At such exorbitant temperatures and high heat transfer rates, the nozzle internal surfaces are severally stressed thermally. Though propellant combinations are usually selected so that the product species do not contain a significant amount of free oxygen, in many cases species such as water vapour or carbon dioxide become highly reactive at elevated temperatures. This causes severe deterioration and degradation of the nozzle contour surfaces if they are not protected satisfactorily. The result of these processes is thermochemical erosion of the nozzle. Erosion of the nozzle internal surface can be contributed by both thermal and mechanical phenomena. Mechanical erosion is the removal of material by physical impact of condensed phase particles like aluminium in the exhaust plume gases. This could be a significant means of material removal for metallized solid propellant rocket motors where metal loadings can be as high as 20% of the total propellant grain weight [9]. Since erosion cannot be fully eliminated in ablatives, predictable erosion is the design concept. The ablative composite liners should erode at a rate which can be predicted and assessed with reasonable accuracy and this erosion rate should be repeatable over different missions. The net effect of uncontrolled chemical and mechanical erosion is a decrease in system performance since both chamber pressure and thrust levels decrease as a result of the enlargement of the nozzle throat. The erosion of the nozzle throat insert leads to a decrease in the operating pressure of the motor and results in a decrease in the delivered energy to the vehicle.

The space capsules after completing their mission in space returns to the earth at very high velocities of the order of 8 km/s and more. During this return journey, while reentering the earth's atmosphere, the external surfaces of the capsule experiences very severe aerodynamic frictional heating. At this condition, the ambient temperature of the air in contact with the module can be heated to very high temperatures and the air will generally be in an ionized state. Adequate thermal protection is required to be provided to the capsule to withstand such hostile conditions [10].

During atmospheric reentry, space vehicles are subjected to severe aerodynamic heating, and their successful return through the earth's atmosphere largely depends on the provision made for reducing aerodynamic heat transfer to the structure. The high heat flux condition as encountered during atmospheric re-entry warrants efficient thermal protection systems (TPS). Ablatives form a class of TPS, which undergoes physical, chemical and mostly endothermic transformations [11]. The latent heat of evaporation of the resin allows extremely high temperatures to be withstood for short periods in the case of rockets and other reentry space vehicle systems [12].

Ablative composites, a class of fibre reinforced polymeric composites, are the best candidate materials for solid rocket motor nozzles, liquid engine throats and reentry thermal protection systems to protect the structures from the extremely severe operating conditions of high temperature, pressure and particle impingement. Most commonly used ablatives are composed of either carbon or silica as the reinforcement fibre and phenolic resin as the matrix in the composite. Ideal ablatives have relatively low thermal conductivity but high heat of ablation coupled with low erosion rate and low mass loss on operation. These high performance composites are indispensable in solid rocket motor nozzles, liquid engine throats, control thrusters, missiles, reentry nose tips and leading edges. Ablatives create a passively cooled environment inside rocket motor nozzles and over reentry surfaces, thus protecting the launch vehicle motors and space vehicle structure from high temperature environments. While the metallic structure provides the necessary structural capability, high performance ablative composite materials are required for thermal protection. Ablative composites are processed using a complex processing cycle starting from impregnating the fibres with phenolic resin followed by moulding or winding prepreg tapes over metallic mandrels before polymerization under pressure in an autoclave or in a hydroclave. Compared to inorganic polymers and metals, polymeric ablatives have some intrinsic advantages like high thermal shock resistance, low density, high mechanical strength and good thermal insulation capabilities.

Ablation is an orderly heat and mass transfer process in which a large quantity of heat is dissipated away in a very short period of time by sacrificial loss of the material itself. Since heat transfer, mass transfer, evaporation, vapourisation, sublimation, pyrolysis, transpiration, surface regression, deformation, dimensional changes and shape changes are involved, the process of ablation is quite complex. Most of the reactions are inherently endothermic expending a large amount of energy thereby protecting the base structure.

When the hot exhaust gases from the solid rocket motor pass through the nozzle, the ablative is subjected to a very high heat flux as the surface temperature increases rapidly. Due to the low thermal conductivity of the material, the temperature builds up on the surface rather than the heat getting conducted to the backup structure. As the temperature near the surface reaches the pyrolysis temperature of the resin in the composite, decomposition of resin takes place. This leads to the formation of char on the surface of the ablative. During the operation, the extent of char increases and the char front advances into the thickness of the material with increasing exposure time. The surface material starts eroding and the erosion of the material can be due to the thermal degradation of the material and/or due to the mechanical erosion caused by particle impingement due to the metallic particles of the solid propellant flowing along with the hot exhaust gases. As the layer on the surface erodes, the next layer gets exposed and the process continues.

During pyrolysis, the volatile gases evolving at the reaction zone finds its way through the charred zone taking away significant amount of heat. The melting of the resin as well as the fibres also consumes some heat. With all these processes, a large quantity of heat is expended with sacrificial loss of material, thereby, protecting the metallic substrate from thermal degradation. As the ablative composite is exposed to heat, it acts as a heat sink and its temperature starts rising. At the pyrolysis temperature, the decomposition of the composite starts evolving gases, leaving the rigid porous carbonaceous substance called passive char [13].

During the further advancement of the heating zone, the evolving pyrolysis gases absorb the heat from the passive char layer and dissociate into the solid substrate. This fills the porous char and builds pressure in the porous cavities. As the pressure exceeds a threshold limit, char spallation takes place. All the above reactions are of endothermic in nature [13].

1.2 Motivation and scope of the research work

Ablative systems are basically designed based on thermal considerations but the structural properties also play a vital role during the operating conditions. These composites are processed using a wide range of sophisticated processes using specialized processing equipments. The major processes include preimpregnation, tape layup, tape winding, moulding, curing and machining. The main process equipments used for processing include preimpregnation plant, tape winding machines, hydraulic presses, autoclave, hydroclave and ovens. There is a sizeable number of key process variables which are to be carefully selected based on the end product requirements. Presently, these are fixed based on the limited laminate level experiments involving a very limited number of process variables. The processes being followed by different agencies have evolved over a period of time by trial and error methods and through processing experience. Process developments in the past have been mainly based on previous experience of similar products and through limited tests carried out at the laboratory level.

As the research and development of ablative composites have been predominantly focused in the aerospace sector limiting its applications to rocket nozzles and reentry capsules and missiles, the developments were not readily published in the open literature domain. As most of the products were for strategic applications, the new developments were always considered as classified and controlled information. Though many exotic ablative products have been developed and successfully used in various applications by many agencies, not much parametric level research was undertaken to investigate the influence of many crucial raw material and process parameters. Not much work has been reported on the correlation of process variables on the final properties of the ablative liners.

At present, ablative composites are designed purely based on thermal considerations. The thickness of the thermal protection system is decided based on empirical relations, technical judgements, experience and are validated by limited number of ground tests. For instance, the thickness of the thermal protection system of a rocket motor nozzle is designed by providing a margin of 0.2 to 0.25 over the char depth obtained during a static ground firing test. Similarly, measurements of erosion and char depth of an ablative in a plasma arc jet test or a kinetic heating simulation test are used as input to decide on the thickness of a thermal protection system for a reentry capsule’s outer surface. Testing of ablatives in the full scale rocket motor nozzles in their real operating environment are prohibitively costly and needs a lot of safety precautions to be taken.

The mechanical properties of the ablatives like compressive strength and interlaminar shear strength are not considered for design as only the thermal properties are emphasized. This is primarily due to the fact that in almost all solid propellant rocket motor and liquid propellant engine designs, a rugged metallic backup structure is provided to take care of the structural and aerodynamic loads during operation. As a result, large design margins exist in the system leading to increase in inert weight. If one needs to exploit the mechanical strength properties of an ablative, a more vivid understanding on the influence of thermomechanical properties on the functional performance of the ablative is necessary. In order to provide a better theoretical base for process design, it is desirable to have a better understanding of the effect of the critical raw material and process parameters on the thermal and mechanical properties and functional performance of the ablative composite either in isolation or in combination. Very little optimisation efforts have been reported in literature on ablative processing.

The proposed research work aims at bridging this obvious gap, to the maximum possible extent, in the understanding of the dependence of the properties and performance of the ablative composites on the raw material properties and process parameters. By studying the sensitivity of the most critical raw material and process parameters on the important thermal, physical and mechanical properties of ablative composites, the important factors can be identified and optimized to obtain consistent and repeatable performance for the ablatives.

Initially, a detailed literature survey and visits to ablative processing labs were carried out to understand the different processing techniques and their process variables being followed currently. Though different products are synthesized through different techniques, there is a general process sequence for all ablative composites. The entire spectrum of process variables were enumerated and broadly classified into critical and noncritical parameters depending on their likely influence on the final product properties. Subsequently, the parameters were identified for further deeper investigation. Many laminates were processed using the different methods to understand the intricacies of the system. The different ablative laminates were realized by varying the critical process parameters. Specimens were fabricated from these test laminates. The matrix of the critical physical, thermal and mechanical properties required for the design of ablative composites was firmed up and the evaluation of properties for different laminates was done.

From the available limited literature, the effect of fibre orientations in an ablative product and the fibre architecture in the laminate plies were identified for further studies. The effect of ply orientation and comparison of properties of pattern-cut with bias-cut tape wrapped components were the two major studies undertaken. To validate the sensitivity of the chosen process parameters, subscale level hot tests were also carried out.

The resin content, volatile content and the degree of advancement of resin were the major raw material parameters influencing the properties and functional performance of the ablative composite. After initial studies, resin content was chosen for detailed investigations as volatile content and degree of advancement were properties largely controlled by the processing conditions and was not found to be influential. On the other hand, the resin content in the prepreg, or indirectly, the fibre content was found to have a significant influence on the physical, thermal and mechanical properties of the ablative. Among the different process stages, polymerisation or curing is the most critical stage as the consolidation of the composite occurs during this phase and the properties are getting achieved. After reaching the cured stage, further changes in the characteristics of the composites are unlikely. Hence, more perturbations were performed on the cure temperature and cure pressure and this has yielded good insights. The effect of temperature on the mechanical properties was also investigated as the ablative is expected to perform at high temperatures during its functional regime. The composite may not be put into its operating environment immediately after its realization. Due to several reasons, the mission may be at a later date. Under such situations, it would be desirable to have an understanding of the effect of ageing on the properties of the ablative composite. For this, limited ageing studies were also conducted on the specimens made from these composites.

1.3 Organization of the thesis

A brief introduction to composites in general and ablative composites in particular forms the first chapter. The broad classification of composites, their applications, advantages, characteristic features and limitations are explained. The process of ablation is explained along with the desirable features of ablative composites. The motivation for undertaking this research project is also explained in the introduction. The scope of the present study is defined followed by contributions of this thesis to the knowledge on ablative composites.

In chapter 2, a detailed review of the published literature on the processing and properties of ablative composites is attempted. Many researchers have been working on efforts for property enhancements using additives and fillers. Sensitivity studies on some process parameters have already been attempted by a few researchers. These have been studied and the applicability to the present research work has been perused. An attempt has been made in this chapter to review the literature on ablative composite processing aspects, property evaluation, efforts to improve the properties and functional performance and the related studies.

In chapter 3, the objectives and the scope of the present work are enlisted. The research methodology adopted for the investigations is also elaborated.

In chapter 4, the selection of raw materials, namely, carbon and silica reinforcement and phenolic resin and their salient properties are discussed. The process of synthesis of the ablative composites is elaborated in detail. The different process sequences with the detailed process parameters and quality control check points are elaborated. A brief description of the process equipments, the details of the mandrels, toolings, fixtures and templates and the precautions related to safety are given in this chapter. The difficulties encountered during the experimental work and the process of overcoming them is also mentioned. The mode of selection of the critical process parameters identified for further investigations is explained in this chapter.

In chapter 5, the details of sensitivity studies performed on the selected critical parameters are elaborated. The characterisation and testing of the samples fabricated from the ablative composites are detailed. After processing, the specimens were fabricated as per the ASTM and other applicable standards. Details of testing of these specimens for thermal, physical and mechanical properties are given in the chapter. Salient features of the test setups and fixtures are enlisted. The structural health of the composite and the specimens were checked by nondestructive evaluation techniques, the details of which are also included in the chapter.

In chapter 6, the results are presented and the observations are discussed. The inferences drawn from the experimental results are given with technical explanations. The sensitivity or insensitivity of the different parameters under consideration is explained. The most critical factors are identified and quantified and the optimum ranges for few of the process parameters and raw material properties are zeroed in.

Chapter 7 gives the conclusions from the study and suggests a few areas which hold significant potential for further research.

1.4 Contributions from the research

The most crucial factors affecting the material properties and functional performance of carbon phenolic and silica phenolic were identified and quantified. Specific studies on the sensitivity of key variables on the final performance of ablatives are not available at present. The outcome of this research work is expected to contribute significantly to the proper and better understanding of the critical process parameters which significantly influence the final product characteristics. This shall enable the designers to optimize the dimensions of the ablatives used in solid rocket motor nozzles and thermal protection systems for reentry vehicles so that the inert weight is minimised. The results are also expected to significantly reduce the cost and/or duration of processing of ablative components. This shall lead to a more scientific and technical process design philosophy eventually leading to better ablatives with superior thermal and mechanical properties. Significant gains in terms of cost, process cycle time and inert mass are expected. Since most of the specific process parameters and raw material properties are still kept as closely guarded proprietary information in the international scenario, this information shall prove to be valuable to process engineers working in the field of ablative thermal protection systems.

CHAPTER 2

REVIEW OF LITERATURE

Ablative composites are a specialized category of composites which find very specific applications mainly in strategic applications of the aerospace and defense sectors. Though there is a large volume of published literature available for polymer matrix composites, research publications in the public domain on ablative composites are much less due to their important strategic nature. Most of the research work in this sector is of sponsored nature and of classified category. Hence little information is available in the public domain for reference. Limited coupon and laminate level studies involving a few variables have been reported by some researchers; however, a critical appraisal of the effect of these variables on the thermomechanical properties of ablative composites and functional performance in solid rocket motor nozzles, liquid engine throats or thermal protection systems of reentry vehicles is not available. Basic research on the properties of fibres and on different resins has been done exhaustively, but its consequential influence on the functional performance of ablatives in rocket motor and reentry applications is not widely reported. On the other hand considerable research with promising results has been done on the development of different resins for ablative applications. The processing equipments for ablative composites have been developed by many nations. These are mainly custom-made and patented information on certain process equipments is available. On the characterization of ablatives, a few research papers are available on the work done at the laboratory level but not much information is available on the ablative products used in the launch vehicle and space craft missions. In this chapter, a comprehensive review of the available literature related to the research problem is attempted and presented.

2.1 Ablation and ablative materials

Ablative materials are employed as a traditional thermal protection mechanism in almost all the space launch vehicles and reentry missions. All NASA planetary probes were shielded from the severe heating encountered during hypersonic flight by ablative protection systems [14, 15]. Organic resins are the most preferred choice as the matrix for ablative TPS. As the thermal protection system is exposed to high heat flux, the resin pyrolyses generating gaseous products like hydrocarbons that permeate the solid diffusing towards the external heated surface and proceed into the boundary layer, where the heat transfer processes take place. The resin pyrolysis continues and finally results in the production of a carbonaceous residue known as char. The whole process is endothermic absorbing large quantity of heat in a very short period of time. The pyrolysis gases percolate towards the surface and in the process get heated transferring heat from the solid to the gas. The transformations and energy accommodation mechanisms of an ablative TPS is schematically illustrated in Figure 2.1.

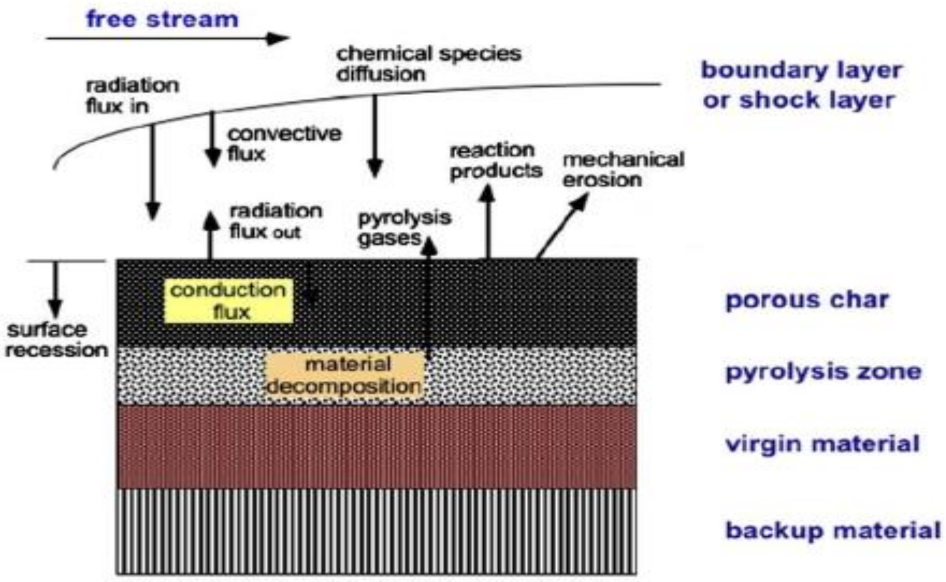


Figure 2.1: Schematic illustration of the basic ablation process [15]

The gases of pyrolysis after entering the boundary layer alter the convective heating. They undergo chemical reactions with the boundary layer gases and influence the heat transfer scenario in the boundary layer. These chemical reactions generally erode the surface of the ablative thermal protection system leading to surface consumption and surface regression. Vapourisation and sublimation reactions are endothermic while oxidation reactions are exothermic in nature [14].

The thermal response of ablative composites is unique and thus this elite class of composites play a very important role in space missions especially reentry operations. When these exotic materials are exposed to extremely high temperatures, not only their surface and structure but also their intrinsic features can be protected from decomposition, which can occur at these temperatures [16]. The ablation of material depends on its intrinsic conditions as well as the extrinsic conditions like thermal, mechanical and chemical factors. Ablation is an endothermic and erosive process which involves complex physical and chemical reactions [17].

Evans [9] has also enumerated the several processes that can affect the nozzle erosion rate at high pressure and high temperature conditions as shown in Figure 2.2. These processes include intense convective and radiative heat transfer to the nozzle surface, rapid rise of surface temperature to elevated level due to these high heat fluxes, turbulent transport of gas phase oxidizing chemical species from core region to the nozzle surface, heterogeneous reactions of these oxidizing species with the exposed graphite surface, strong shear flow induced removal of product species from heterogeneous reactions and impact of molten particles on the nozzle material. Each of these processes has an important effect on the erosion rate of nozzle materials. There are also strong coupling effects among the above processes which make the process of ablation very complex.

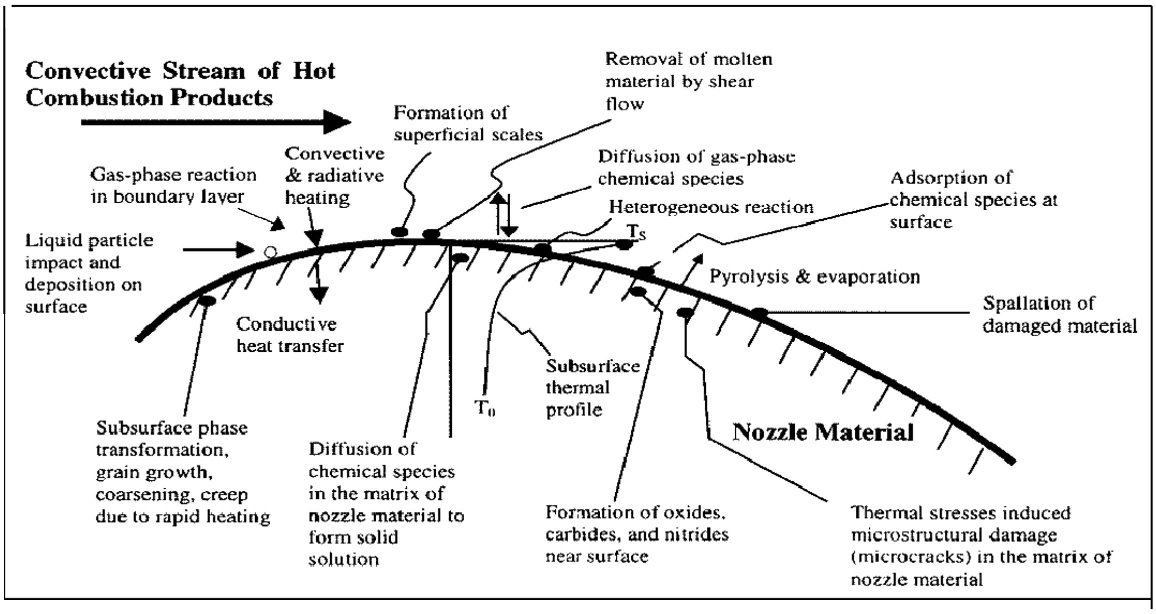


Figure 2.2: Chemical and mechanical processes related to rocket nozzle erosion [9]

In rocket motor applications, polymer based composites are ideal as they have good insulation properties which helps to avoid excessive heat transfer to the backup material. The energy transferred from the product stream to the composite material is contained in a thin region close to the surface where it causes ablation of the composite material. Figure 2.3 shows typical processes associated with the ablation of polymeric composites. As the temperature in the surface region increases from convective and radiative heat transfer, the material in the near surface region begins to degrade, removing energy through endothermic decomposition and pyrolysis reactions. Further pyrolysis occurs as the material heats to higher temperatures. The gas evolved from the decomposition of the composite material enters the boundary layer zone, leaving a charred layer of material on the surface containing the fibre reinforcements. As the fibre reinforcements are heated further, chemical reaction begins to occur also from the heterogeneous attack. The pyrolysis of the matrix material and chemical attack of reinforcement fibres may be driven to completion, given enough energy transfer and available oxidizing species leaving a char layer on the surface. The char layer is removed by the continuous heating and convective cross flow resulting in surface recession.

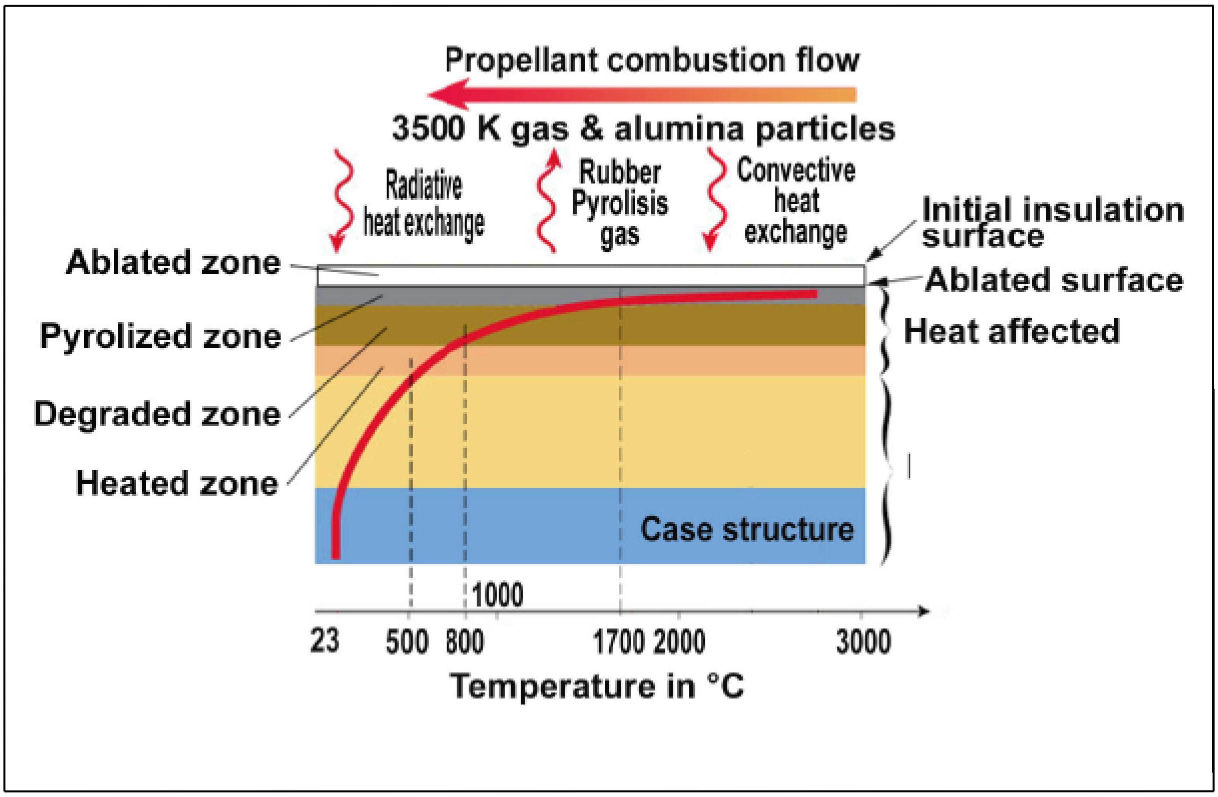


Figure 2.3: Ablation processes of reinforced-polymeric composites [18]

A review of the literature shows that there are two categories of ablative materials- melting and nonmelting. In the thermoplastic based melting ablatives, the liquid is removed immediately after the formation and a fresh surface gets exposed. This is not the most efficient mode of thermal protection[19]. In nonmelting and unreinforced materials, mechanical ablation precedes chemical ablation. As the temperature increases, the mechanical strength decreases. Sublimation becomes appreciable at higher temperatures like 3000 K [20]. Nonmelting ablatives are synthesized from char forming thermosetting resins, providing multiple layers of protection. These are suitable for reentry vehicles, probes and ballistic missiles where the operating environment is of high heating rates and short duration. However, these composites are characterized by low strength and stiffness and hence are reinforced by fibres and sometimes fillers. Carbon phenolics are the widely used ablative composite in this category [21].

Maurizio Natali *et al.* [7] in a review of the polymeric materials for thermal protection systems and propulsion devices have given a broad overview of ablative materials used in aerospace industries. According to the mode of interaction with the environment, the energy can be dissipated in different ways. Ablative TPS can be further bifurcated into organic polymeric materials and inorganic oxides and metals. Non-ablative TPS are limited to relatively mild and medium hyper thermal environments only. Metals like Rhenium were used successfully in liquid fuelled engines for upper stages for launchers. Ceramic based TPS has been successfully used as heat shield material in reentry mission of Space Shuttle Orbiter (SSO).

Reinforced polymer composites consist of fibres with high strength and modulus in a polymeric matrix. There are clear boundaries between the fibres and the matrix material, allowing each component to maintain its original material properties while forming a composite that has properties far superior to either of the individual components. Fibre reinforcement materials can include silica glass, aramids, or carbon fibres. Matrix materials usually include phenolic or epoxy resins. Components made of these composites are either compression molded from preimpregnated materials or tape wrapped for larger nozzles. The combination of low density and high strength make these materials useful for not only nozzle throat applications, but also for casing insulation and casing/nozzle structure materials.

When carbon phenolic and silica phenolic composites are subjected to high temperature, the phenolic resin starts pyrolysing from 250°C onwards forming porous char. Charring continues till all elements other than carbon have been driven out in the form of decomposition products. Oxides of carbon are also formed. The volatiles while passing through the porous char into the exhaust stream carry away a large quantity of heat. The thermomechanical response of ablative composites has been studied by many researchers and different models were proposed by Shi Shengbo [22, 23], Suvillan [24, 25], Matsuuara [26] McManus [27, 28] and others.

2.2 Reinforcements for ablatives

Though many reinforcements were experimented by many researchers in many different forms like fibres, chops, strands, flakes and fabrics, the most commonly used reinforcements are carbon and silica in the fabric form.

Each ablative material has its own characteristic advantages and disadvantages in terms of its properties like density, ablation temperature, shear strength and pyrolysis rate and in terms of the external environmental conditions like heat flux, velocity of the hot gases, mechanical shear forces, temperature, pressure and vacuum. Carbon based materials have been considered as promising candidates for severe environments with high temperatures and high pressures due to their high temperature capability above 2000°C, high thermal shock resistance, good ablation resistance with low density and hence less weight[29]. Carbon fabric is a common choice as reinforcement due to its ability to resist high temperature erosive aerodynamic shear forces because of its high thermal stability, low thermal conductivity and higher interlaminar shear strength (ILSS) in the composite form [30].

Carbon fabric can be made from polyacrylonitrile (PAN), pitch or rayon route. From the literature, it is observed that all the three routes have been used for development of ablative composites but rayon based carbon fabric is preferred by most designers. Rayon based carbon fabric reinforced phenolic composites offer a combination of low thermal conductivity and predictable char properties which results in significant performance advantages when used in solid rocket motor nozzles and reentry heat shields. Historically, the aerospace industry has utilized textile grade rayon as the precursor for phenolic impregnated carbonized rayon fabric. Textile grade rayon was found to be attractive based on the ease with which it could be processed carbonized fibre, ready availability, relatively low cost and suitable fibre dimensions [31, 32]. Tauriello and Doyle [33] have reported that no other material system offers a combination of properties and performance to match carbonized rayon phenolic ablatives citing many major launch vehicle experiences including NASA’s Space Shuttle programme. The focus primarily is on risk reduction and reuse of legacy designs for the major space fairing nations.

Rossi and Wong [34] have reported the significance of rayon yarn cross section and weave pattern for aerospace applications. They have studied the possible alternatives to rayon for fabric precursors. Due to the poor performance of demonstration hardware using these materials, they have concluded that none of these materials can be a replacement for rayon based carbon fabric. Rayon is made from a cellulose acetate viscose. The manufacture of rayon fibre is normally done in a continuous process, where by controlling the resident time and flow rates through the sequential tanks, the desired properties are achieved. The aerospace grade is intermediate in processing conditions between the stronger commercial fibre and the lower strength, high sheen grade used in fabrics. A major requirement of the aerospace grade rayon is that, when carbonized, it must produce a fibre with crenulated cross section. Such a cross section will provide good interlaminar shear and across ply tensile strength for nozzle applications. It is reported that though aerospace rayon is not the strongest fibre especially after carbonization and graphitization, fibre strength is not the determining factor for nozzle applications. The fibre has to have just sufficient strength to withstand the stress from the hot gas pressure and thermal expansion. Rayon based fabric reinforcements develop relatively low stress since they have low values of elastic modulus. Hence, they are the favourite choice of the nozzle designer.

Rayon fibres are processed through a spinning operation, in which the rayon viscose is drawn through a spinneret that contains multiple fine holes, each hole creating an individual filament. After drawing the filaments, they are dried, pulled and twisted to form a yarn. 1100 denier with 490 filaments and 1650 denier with 720 filaments are the aerospace rayon specifications. The yarns are weaved in three different types of harness constructions, 8 Harness Satin (HS) weave, 5 HS weave and the plain weave. 8 HS weave is the most common construction for nozzle applications since it gives the best drapability characteristics for the fabric during processing.

PAN and pitch made from oil base or coal base have also been tried as precursors to produce carbon fabric [35]. PAN fibre is wet spun using a suitable solvent, dried, stretched, air stabilized at 430°C and carbonized at 1600-1700°C. High strength, stiffness and thermal conductivity differentiate PAN fibres from rayon based carbon fibres. They are spun in a cylindrical fashion but become distorted in shape after carbonisation. The major disadvantage of using PAN based fibres with phenolic resin is that the interface between the fibre and the matrix develops only about half the strength of rayon based carbon fibres and phenolic resin. Weak fibre to matrix bonding leads to reduced interlaminar shear strength and this can eventually lead to delaminations, an unacceptable condition for rocket nozzles.

Pitch fibres are melt spun, carbonized and stress graphitized at very high temperatures. These fibres are circular but they tend to split axially after graphitization. Very high modulus and very high thermal conductivity are the characteristic features of these fibres. Due to the higher thermal conductivity of these fibres, the composite when used in rocket nozzles exhibit larger unacceptable char depths. Thus higher thermal conductivity reduces the thermal margins and lower shear strength reduces the structural margins for delaminations, higher density increases the weight and higher stiffness increases the bondline stresses. These observations make rayon based carbon fibres the favourite over PAN and pitch based fibres.

Interfacial properties of spun carbon phenolics are significantly greater than those of the filament carbon phenolic composite. A comparison of interfacial, thermal and ablative properties between spun and filament yarn type carbon phenolic composites were studied by Park, Cho and Kang of South Korea [36]. Their experimental results suggest that use of spun yarn type carbon fabrics heat-treated at low carbonization temperature as reinforcement in a phenolic composite may significantly contribute to improving the interfacial, thermal, and ablative properties of carbon phenolic composites.

2.3 Matrix resins for ablatives

Due to their inherent characteristics of high char yield and char retention strength phenolic resins, polyimides and polybenzimidazole are candidate matrix materials for ablative applications. The heat absorbed due to decomposition into char and gases are indicated by the heat of pyrolysis of a resin system. Heat of pyrolysis is very high for the composites synthesized using these resin systems. As the external surface is subjected to very high temperatures, pyrolysis of the outermost layer begins followed by charring of the layer. The pyrolysis zone advances gradually towards the inner layers and removal of the softened char material on the outermost surface begins due to the aerodynamic shear. This process is called mechanical ablation. The extent of char removal by mechanical ablation depends on the inplane shear strength and the severity of aerodynamic surface shear [37 - 40].

Researchers have reported that the most critical parameters for the selection of an optimum ablative system are the ablation temperature at which the material degradation begins and the material overall density [41, 42].

Phenol formaldehyde resins (PF) or phenolic resins are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. It is synthesized by reaction of phenol and formaldehyde directly to produce a thermosetting network polymer or by restricting the formaldehyde to produce a pre - polymer known as novolac which can be moulded and then cured with the addition of more formaldehyde and heat [43, 44]. There are many variations in both production and input materials that are used to produce a wide variety of resins for special purposes. Phenolic resins are formed by step growth polymerization. Step growth polymerization refers to a type of polymerization mechanism in which bifunctional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. When the molar ratio of formaldehyde to phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule and the system is entirely crosslinked. This is the reason why novolacs with formaldehyde to phenol ratio <1 do not harden without the addition of a cross-linking agents, and why resols with formaldehyde to phenol ratio >1 will harden without the addition of crosslinking agents. Phenolic resin is the preferred matrix material due to its high char yield and high char retention ability. During the endothermic pyrolysis, phenolic resin forms higher char than other resins [45]. This unique property of phenolic resins is utilized in ablative composites.

Phenolic resin is an important thermosetting matrix with good stiffness, thermal resistance, chemical resistance and long pot life. On the other hand, cured phenolic resins are highly brittle, which limits their utility in many composite applications. The incorporation of nanofillers into phenolic matrix is gaining significant interest in the structural composite application, where strength, stiffness, durability, lightweight, design and process flexibility are required such as in aerospace and automobile industry. The inherent brittle nature of the phenolic matrix can be improved by the incorporation of nanofillers in the matrix. The realization of nanofiller reinforced phenolic resins with high thermal stability requires a homogeneous dispersion and strong interfacial interaction between the nanofiller and the polymer matrix. Generally nanoparticles have a tendency for agglomeration because of the weak Van der Waals force of attraction. Surface modifications of nanofillers are an effective way to improve interfacial interaction between the nanofillers and the phenolic matrix, which in turn leads to better filler dispersion, and enhanced mechanical performance to the nanocomposites [46].

2.4 Ablative processing and characterization

Donald A. Peterson *et al.*[47] evaluated the erosion resistance and charring characteristics of silica reinforced ablative materials made of polyimide resin at different fabric orientations as nozzle sections of a storable propellant (nitrogen tetroxide and an equal blend of unsymmetrical dimethyl hydrazine and hydrazine) rocket engine. Quartz reinforcement was determined to have the greatest resistance to erosion, but a low-cost silica powder filled material was also high in erosion resistance. A fabric orientation of 60° to the nozzle centerline resulted in low char depth and high erosion resistance. The fabric layup angle to the gas stream should be minimized to minimize char depth and reduce engine weight. A 0° helix angle used for rosette layups resulted in delaminations and severe erosion.

Many researchers have tried to enhance the mechanical and thermal characteristics of ablative composites by using different techniques. The most common method attempted was the inclusion of different types of fillers in the resin. Though at the specimen level these additives showed encouraging results, these could not be scaled up satisfactorily to the full scale product level in a consistent, repetitive and uniform manner. Chidley and Seade [48] had attempted to study the effect of additives on the behaviour of silica phenolic composites. They used iron, iron oxide and chromium oxide as additives in phenolic resin. Composites containing chromium oxide exhibited the least reduction in char depth. The chromium oxide particles did not appear to interact appreciably with either carbon or silica during exposure in the rocket motor. The effect of iron was an overall char depth reduction of about 10%. Microscopically observed interactions between the iron phase and silica were highly supportive of a mechanism of silica reduction by carbon dissolved in iron as postulated. The largest reduction in the char depth, ranging up to 30%, was observed in composites containing ferric oxide. Results of microscopic examinations were consistent with the hypothesis that the decrease in char depth was due mainly to heat absorption by endothermic reduction of iron oxides. Subsequently, not much progress has been reported with metallic or metallic oxide additives.

Ding *et al.* [49], in 2015 have reported improved ablation resistance of carbon phenolic composites by introducing zirconium silicide particles. They investigated the effect of zirconium silicide on the thermal degradation behavior of phenolic and its role on the ablation resistance of carbon phenolic composites. It was investigated by first introducing these particles into phenolic, and then into carbon phenolic composites. Thermogravimetry (TG) analysis illustrated that the residue yield of phenolic at high temperatures is increased by the introduction of zirconium silicide particles. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses revealed that the increased residue yield is attributed to the reactions between these particles and pyrolysis volatiles. Therefore, partial carbon and oxygen elements in the volatiles remain in the thermal residue in the forms of amorphous carbon, zirconium oxide and silicon dioxide respectively. Moreover, the ablation resistance of carbon phenolic composites is significantly improved by the introduction of zirconium silicide particles with formation zirconium oxide and silicon dioxide during the oxygen-acetylene ablation process.

Jingjing Si *et al.* [50] in 2013 have attempted to enhance the thermal resistance and char yield of phenolic resin composites by low loading of graphene oxide. Li Wei Dong [51] *et al.*used basalt fibres to elevate the ablation, thermal, and mechanical properties of phenol formaldehyde ablative composites. Bahramian, AR [52] *et al*. reinforced kaolinite in the phenolic resin to improve the thermal stability, endothermic capability, and ablation performance of the fabricated ablative composites.

Harinath and Srinivasa Gupta [53] in 2013 reported an experimental investigation carried out on manufacturing and testing of ablative silica phenolic laminate by varying the different parameters with and without reinforcement of micro silica powder as filler material by changing the ply orientation of 0 and 35° rosette. The filler material of up to 15% is added and the properties evaluated and compared to standard laminates. In comparison with unreinforced filler laminate, specific gravity was reported to have increased at 20.87% & 12.76% for 0° overlap and 35° rosette reinforced filler laminate respectively. Parallel ply orientation fabrics of reinforced filler laminate had decreased the void content to the order of 68.84% as compared to unreinforced filler parallel ply laminate.

Yaxi Chen *et al.* [54] introduced Zirconium diboride in the phenolic resin with the help of ethanol solvent. Char yield of phenolic resin could be improved but thermal stability of phenolic was not enhanced. Wei Huazhen *et al.* [55] used modified Polyhedral Oligomeric Silsesquioxane (POSS) in carbon phenolic composite to increase ablation properties. Yu Liu *et al.* [56] introduced phenyl modified POSS in carbon phenolic composite to improve the mass of ablation and erosion rate.

Recent developments in nanoscale material production have generated a relatively new class of polymeric composite materials, nanocomposites [57]. Nanocomposites refer to the reinforcement materials having one dimension that is nano in scale. Nanosized particles have a very high specific surface area, compared to traditional reinforcement materials. The large interfacial area increases the mechanical properties significantly and also help with erosion resistance. Nozzle assemblies (entrance, throat, and exit cone) made of montmorillonite organoclays (natural clay), carbon nanofibres, and polyhedral oligomeric silsesquioxane(inorganic/organic compound) containing reinforced nanocomposites have been tested in solid propellant motors showing very promising results in the laboratory level [58].

Nanoparticles in their purest form are reported to have exceptional fundamental properties. Their high surface area-to-volume ratio, especially for nanotubes, makes them perfect ablative and reinforcement materials. Addition of proper nanoparticles in polymer matrix can enhance ablative and mechanical properties of polymer matrix composites. Many researchers have reported their findings on the effects of nanoparticles on ablative properties [59-65]. The typical nanoparticles used for ablatives are single walled and multi wall carbon nanotubes (SWCNT and MWCNT), carbon black and nanoclays.

Patton *et al*. [66] modified carbon fibre-reinforced phenolic composites with carbon nanofibres (CNF). It was observed that the nanoscale dimensions of the vapor grown CNF caused major changes in the heat transfer rates and affected the resultant combustion chemistry.

A novel flake graphite was introduced into barium phenolic resin by Yu and Wan [67]. Nanocomposites were made by roller coating technology and its ablation property was tested under long pulse laser radiation. It was observed that the size of the graphite flake affected the ablation rate. Srikanth *et al*. [68]

prepared ablative nanocomposites by introducing nanosilica into the phenolic resin with carbon fibre reinforcement. Ablation resistance of nanocomposites increased with the nanosilica content up to 2% by weight. However, beyond this point ablation resistance was decreased. The ablation performance, thermal decomposition, and temperature distribution through the thickness of asbestos/phenolic composites modified with layered silicate were compared with traditional asbestos/phenolic composites by Bahramian and Kokabi [69]. Nanofillers were introduced at 3, 4, and 6 % loadings. Test samples were tested at the heat flux of 900 W/cm^2. The 6% nanocomposite samples showed the best ablation performance [69]. Natali *et al.* [70 – 72] have carried out extensive studies on nanofillers, CNTs and other additives. Their results included thermogravimetric analysis, evaluation of the heat capacity, oxy-acetylene test, and the post burning morphology. They observed better performance in nanomodified samples. Koo *et al.* [73] prepared ablative nanocomposites by using organoclay, POSS, and CNF with and without carbon fibres in a phenolic resin. The combination of high loading of organoclay in phenolic resin and high loading of CNF in phenolic resin showed better ablation performance [73]. As the amount of nanoparticles increase, the viscosity of polymer resin increases rapidly. There is significant challenge in processing fibre reinforced composites using highly viscous polymer resins. On the other hand, lower loadings of MWCNT and POSS in polymer resin provide similar performance as that of higher loadings of organoclays and CNF [70-73]. MWCNT are easier to produce and therefore are available in much larger commercial quantity at a more affordable price than POSS. The constant increase in production rate of MWCNT has significantly decreased the cost in recent years. Koo *et al*. provided a comprehensive review of literature on polymer nanocomposites as advanced ablative material. This review indicates that there are no attempts in developing composites consisting rayon based carbon fabric, MWCNT, and phenolic resin [73].

Tate *et al.* [74] prepared ablative nanocomposites by incorporating MWCNT into phenolic resin and then impregnating them into rayon based carbon fabric. MWCNT were blended into phenolic resin at 0.5, 1 and 2 % loadings using a combination of sonication and high shear mixing. Test specimens were tested using oxyacetylene at a heat flux of 1000 W/cm^2 for 45 s. They have reported that 2% loading showed reduction in mass loss, recession in length compared to other samples.

Zuo Jia Wang *et al.* [75] experimented with MWCNT mixed in phenolic resin. They reported effective reduction in thermal erosion and improvement in the mechanical properties of the composites. Low filled and high filled layered silicate polymeric nanocomposites were introduced as new class of ablative materials by Azin Paydayesh *et al.* [76 - 77]. They also used nanoclay in asbestos phenolic composite to improve the mechanical properties and toughness of the composite.

Naderi, A. *et al.*[78] investigated the thermal behavior of carbon fibre/phenolic resin composite in presence of nanozirconium dioxide to determine the potential application of new modified composite material as thermal protection system.

Robert, TM *et al.* [79] in 2014 have modified silica phenolic composites with nanoclay and evaluated their mechanical properties and thermal response under simulated atmospheric reentry conditions. Bharati *et al.* [46] have reported that the addition of optimum concentration of nanoclay (cloisite 30B) and graphene in silica phenolic ablative composite system enhances the char yield.

Mechanical and ablation properties of nanosilica modified carbon fibre/phenolic composites have been investigated by Mirzapour *et al.* [21]. Nanosilica/carbon fibre/phenolic nanocomposites were prepared using chopped carbon fibre, phenolic resin and nanosilica by compression molding. The ablation properties of composites were tested in an oxyacetylene torch. The results show that the linear and mass ablation rates of the composites after modifying with 5% nanosilica decreased by 23.55% and 61.11% respectively. Microstructure investigations and X-ray diffraction studies revealed that nanosilica reacts with char at high-temperature, forming ablation resistant silicon carbide. Mechanical analysis showed that the bending strength of the nanocomposite increases by about 13% after adding 3% nanosilica.

Hybrid carbon fibre phenolic matrix composites containing carbon nanotubes and silicon carbide particles were characterized against oxyacetylene torch test to investigate the individual and combined effect of particulate reinforcement on ablative properties by Saghara.A [80]. The composite containing 5% silicon carbide particles reduced the ablation rate to 33% while the one containing 0.1% carbon nanotubes lowered the rate to 9%. The combined effect of 5% silicon carbide particles and 0.1% carbon nanotubes resulted in 43% reduction in ablation rate. In terms of weight fraction of the two particulate reinforcements, the effect of carbon nanotubes on ablation properties was found to be significantly greater than silicon carbide particles while their combined incorporation synergically improved the ablative properties.

Though many studies indicated improvement in the laboratory level, these could not be effectively and economically scaled up to the ablative product level due to practical limitations.

Jong Kyoo Park and Tae Jin Kang [81] have investigated the thermal and ablative properties of PF composites reinforced with carbon fibres heat treated at low temperature have been investigated. Low temperature carbon fibres (LTCF) were obtained by a continuous carbonization process from stabilized PAN fibres at 1100°C. The properties of LTCF reinforced PF (LTCF-PF) composites are compared with those of high temperature carbon fibre (HTCF) reinforced PF (HTCF-PF) composites. The thermal conductivity of the LTCF-PF composite is lower than that of HTCF-PF composite by about 35 and 10% along the directions parallel and perpendicular to the laminar plane, respectively. It was found from the ablation test using an arc plasma touch flame that the erosion rate is higher by about 30% in comparison with HTCF-PF composite. The results suggest that use of LTCFs as reinforcement in a composite may improve the thermal insulation of the composite but decrease the ablative resistance.

The mechanism of mass loss and endothermic properties of silica fibre reinforced phenolic composites during ablation were investigated by Shengbo Shi *et al.*[82] in 2016. Variations of the ablation properties of the silica fibre reinforced phenolic composites versus thermal exposure time were calculated and analyzed. They have concluded that it is necessary to increase the specific heat capacity and the content of silicon dioxide in the ablative material when designing silica-reinforced composites, which would improve the heat absorbing capacity of the thermal protection material.

Some researchers have worked on the machinability aspects of composites in general and a few have worked on ablatives as well. Khashaba [83] in 2012 had studied the effects of drilling parameters in drilling polymeric composite materials. Delamination associated with drilling can often be a limiting factor resulting in reduced structural strength, poor assembly tolerance and has the potential for long term performance deterioration. He had studied the parameters like feed, speed, drill geometry, drill wear along with composite material parameters. Factors affecting delamination onset, delamination mechanisms and measurements are considered and a few delamination-free techniques for drilling are suggested. However, in ablative composites for rocket nozzles and reentry vehicles, need for drilling is limited.

Sreejith *et al.* [84] had studied in detail the thermal aspects of machining SP ablative composites. It was reported that machining of SP ablatives was inherently difficult due to the diverse fibre and matrix properties, inhomogeneous nature of the composite and high volume fraction of the fibres in the matrix. Since the material was a poor conductor of heat, the heat generated during cutting was not properly dissipated. The same research group had studied in detail the effect of poly crystalline diamond (PCD) tool behavior during machining of CP ablative composites [85, 86].

Bibin John *et al.* [87] in 2011 had processed and characterised medium density ablatives for reentry applications. They studied the thermal response under moderate atmospheric reentry conditions. This article described the processing of silica fibre reinforced phenolic syntactic foams containing varying concentration of silica fibre and different specific gravities. The compositional dependency of the mechanical, dynamic mechanical, thermal and thermophysical properties of the foam composites were also examined. Thermal response of the ablatives was studied by simulating a moderate atmospheric reentry heat flux history on the specimen with maximum heat flux of about 40 W/cm^2 for duration of 600 s. Material surface behaviour, mass loss and flammability were studied and correlated to the functional requirements of a typical flight.

Phenolic and silicone based syntactic foams have been successfully used for thermal protection of atmospheric reentry space vehicles and to prevent structures from the extreme heat flux of rocket exhaust plumes. Also, in a given composition of resin and filler, it is further possible to tailor the mechanical properties and density by varying the nature and composition of the fillers and the extent of compaction. Thus, density can be maintained a minimum by limiting the extent of mechanical compaction for achieving the minimum required structural strength. This leaves high porosity in the system, resulting in low thermal conductivity, rendering them suitable for use as passive thermal insulation materials as well as ablative systems.

In many aerospace and military applications using thermal insulating materials with anti-ablation performances, lowering the thermal conductivity of a composite of interest is primarily more important than maintaining its mechanical strength. Cho D and Yoon B.I [88] had reported the microstructural interpretation of the effect of various matrices on the ablation properties of carbon fibre reinforced composites. Park and Kang [89] reported that use of low temperature carbon fibres heat treated at 1100°C as reinforcement of the phenolic composite improved the insulation property of the composite. Lowering the thermal conductivity of a carbon phenolic composite was successfully achieved by controlling the thermal conductivity of carbon fibres rather than phenolic matrix because the conductivity of carbon fibres was much greater than that of polymer matrix and it was also effectively managed through a variety of heat treatment processes. Some researchers have reported results of processing carbon fibres with less thermal conductivity [90-96].

Winya *et al.* [97] in 2013 have studied some factors affecting the ablation rate of phenolic resin/fibre glass. They have concluded that the ablation rate was affected by the amount of phenolic resin, curing time, interaction between amount of resin and curing time and interaction between curing temperature and curing time and three way interactions between these variables. For the particular type of phenolic resin and the reinforcement of synthetic fibre glass, they had suggested that 75% of phenolic resin at a curing temperature of 160°C for a curing time of 35 minutes gave an ablation rate of 0.121 mm/s. Firouzmanesh.M.R. and Arefazar.A [98] in 2003 have investigated the thermal stability and ablation behavior of carbon/epoxy novalac composites.

Winya, Chankapoe.S. and Kiriratnikom [99] in 2012 had studied the ablation, mechanical and thermal properties of a rocket motor insulation material from phenolic resin matrix and different synthetic fibres and fibre glass. They had reported a density of 1.66 g/cc for synthetic fibre/phenolic composite and 1.41 g/cc for fibre glass/phenolic composite.

Pulci *et al.* [14] in 2010 had developed a carbon phenolic ablative thermal protection system fulfilling the thermal and mechanical requirements corresponding to the actual loads experienced by a space vehicle during a moon to earth reentry. They used a resole resin coupled with graphite felt and graphite foam. They made a carbon phenolic composite made of rigid nonwoven graphite felt impregnated with a resole phenolic resin which can act a very effective thermal protection system upto 2000°C. They had carried out a multistage curing cycle at different temperatures to obtain a complete cure of the phenolic resin and to allow for an efficient impregnation of the porous graphite reinforcement, thus achieving optimal microstructure and the highest mechanical properties.

Wang *et al.* [100] in 2012 had prepared carbon fibre reinforced phenolic based composites by laminating molding. The variation in mechanical characteristics of composites was evaluated with heating temperature. The microstructure of composites at different temperatures was observed by optical microscope and scanning electron microscope. The results showed that the main weight loss range of carbon phenolic is from 300 to 800°C. The weight loss at temperatures below 700°C was due to the pyrolysis of the resin and the weight loss after that temperature was mainly by oxidation in the fibre phase. They had reported that with the heat treatment temperature rising, the bonding at the interface of carbon fibres and resin matrix weakened and in the pyrolysis temperature range, the ILSS of carbon phenolic showed a rapid drop with increase in temperature and then decrease in the rate of ILSS became relatively slower. They had also concluded that the fibre oxidation had little influence on the ILSS.

Patton R.D *et al.* [101] had studied in detail the ablation, mechanical and thermal properties of vapor grown carbon fibre composites. These properties were evaluated to determine the potential of using this material in solid rocket motor nozzles. Composite specimens with varying fibre loadings (30-50%) including one sample with rayon carbon fibre plies were prepared and exposed to a plasma torch for 20 seconds duration with a heat flux of 16.5 MW/m^2 at approximately 1650°C. Low erosion rates and little char formation were observed confirming that these materials were promising for rocket motor nozzle materials. When fibre loadings increased, mechanical properties and ablative properties improved. The composites had low thermal conductivities (approximately 0.56W/mK) indicating they were good insulating materials. They had reported that if a 65% fibre loading in composite could be achieved, then ablative properties are projected to be comparable to or better than the composite material currently used on the Space Shuttle Reusable Solid Rocket Motor (RSRM).

Kitinirunkul *et al.* [102] had investigated the influence of the amount of phenolic, curing temperature and curing time on the mechanical properties of the composite made from a synthetic fibre impregnated with phenolic resin. For the particular combination of reinforcement and matrix they had concluded that a 75 wt % of phenolic resin cured at 140°C for 15 minutes gives the highest tensile mechanical properties.

Many researchers have attempted using different reinforcements with phenolic and other resins [103-108]. Mithil Kumar.N. and Venkatareddy.G [104] in 2009 have developed coir/glass hybrid composites using compression moulding technique. Hybrid fibres possess better mechanical properties than single fibre composites [105].

Sonia Fonseca *et al.* [109] in 2015 had studied the effect of fibre angle in the ablative behavior and thermal conductivity of carbon phenolic in nozzle extensions. They extracted samples of the Carbon Reinforced Carbon Fibre (CRCF) from performs obtained by biased and parallel tape wrapping processes with a resol type phenolic resin used as a matrix. Ablation tests were carried out in a plasma torch and compared. They have indicated that the fibre angle is an influencing parameter to determine the ablative properties and the thermal performance of composite wrapped structures.

Few researchers had attempted investigations on the effect of prepreg parameters and process parameters on the final thermal and mechanical properties of ablative composites. Kim *et al.* [110] had tried to apply compression in the thickness direction to the composite prepreg using a compression jig to supplement the low autoclave pressure. They have reported that the through thickness coefficient of thermal expansion (CTE) changed drastically with respect to the compaction amount and the void content of the carbon phenolic composite laminate showed different characteristics from the ordinary fabric laminates with respect to the autoclave pressure and jig pressure. This was significant since the thick axisymmetric structure of the composite nozzle induces high thermal residual stresses due the large difference in CTE between in plane and out of plane values. Better ILSS reduces the possibility of delaminations and prevents interlaminar failure of the composite nozzle.

Warga *et al.* [111] had studied the effects of process deviations on the performance of ablative solid rocket motor components. They had tested statically a submerged nozzle assembly by deliberately introducing defects like wrinkles, delaminations, resin pockets, density variations and voids. The mechanical and thermal properties of the discrepant areas were determined prior to the static test and the surface regression associated with each of these areas was measured after the test. Water infiltration was the most dangerous discrepancy which seriously affected the performance. Resin pockets, wrinkles, voids and metallic inclusions were much localized and less severe in their effects. Other deviations could not significantly affect the performance of the ablative composite.

Regarding the ply orientation of ablative liners, exhaustive investigations are not reported. However, clear mention is made in some technical papers which deal with the development aspects of ablative nozzles which were used in Space Shuttle of US, Ariane launch vehicles of European Space Agency (ESA) etc. Graves *et al.* [112] had discussed the advances in the process technology for ablative composite materials used in solid rocket motors of Space Shuttle. They had reported that carbon phenolic components with ply angles oriented perpendicular to the gas flow can develop magnitudes of fibre tensile strain that exceed the capability of the material so that the fibre can fail in mechanical spallation. Such a condition is highly undesirable since it leads to nonuniform surface causing severe flow disturbance and anomalous erosion. Their analysis and subscale and full scale tests showed significant reduction in fibre strains can be achieved by orienting the plies from 30 to 60º away from the flow. It was also reported that ablative composites with plies oriented between 30 to 60º to the flow were relatively insensitive to material and process variations, unlike ablatives with plies oriented perpendicular to the flow.

Research conducted for the improvement of Space Transportation System (STS) nozzles have brought to light interesting observations on the erosion performance of carbon phenolic ablative nozzle liners [113-114]. They had identified sodium content in the carbon fabric as a major factor affecting nozzle erosion. When the levels of sodium carbonate increased beyond 1400 ppm, in and on the surface of the Carbon fabric used for impregnation with phenolic resin, the thermal decomposition rate of the carbon fibre increased substantially. They eventually decreased the fibre load carrying capability of the fibres, thus contributing to poor erosion performance of the ablative nozzle liners. When the sodium content was controlled, the magnitude and frequency of pocketing erosion in the nose inlet portion of the nozzle was reported to be lesser.

Another interesting observation from this study was that the carbon phenolic plies in the nozzle liners were separating and lifting, in what they termed as ‘ply lifting phenomena’. When the plies were parallel to the axis or were oriented at an angle of 0 to 20º to the angle of the flow, plies showed a tendency to separate and lift themselves. However, ply lifting was never reported with components whose ply angles are greater than 20º to the nozzle flow. Liners which are having plies parallel to the centerline were observed to be sensitive to cure cycle and material variations. In depth details of the same are not available in published literature.

Bruno D’Andrea and Lillo Francesca [115] had further investigated these aspects by analyzing pocketing erosion of SRM Nozzles by extended thermal and mechanical tests. Pocketing erosion is a form on highly uneven surface regression of an ablative composite during the operation of solid motor nozzle. They were unable to find a real unique repeatable reason for pocketing erosion by their studies. They had suggested that the irregular sewings distributed along the circumference and in the thickness could be contributing to this undesirable phenomenon. The dispersed wrinkles in the ablative liner may have caused local distortion of the carbon fibres leading to further erosion.

The lack of reliable, statistically significant material property data for carbon phenolic and silica phenolic was always a constraint for nozzle designers. Few researchers have worked in the area of characterization of polymer composites in general and ablative composites in particular. Canfield *et al.* [116] worked on determining the critical properties for analysis and evaluated the existing data to identify deficiencies. Tianbo *et al.* [117] prepared carbon fibre reinforced phenolic based composites by laminate moulding and the variation of mechanical properties and microstructure were evaluated. His results showed that the main weight loss range of carbon phenolic is from 300 to 800°C.

From the available literature, it was observed that no focused effort had been made to critically identify and evaluate the sensitivity and influence of the various raw material and process parameters on the critical properties and functional performance of ablatives. Hence, to bridge the obvious gap, a study has been attempted to identify the most influential parameters which have a significant bearing on the properties and functional performance of ablative composites. Of the large number of raw material and process parameters, the most critical ones were selected. The effect of fibre orientations in an ablative product and the fibre architecture in the laminate plies were identified for further studies. The effect of ply orientation, comparison of properties of pattern-cut vs. bias-cut tape wrapped components were the two major studies undertaken. To validate the sensitivity of the chosen process parameters, subscale level hot tests were also carried out.

The resin content, volatile content and the degree of advancement of resin are the major raw material parameters influencing the properties and functional performance of the ablative composite. After initial studies, resin content was chosen for detailed investigations as volatile content and degree of advancement were properties largely controlled by the processing conditions and was not generally influential. On the other hand, the resin content in the prepreg, or indirectly, the fibre content was found to have a significant influence on the physical, thermal and mechanical properties of the ablative. Among the different process stages, polymerisation or curing was the most critical stage as the consolidation of the composite occurs during this phase and the properties are getting frozen. After reaching the cured stage, further changes in the characteristics of the composites are unlikely. Hence, more perturbations were performed on the cure temperature and cure pressure and this has yielded good insights.

CHAPTER 3

OBJECTIVES AND METHODOLOGY

Ablative systems are basically designed based on thermal considerations but the structural properties also play a vital role during the operating conditions. There is a sizeable number of key process variables which are to be carefully selected based on the end product requirements. The processes being followed by different agencies have been evolved over a period of time by trial and error method and through processing experience. Process developments in the past have been mainly based on previous experience of similar products and/or by very limited coupon level or laminate level experiments.

Though many ablative products have been developed successfully, not much parametric level research was undertaken to investigate the influence of the crucial raw material and process parameters. Not much work has been reported on the correlation of process variables on the final properties and performance of the ablative liners. In order to provide a better theoretical base for process design, it is essential to have a better understanding of the effect of the critical raw material and process parameters on the thermal and mechanical properties and functional performance of the ablative composite either in isolation or in combination.

The motivation of the present research work is bridging this obvious gap in the understanding of the dependence of the properties and performance of the ablative composites on the raw material properties and process parameters. By studying the sensitivity of the most critical raw material and process parameters on the important thermal, physical and mechanical properties of ablative composites, the important factors can be identified, monitored and optimized to obtain consistent and repeatable performance for the ablatives. Significant gains in terms of cost, process cycle time and inert mass are expected. Since most of the specific process parameters and raw material properties are still kept as closely guarded proprietary information in the international scenario, this information shall prove to be valuable to process engineers working in the field of ablative thermal protection systems.

3.1 Objectives and scope of the research

The main objective of the research is to identify and quantify the most crucial factors affecting the material properties and functional performance of CP SP ablative composites. CP and SP were selected for the study because they were the most commonly used ablatives. Considering the gaps identified from literature, the following objectives were framed.

- To carry out total characterization of the reinforcement fibres (carbon and silica) and matrix resin (phenolic) and identification of the critical properties influencing the composite properties and to quantify the influence of these properties by laminate level studies.
- To carry out the impregnation of the carbon and silica fabric with phenolic resin and characterize the carbon phenolic and silica phenolic prepreg to identify the critical properties influencing the composite properties.
- To process ablative liners using the standard process sequence and identify the critical process variables in each stage. Sensitivity studies on the chosen variables to quantify the influence of these variables on the properties and performance of the ablative composites.
- To estimate the effect of other related factors like effect of temperature and effect of ageing on the properties of the ablative composites.

3.2 Experimental methodology

A detailed literature survey of the current raw materials, processing techniques, equipments and an actual on-the-job study at the processing labs was conducted to understand the different processes and the process variables being followed currently. The raw materials were characterized completely and the most influential parameters were identified for further investigations. This was followed by the impregnation of the reinforcement fabrics with the matrix resin and the total characterization of the prepreg for the volatile content, resin content and advancement parameters. The entire spectrum of process variables were enumerated and broadly classified into critical and noncritical parameters depending on their likely influence on the final product properties. Then, the chosen parameters for sensitivity studies were subjected to deeper investigation. Composite laminates and liners will be prepared using carbon fabric/silica fabric and phenol formaldehyde resin by varying the different parameters selected for the study. The important thermostructural properties required for an ablative were identified and the test methods and procedures were finalized.

Processing of the ablative composites was done following the standard process in which the chosen variable alone was changed each time and its effect studied. Laminates after processing were subjected to nondestructive evaluation techniques like visual inspection, alcohol wipe test and ultrasonic (pulse-echo and through transmission) testing to study the integrity and uniformity. After ensuring that the laminates are defect-free, specimens were fabricated from them as per accepted standards. Evaluation of mechanical and thermal properties was completed and the results tabulated. Apart from density, the crucial mechanical properties like compressive strength, modulus and interlaminar shear strength were studied. Heat of ablation, erosion rate, thermal conductivity and specific heat are the thermal properties which were evaluated. From the results of the tests, the effect of each variable on the composite properties was quantified and inferences made accordingly.

CHAPTER 4

PROCESSING OF ABLATIVE COMPOSITES AND SELECTION OF CRITICAL PARAMETERS

Ablative composites are synthesized from the basic raw materials of carbon or silica fabric reinforcement and phenolic or similar resins. The process may be in different routes but, in general, the following major steps are common for all routes.

1. Characterisation and testing of raw materials - carbon/silica fabric and phenolic resin
2. Impregnation of fabric with phenolic resin to obtain the prepreg
3. Testing of the prepreg and acceptance
4. Conditioning and cutting of the prepreg to the required size and shape into plies, tapes, chops or strands
5. Tape winding, layup or moulding of the prepreg on the mould or mandrel
6. Consolidation, vacuum bagging and curing (polymerisation)
7. Extraction, machining and specimen preparation
8. Nondestructive testing and evaluation of properties

The equipments, fixtures, toolings and process varies from product to product and from application to application, but by and large the sequence remains the same.

In each stage, there are a number of process parameters and allied factors that are likely to influence the mechanical and thermal properties of the ablative composite during the processing sequence as well as during their functional performance in the actual service conditions. In each of these stages, the different parameters were scrutinized and their likely influence was assessed. The most critical and important factors were identified and selected for further detailed investigations.

4.1 Materials

Among the various probable choices for the constituent fibre and resin of an ablative composite, there are clear favourites for applications in the aerospace sector especially in the internal surfaces of the solid propellant rocket motor nozzles, liquid propellant engine throat inserts and external surfaces of the re-entry vehicles. For reinforcements, carbon fibres and silica fibres are widely used. As explained in chapter 2, carbon fibres processed from rayon have distinctly superior characteristics than other fibres and are currently being used worldwide for the synthesis of ablative composites for launch vehicle and reentry applications [31-34]. Hence rayon based carbon fabric was selected for processing of ablative composites. Rayon is the precursor for this fibre and it is spun into filament yarns. After spinning or drawing, the filament yarns are carbonized at specified temperatures in two or three stages to drive out elements other than carbon. The basic raw material is initially carbonized in oil medium and subsequent carbonization is carried out in high temperature furnaces. Fabric is woven from twisted rayon rovings.

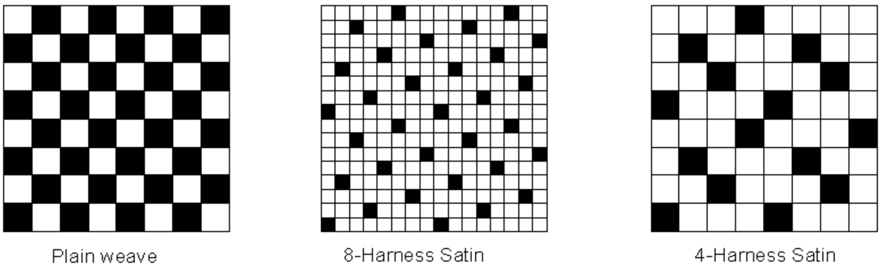
Rayon fabric is basically a carbohydrate known as cellulose having a chemical formula $(C_6H_{10}O_5)_n$. H_2O. The conversion of rayon fabric to carbon fabric is realized through a controlled thermal decomposition process under inert atmosphere. It is a multi stage process involving physical desorption of water, dehydration from cellulose unit, molecular rearrangements and aromatization.

Further treatments like sizing are done on the carbon fibres to improve the ability to handle them. The carbon fabric was procured from a standard manufacturer, M/s. Aerospace Materials Private Ltd and was characterized for all its properties before processing the ablative composites.

4.1.1 Characterisation of carbon fabric

a) Type of weave:

There are different types of weaves used for converting the carbon and silica fibres into bidirectional fabrics. Figure 4.1 shows the three most common weave patterns; 4.1 a) shows a plain weave, 4.1 b) and c) shows an 8- Harness and 4-Harness satin weaves respectively. Figure 4.2 depicts the fabric architecture in the different types of plain, twill and satin weave patterns. The basic difference is in the layout of the fibres in the two mutually perpendicular warp and weft directions. In a simple plain weave, it is the one up-one down construction of fibres while weaving whereas in an 8 Harness Satin (HS) weave, it is one up-seven down and in a 4 Harness Satin weave it is one up- three down and so on. To achieve high drapability while making complex composite parts satin weave with 8 Harness was chosen for the study.



a) 1 up & 1 down yarn. b) 1 up & 7 down yarn. c) 1 up & 3 down yarn.

Figure 4.1: Types of weave

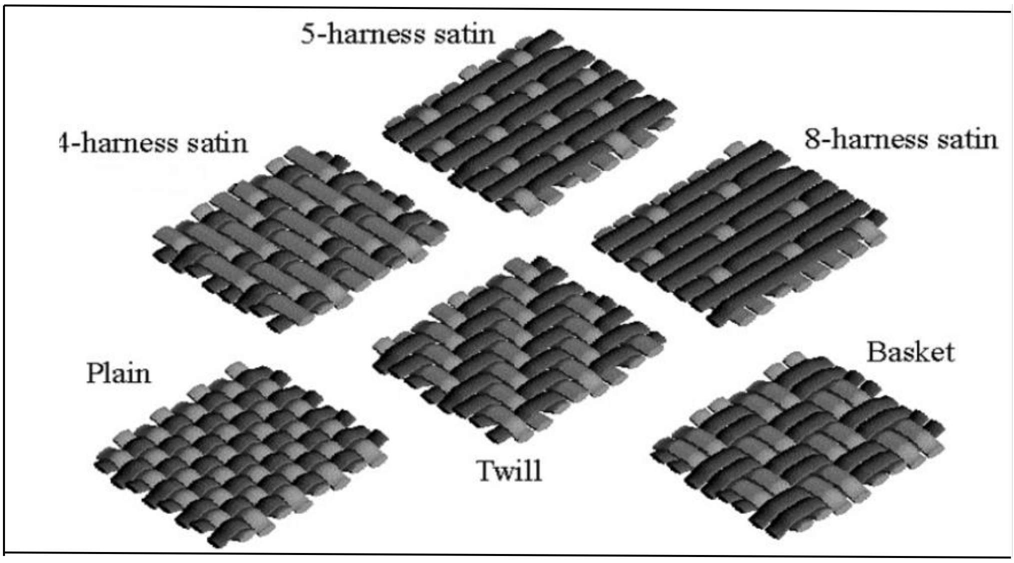


Figure 4.2: Types of satin weave

The 8-harness satin weave is confirmed by the use of needle and zoom glass. The basic construction of 8HS weave is given in Figure 4.3.

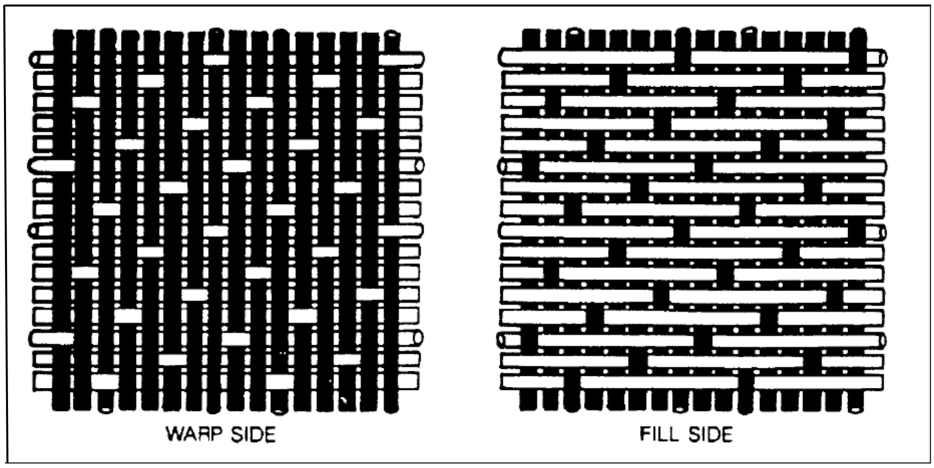


Figure 4.3: 8 HS satin weave-basic construction

b) Carbon content

Carbon content is an important parameter affecting the performance of the fabric as it affects the ablative characteristics significantly. Carbon content was evaluated using a CHN Elemental analyser which has a detection range of carbon in the range 0.01 mg to 3.5 mg. Thermal Conductivity Detector is used in this equipment which has an accuracy of 0.3% and a repeatability of 0.3%. Elemental analyzer is mainly for the estimation of carbon, hydrogen, nitrogen and sulphur content in different types of compounds, carbon fibre and carbon fabric. An exactly known weight of the sample (approximately 0.1 mg) was combusted in an atmosphere of pure and dry oxygen in the presence of tungsten oxide which acts as a catalyst. The oxides of carbon, hydrogen and nitrogen formed were passed through a chromatographic column where stepwise separation of the gases CO_2, H_2O and N_2 take place. These gases entered the detection chamber where the concentrations of individual components were measured as a function of their thermal conductivity.

A bunch of yarn from the fabric was extracted and two knots were made at the ends. After rigidising, the knots were cut off. The samples were kept in glass sample tubes and dried in pre-heated oven at 120°C for 30 minutes to drive away moisture. Immediately after drying and cooling, the samples were transferred to a tin boat in the equipment. Weights were taken using a microbalance and the sample was transferred to the auto sampler. 24 samples were evaluated and the carbon content was observed to be ranging from 92.52% to 98.43%.

c) Ash and sodium content

The organic parts of the carbon fabric were removed by heating the sample in furnace at 900^0C in presence of air. The residue was the ash content in the fabric. One of the content in the ash was sodium which was one of the critical parameters of interest in view of erosion performance. The residue was dissolved in dilute hydrochloric acid and the sodium content in the solution was estimated by flame emission technique.

Sodium, which was present in the fabric as an undesirable impurity had a significant bearing on the erosion characteristics of the ablative [113]. The content of sodium was evaluated along with the ash content as per ASTM C 561 91. About 1 g of dried carbon fabric was heated at 120°C for an hour in a forced air oven. Further it was subjected to 950°C for two hours in a platinum crucible. The sample was removed from the furnace and after reaching ambient temperature, the weight was taken and the ash content was determined. Ash content varied between 0.20 to 0.25% in all the samples and hence a perturbation study was not attempted as this was negligible. In addition, there was no reported evidence of the influence of ash content on the ablative performance. However, a lower content of the ash is desirable. After this process, 10 ml of dilute hydrochloric acid was added to the ash in the crucible. The flame photometer was calibrated using 1 and 10 ppm standard solutions to obtain the calibration curve (emission signal vs. concentration). Then the sample solution was evaluated for sodium content. 10 samples were tested and the values were found to be ranging from 332 to 944 ppm.

d) pH value:

The fabric samples having weight 2.5 g were soaked in boiling water for 30 minutes for extraction of fabric pH. The pH content in the water was measured for pH estimation using digital pH meter. pH value was generally stable for different types of fabric and hence further investigations on this parameter were not attempted. Significant dispersion in pH values were not seen in the samples characterized.

e) Specific gravity

The specific gravity of carbon fabric was evaluated using Archimedes principle. The weight of fabric in water was evaluated after complete removal of air bubbles present in the fabric. The air bubbles in the fabric were removed by heating the immersed fabric.

f) Mass per unit area

The mass per unit area of the fabric is a basic parameter of the fabric. It is represented in grams per square meter (gsm). A small size of the fabric (100 mm long and 100 mm wide) was taken from either side of the roll and the weight was measured. The measured value is converted into 1000 mm x1000 mm for reporting the mass per unit area in gsm.

g) Thread count

Thread count was estimated on both warp and fill directions by using needle with zoom glass and counterchecked by unweaving one inch fabric and physically counting the fibres in the warp and fill directions.

h) Thickness

The thickness of the carbon fabric is having a minor influence in the resin pickup during impregnation of the fabric with the resin. Thickness of the fabric was measured using Federal thickness gauge as per ASTM D 1777. The Federal thickness gauge has a presser foot with a diameter of 8.9 mm (0.35 inch) which applies a pressure of 0.69 Mpa (10 psi). The sample is placed under the anvil of the Federal thickness gauge and the presser foot is lowered. After 10 seconds, the gauge reading to the nearest 0.001 mm is noted. But the thickness is controlled by the filament yarn size as well as the weave pattern. Areal weight or mass per unit area (gsm) of an accurately cut 100 mm long and 100 mm wide fabric sample was measured using a highly sensitive balance. Fabric thread count in the warp and fill directions were also done manually for confirmation. These parameters were very difficult to change and hence were not amenable for perturbation studies. Manual impregnation of the fabric for higher thicknesses was practically difficult as it caused nonuniform wetting of resin. Impregnation plants are designed for standard thicknesses of the fabric and cannot be altered for highly variable thicknesses. Further, these parameters are not expected to drastically influence the mechanical and thermal properties or the functional performance of the ablative composites.

i) Tensile breaking strength of the fibres in the reinforcement

Tensile breaking strength of the fibres in the carbon fabric was evaluated as per ASTM D 5035 standard. Specimens were prepared for both warp and fill direction and tested for breaking strength. Paper tabs were used during testing for uniform load transfer as well as for better holding of specimen. The width in the testing direction was maintained as 25.4 mm (1 inch). Figure 4.4 shows the specimens prepared with the end tabs and the test fixture set up showing the gripping arrangement in the UTM.

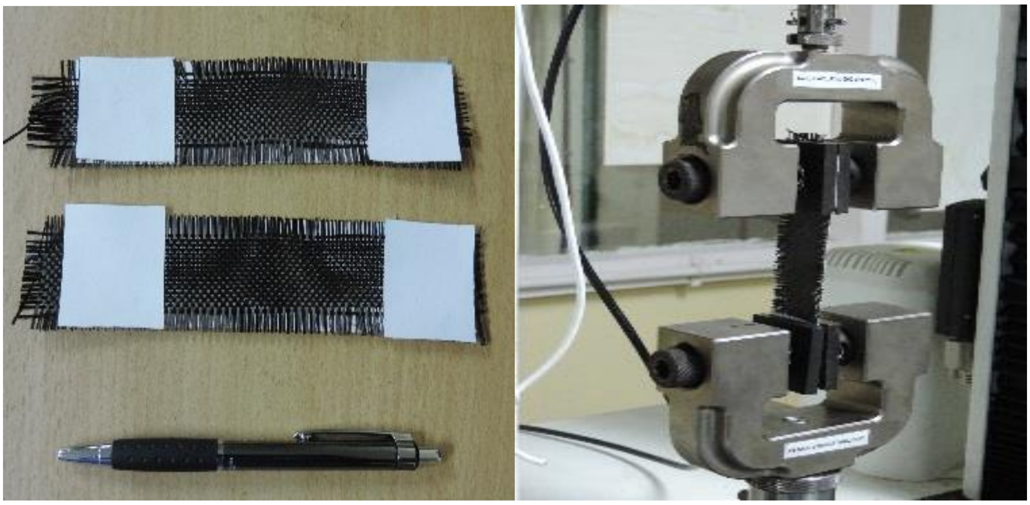


Figure 4.4: Specimens and test setup for evaluating Tensile breaking strength of a fabric

The summary of tested values are tabulated in Table 4.1

Table 4.1: Tested properties of carbon fabric

	Property of the fabric	Minimum value	Maximum value
1	Carbon content , %	92.52	98.43
2	Sodium Content (ppm)	332	943.75
3	pH	7.6	8.39
4	Ash content (%)	0.20	0.25
5	Breaking strength (kg/inch)	28	129
6	Areal weight, (gm/m^2)	292	300
7	Thread count (ends or picks/inch)	50	52
8	Thickness (mm)	0.328	0.332
9	Specific Gravity	1.75	1.765
10	Weave pattern	8HS	

From the experience of processing ablative composites and from the limited information available from literature, pH value, specific gravity and ash content are likely to be insensitive to the properties and performance of the ablative composites. Thickness and type of weave are standard features of specific types of fabrics. Breaking strength of carbon fabric is not very critical and sufficient strength requirement for withstanding the tension for pulling the fabric through the impregnation plant is the only requisite. It does not contribute significantly to the mechanical properties of the carbon fabric as such. Hence, these parameters were not chosen for further perturbation studies.

Accordingly, the following two parameters were selected for further in-depth sensitivity studies.

1. Carbon content in the fibres in the fabric reinforcement
2. Sodium content.

4.1.2 Characterisation of silica fabric

High silica fabric was the second type of reinforcement chosen for the experiments. Silica fabric is being produced by acid leaching of glass fabric. The

E-glass fabric, the basic raw material, is leached with hydrochloric acid for the removal of non-siliceous matter. E-glass (lime alumina borosilicate glass) originally has a silica content of 52 to 56%. During leaching, all metallic oxides other than silica, are converted into respective metallic chlorides. These metallic chlorides are removed during washing, leaving silica alone. The E-glass rolls are joined together for continuous production with proper stitching. Leaching is carried out in an extractor maintaining the acid concentration at 7-8N and temperature at 75-85^{o}C. The minimum residence time required for the E-glass fabric in hydrochloric acid is 4 hours to ensure complete removal non-siliceous content. The leached fabric is immediately fed to the washing tank and the drying unit at the same speed. The consolidation of leached fabric is carried out at elevated temperature in a multi zone electrically heated furnace. The leached fabric from drier needs consolidation since considerable mass loss is happening during leaching process. High silica fabric of aerospace grade was procured from M/s. Valeth HighTech Composites and was thoroughly characterized.

a) Silica content: A known weight of silica fabric sample was fused at 900^{0}C for an hour in a platinum crucible. The fused sample was digested with 10 ml of 1:3 concentrated sulphuric acid and hydrofluoric acid and boiled in hot plate till complete evaporation. The non-siliceous matter was left out as residue which was weighed and silica content was estimated.

b) pH value: 2.5 g of sample was boiled in distilled water for 30 minutes. The boiled water was filtered and the extract was used for pH estimation using digital pH meter.

c) Thickness: Thickness of the fabric was measured using a digital Federal thickness gauge. Thickness was measured randomly in both ends across the width of the fabric at 10 locations.

d) Specific gravity: The specific gravity of silica fabric was evaluated using Archimedes principle. A preweighed sample was boiled in water by keeping it in an oven for complete removal of air bubbles.

e) Weight (gsm): The weight per unit area of the fabric was measured from both ends of the roll and reported.

f) Tensile breaking strength: Breaking strength in both the warp and fill directions on each end were tested. Five samples were prepared for each direction. The holding of fabric was provided with paper tabs and the test was carried out up to failure of fabric.

g) Thread count: Thread count was estimated on both the warp and fill direction by using needle with zoom glass and counterchecked by unweaving a small sample of the fabric and physically counting the fibres in the warp and fill directions.

h) Areal shrinkage: The effectiveness of consolidation was measured by measuring the areal shrinkage. A sample size of 150 mm x 150 mm was kept at 1000^0C for 30 minutes in muffle furnace. The difference in area prior and after heating was taken for estimation.

The results of characterization of the silica fabric are tabulated in Table 4.2.

Table 4.2: Tested properties of high silica fabric

	Parameter	Minimum value	Maximum value
1	Silica content, %	95.04	98.90
2	Breaking strength (kg/inch)	22	38
3	pH	3	3.5
4	Areal weight, (g/m^2)	580	720
5	Thread count (Ends or picks/inch)	43	50
6	Thickness (mm)	0.50	0.70
7	Specific Gravity	1.90	2.10
8	Weave pattern	8HS	

In the case of silica fabric which is used in the less critical regions of the nozzle, there are no major parameters which can be really varied to study their effect on the functional performance. Similar to the carbon fabric, 8 HS weave is generally chosen for aerospace ablative applications. The thread count, mass per unit area and thickness have been standardized over a period of time and are well known to have limited influence on the final properties and performance. Silica content is achieved by repeated leaching of glass fabric to remove the impurities. Only high silica fabric is used in aerospace ablative applications. Silica content lower than 95% is not used in any of the rocket or reentry applications but is utilized only in insulation applications. The thickness, mass per unit area and thread count are also largely insensitive as discussed in the previous section. Hence there was not much scope for perturbation of silica fabric parameters. The only parameter which was likely to affect the mechanical or structural properties of the fabric and hence the composite was the tensile breaking strength of the fabric. Though it was known that a higher strength of the fabric obviously leads to higher strength in the composite, an effort was made to quantify the influence of breaking strength on the mechanical properties of the ablative composite.

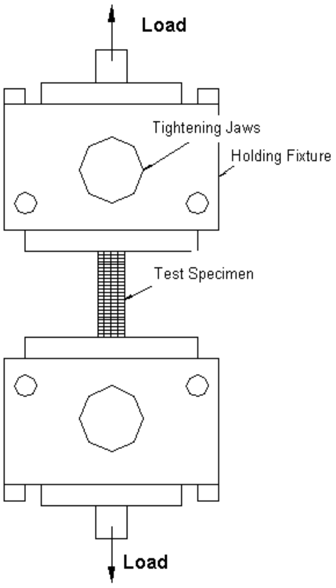


Figure 4.5: Test set up for evaluating tensile breaking strength of a fabric

The specimens bonded with end tabs similar to the procedure followed for carbon fabric. A test fixture shown in Figure 4.5 was used for evaluating the tensile breaking strength of silica fabric. The fabric was cut into 25.4mm (1 inch) wide strips and the ends were bonded with bond tabs for proper gripping on the fixture. Ends tabs also served to reduce the stress concentration near the grips. After the specimen was properly aligned with the load axis in an UTM, it was loaded in tension at a rate of 15 mm/min till failure. The load at failure was recorded and the breaking strength per unit width was computed.

4.1.3 Characterisation of phenolic resin

A high temperature curing resol type thermosetting phenolic resin was chosen for processing ablative composites for this study. This resin was reported to have excellent char strength and good ablative properties. Both carbon phenolic and silica phenolic composites were processed using the same resin. The basic process involves melting of phenol and charging formalin into the reactor at the desired mole ratio in the presence of a catalyst. The resin is formed by the condensation polymerisation of phenol and formalin. The main properties of the phenolic resin which were expected to have a bearing on the properties of the ablative composites are

1. Viscosity at 30°C, (P/Pa.s)
2. Specific gravity at 30°C
3. Total solid content at 170°C for 30 minutes (%)
4. Volatile content (%)
5. Free phenol (%)
6. Free formalin (%)
7. Point of trouble at 0.863 Sp.gr/10ml.of resin at 30°C

Since these properties were interdependent and perturbing one property would make changes on many other properties, it was not attempted to vary each parameter independently. On the other hand, two different phenolic resin combinations (Resin 1 and Resin 2), with different characteristics were studied by processing carbon phenolic and silica phenolic ablative composites and evaluating their mechanical and thermal properties for comparison. The resins (Resin 1 and Resin 2) were characterised in detail.

a) Viscosity

Viscosity, a temperature dependent property was evaluated at 30°C using Brookfield digital type viscometer following ASTM D 2393-65T. It was determined by measuring the torque on the spindle, rotating freely at a constant speed in the sample at 30˚C.

b) Specific gravity:

Specific gravity (density) of the resin was measured at 30˚C using a Hydrometer as per ASTM D792-13.

c) Solids content

The total solid content in the resin was evaluated by evaporating to dryness at 170˚C for 30 minutes and the solid residue is weighed and the total solid content is determined.

d) Phenol content and formalin content

The phenol in the phenolic resin was estimated by steam distillation, followed by reaction with Bromine and then titration with sodium thiosulphate solution.The method adopted for this purpose is based on ASTM D 1428. Free formalin in the resin was evaluated by treating with hydroxylamine hydrochloride and the liberated hydrochloric acid is titrated against standard NaOH solution.

e) Point of trouble (degree of advancement of resin)

Point of trouble is a very important characteristic property of a resin. It is an indication of the extent of polymerisation that has taken place in the resin. 100 gm of resin was diluted with rectified spirit till the specific gravity of the solution reaches 0.863. 10ml of dilute solution was titrated against distilled water. Appearance of turbidity indicated the end point. The volume of water added for complete reaction was reported as the point of trouble. Higher the value indicates that the extent of polymerisation was less.

The comparison of tested results is tabulated below.

Table 4.3: Tested properties of Phenolic Resins

No.	Property	Resin 1	Resin 2
1	Specific gravity at 30 ^{o}C	1.12-1.16	1.18-1.20
2	Viscosity (cP)	150-300	400-600
3	Degree of advancement (Point of trouble) @ 30 ^{o}C- (ml of water)	6- 10	13- 16
4	Solids content, % at 170 deg C for 30 minutes	60-65	72- 75
5	Free phenol, %	3 -6	18-22
6	Free formaldehyde, %	1-3	0.2- 0.5

Basically, Resin 2 had got a higher solid content and hence higher specific gravity and viscosity. The degree of advancement as measured by the point of trouble was maintained much higher for Resin 2 to ensure better processability. The free phenol % in Resin 1 was kept low at around 6%, while in Resin 2 it was more than thrice that value. The free formaldehyde value on the other hand was kept low for Resin 2 while for Resin 1 it was more than double the value.

So the effect of the combination of phenol content, formaldehyde content, total solid content and other properties was planned to be investigated. The effect of viscosity, degree of advancement and solids content were also decided to be subjected to detailed investigations.

4.2 Preimpregnation process

The first major process in the process sequence of the realisation of an ablative composite is the impregnation of the carbon or the silica fabric with the identified phenolic resin. The resultant intermediate product is called the ‘prepreg’. This is a very critical stage of processing since the intermediate raw material as well as the product is getting formed here. The characteristics of the ablative are largely influenced by the properties of the prepreg.

The process of impregnating the fabric with the resin can be done manually for small quantities but for larger volumes it is done using a mechanised impregnation plant. The plant can be a horizontal or a vertical one. A detailed study of the plants and its influence on the quality of the prepreg was carried out. Compared to the manual impregnation, mechanised system provides better uniformity and repeatability. This in turn leads to higher levels of quality and reliability. Vertical plants are more compact and occupy less floor space than horizontal impregnation plants of similar capacity. Both horizontal and vertical plants give almost similar output with respect to quality and productivity provided the process parameters are closely monitored and controlled. A basic schematic of a typical impregnation plant is given in Figure 4.6.

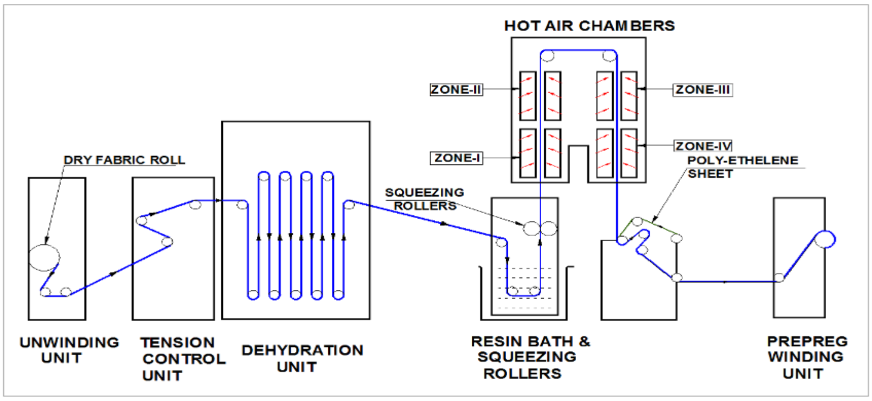


Figure 4.6: Schematic of a typical preimpregnation plant

The raw carbon or silica fabric rolls, known as the dry fabric were unwound in the unwinding unit and was passed through a tension control unit to ensure that the fabric was stretched to the optimum level and no sagging or wrinkling was observed as it passed through the plant. This is important since any laxity in tension leads to folding, wrinkling and similar deformities which leads to nonuniform resin pickup, resin starvation in some regions or nonuniform advancement of resin. All these observations are undesirable as they lead to poor quality prepreg. Both silica and carbon fabric may absorb some moisture when it is kept out in the ambient condition. Hence, the fabric was kept in the rolled condition in sealed containers to prevent moisture absorption. Absorption of moisture is detrimental to uniform resin pickup and advancement. Also, the fabric was passed through a dehydration unit maintained at around 105°C to drive out the any absorbed moisture. Moisture absorption leads to increase in volatile content in the prepreg which in turn increases the wet resin content in the prepreg. Higher volatile content is detrimental since these volatiles have to find an escape route from the layup during curing. Any entrapped volatiles can lead to delaminations and other defects in the composite. Hence dehydration is a critical step in the impregnation sequence.

After dehydration of the fabric, it was passed through the resin bath filled with adequate amount of the identified resin. The resin levels were maintained uniform during the process by periodic replenishment. As the fabric was passed through the resin in the bath, it picked up resin and the prepreg was formed. It was then guided through the squeeze rollers, the gap between which was adjusted to obtain the correct resin pickup. This was fine tuned through a number of trials. The excess resin was squeezed out though the squeeze rollers and the desired amount of resin was impregnated in the fabric forming the raw prepreg. The amount of resin impregnated in the prepreg is the most critical deciding factor of the ablative and mechanical properties of the composite. The resin in the prepreg was still in the less advanced ‘A’ stage where it can freely flow and wet the fabric. Advancement of cross-linking or polymerisation was minimum at this stage. The prepreg was guided through hot air chambers consisting of four different zones maintained at 90°C, 95°C, 100°C and 105°C for consolidation where the resin in the prepreg gets further advanced and it moves from ‘A’ stage to ‘B’ stage. ‘B’ stage of the resin is a stage in which the resin in the prepreg has further advanced and has build up its viscosity. It no longer flows freely in the ambient condition but can flow and further advance on the application of heat and pressure. The final prepreg in the ‘B’ stage was made into rolls and kept in a controlled humidity and temperature environment. The advancement of resin was influenced by the duration and condition of storage. As storage duration and temperature increases, the advancement or polymerisation of the resin in the prepreg progresses. Further cross linking of polymers was controlled by storing the prepreg in cold storages till the next stage of processing. Polythene sheets were used on either sides of the prepreg to prevent contamination and inadvertent adhesion of layers.

The factors other than dehydration temperature, gap between the rollers and heating chamber set temperatures include velocity of the fabric through the plant. This parameter determines the residence time in the plant and it indirectly contributes to the degree of advancement of the resin in the prepreg. These plant related factors can be easily tailored to suit the particular application requirements and a standard set of parameters were followed for the impregnation process. After a few trials, it was decided that sensitive studies by varying the impregnation plant parameters may not yield exciting outputs. With a set of proven plant parameters, the gap between the squeeze rollers was adjusted to obtain different grades of prepreg with different volatile and resin contents. Degree of advancement of resin in the prepreg was maintained constant since varying all the three critical parameters simultaneously leads to an unmanageably large number of trials. Further, varying the polymerisation levels beyond the normal ranges led to processing difficulties. Prepreg with high degree of advancement was already having a higher degree of cure and hence it could not be used for layup or winding trials. Prepreg with very low degree of advancement was not amenable for handling during processing as resin was flowing from the prepreg and the prepreg plies were slipping during layup and winding. Due to processing difficulties, optimum level of CI (degree of advancement of resin in the prepreg) was maintained at 24-26 ml of water for all the trials.

4.3 Characterisation and testing of prepreg

The main properties of the prepreg include volatile content, resin content and the degree of advancement of the resin in the prepreg. Since the prepreg is the real deciding element in the processing of an ablative composite, the study of the prepreg parameters was given utmost importance. The test methods for prepreg volatile and resin content were adopted from the procedure PTM-11 of U.S Polymeric Company.

4.3.1 Volatile content in the prepreg

Three specimens of size 100 mm x 100 mm were randomly cut with a template from the prepreg. These were weighed accurately separately after keeping them in porcelain crucible. Weight of the crucible was measured as W1 g and that of crucible with specimens as W2 g. The specimens in the crucible were introduced into the oven already maintained at 160^0C. After 30 minutes, the specimens were taken out using tongs and kept in the desiccators for cooling to room temperature. All the volatiles in the prepreg was driven out and the crucible with the specimens was again weighted accurately as W3 g. Volatile content was calculated as

$$Volatile\ content, \% = \frac{W2 - W3}{W2 - W1} \times 100 \tag{4.1}$$

4.3.2 Resin content in the prepreg

The procedure for evaluation of wet resin content is different for carbon phenolic and silica phenolic. For silica phenolic, burn off method was used to evaluate the resin content. The specimens after driving out all the volatiles (W3 g) were kept in a muffle furnace at 800°C. Along with this, bare high silica cloth sample weighed accurately in a porcelain crucible was also made ready for burn off. The size of this cloth sample was the same as prepreg sample. The weight of the crucible was measured as Y1 and the weight of the crucible and the high silica cloth sample as Y2. This was done to apply a correction factor to account for the loss of weight of bare high silica cloth at high temperature. The specimen was heated in the furnace till complete burn off was ensured, which was indicated by the specimen regaining the colour of the bare cloth. After complete burn off the furnace was switched off and as the temperature reached 200^0C, the specimens were taken out and weighed again. The weight of the crucible with burnt prepreg specimen was taken as W4 g and that of the crucible with bare cloth as Y3.

Correction Factor was calculated as

$$X = \frac{Y2 - Y1}{Y3 - Y1} \tag{4.2}$$

$$Corrected\ specimen\ weight = (W4 - W1) \times X \tag{4.3}$$

$$Wet\ resin\ content, \% = (W2 - W1) - \frac{[(W4 - W1)X]}{W2 - W1} \times 100 \tag{4.4}$$

For carbon phenolic, extraction method was used to evaluate the resin content. The volatile content was determined by following the procedure described for high silica phenolic prepreg. The other half of the carbon phenolic prepreg was weighed accurately by taking it in a folded filter paper. The weight of filter paper was W1 g and the weight of filter paper with the sample was W2 g. The filter paper with the sample was kept in Soxhlet extraction assembly for extraction of the resin. Extraction was continued until the solvent is clear indicating complete extraction of the resin. The filter paper with the sample is taken out and dried in oven at 100^0C for one hour, after which it is taken out and cooled to room temperature. After cooling it was weighed (W3 g).

$$Wet\ resin\ content.\% = \frac{(W2 - W1) - [(W3 - W1)X]}{(W2 - W1)} \times 100 \tag{4.5}$$

4.3.3 Degree of advancement of resin in the prepreg:

CI which is an indication of relative degree of advancement of the resin in the prepreg was also evaluated. The resin part of the prepreg was dissolved in acetone and was used for the evaluation. The prepreg sample was cut into small pieces and was put into the beaker. 50ml of acetone was poured into the beaker and the pieces were stirred slowly and carefully using a glass rod. Stirring was done until the phenolic resin in the prepreg becomes fully dissolved as indicated by the colour of the solution.

The resin solution in acetone as obtained above was filtered using filter paper, funnel and conical flask. A sample of the filtrate was tested for solid resin percentage. An aluminium foil dish was weighed accurately (W1 g). About 2 or 3 g of the resin solution was poured into the dish and weighed accurately (W2 g). The dish with the solution was evaporated in oven at 160°C for 30 minutes, taken out, cooled in desiccators and weighed (W3 g). The resin solids percentage was calculated.

$$Resin\ solids, \% = \frac{(W3 - W1)}{(W2 - W1)} \times 100 \tag{4.6}$$

This value was ensured to be above 4%. For specimens where this value was below 4 % it indicated the insufficiency of resin that has been digested in acetone. In such cases, excess amount of prepreg sample was taken for extraction in acetone in order to ensure that the resin solid did not fall below 4%.

Once the resin solids percentage was known, a resin solution was made up to 4% solids by addition of acetone. From the 4% solution made, 25ml was pipetted out into a conical flask and was titrated against distilled water added from a burette slowly, simultaneously shaking the flask, till the endpoint when turbidity is developed. The addition was stopped when turbidity was noticed. The volume of distilled water added indicated the Chang's index, which gives a measure of the degree of advancement of the resin in the prepreg.

Of the three important quantifiable parameters of volatile content, resin content and the degree of advancement of the resin in the prepreg (CI), resin content was selected for detailed study. Degree of advancement of resin in the prepreg had to be maintained at a standard rate to enable processing. If the advancement was more, the prepreg would become stiff and rigid and would not be amenable for ply cutting, forming, winding or layup. Processing difficulties prevented varying the Chang's index beyond a small range. Similarly, if the advancement was less, resin in the prepreg would be in the very liquid state with high flowability. This too rendered the prepreg difficult for handling during layup and further processing. The resin dripped out during tape winding and laying and caused ply slippages from the mould. Due to such process constraints, Chang's index in prepreg was maintained in a band of 24 to 26ml of water for all the trials. Volatile content in the prepreg is an important parameter, but since it was included directly in the wet resin content, this too was not selected for perturbation studies. Dry resin content along with volatiles is included in the wet resin content values. Since the wet resin content parameter takes care of dry resin content and volatile content in the prepreg, it was chosen for detailed investigations.

4.4 Conditioning of the prepreg and ply cutting

Once the prepreg was tested and accepted, it was prepared for further processing activities. The prepreg properties are highly sensitive to the storage conditions, time and temperature. As the viscosity in the prepreg builds up with time and temperature, the degree of advancement of the resin in the prepreg also builds up. The prepreg made was stored in a humidity controlled environment at a controlled temperature to avoid rapid polymerisation of the resin till the processing is complete. The prepreg was stored in a cold storage at 4°C till it was taken up for processing. The prepreg was conditioned at 90°C for 30 minutes to drive out any moisture absorbed during the storage. Any moisture absorption alters the volatile content in the prepreg which in turn alters the wet resin content.

After conditioning of the prepreg, it was cut into plies using a template for layup activities and into tapes for tape winding. Though there were no major process parameters likely to influence the properties and performance of the ablative composites, due care was taken to accurately prepare the tapes and plies. A major observation at this stage was that of the possibility of contamination during ply and tape cutting. In some laminates, foreign particles were observed during NDT which was attributed to this stage. Similarly, any oil or grease contamination can lead to delaminations in the laminate. If due care and diligence is given during this stage, good quality composites can be realized. Hence, no parameters were selected from this stage for detailed investigations.

4.5 Processing of ablative liners

After preparation of the prepreg, it was moulded over a shaped mandrel or mould. The mandrel is loaded on the tape winding machine between the head stock and the tail stock. The prepreg in the form of cut plies or continuous tapes were fed through a feed mechanism under controlled tension. Figure 4.7 shows a schematic of the tape winding machine on which the experiments were performed.

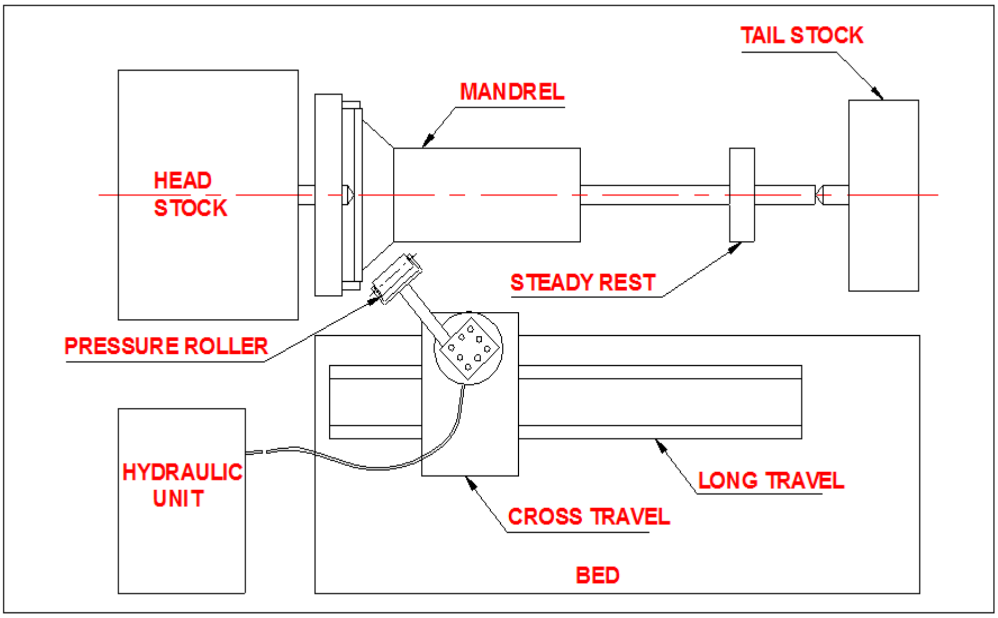


Figure 4.7: Schematic of the tape winding machine

The major process parameters in this stage were related to the winding machine like pitch and speed of rotation. The prepreg was subjected to heat to enable the resin in the prepreg to flow so that proper adhesion between adjacent layers was ensured. A hot air blower was used for this purpose. The heater set temperature was adjusted based on the initial prepreg condition especially the level of advancement of the resin in the prepreg. For the experiments it was set at 200°C and the temperature measured on the layup was around 75 to 80°C. Sufficient care was taken to ensure that the temperature in the prepreg does not cross 90°C to avoid exotherm initiation. For consolidation of layup, Teflon coated rollers were used and roller pressure was monitored. A pressure of 22 to 28 kg/cm^2 was applied for the experiments. Excess roller pressure led to crushing and wrinkling of the prepreg while pressures less than 22 kg/cm^2 was found to be ineffective. Though these parameters are important for efficient processing these can be maintained within certain standard limits. These were mainly related to processing easiness and to avoid process constraints and were not found to be sensitive to the mechanical or thermal properties or functional performance of the ablatives. Hence, these were not selected for further detailed investigations.

However, the ply orientation and fibre architecture are the two major parameters which have been discussed in literature as contributing to the properties and performance of ablatives. The ply orientation refers to the direction of the fibres in the reinforcement of the composite to the direction of the hot gas flow in the nozzle of the solid rocket motor nozzle.

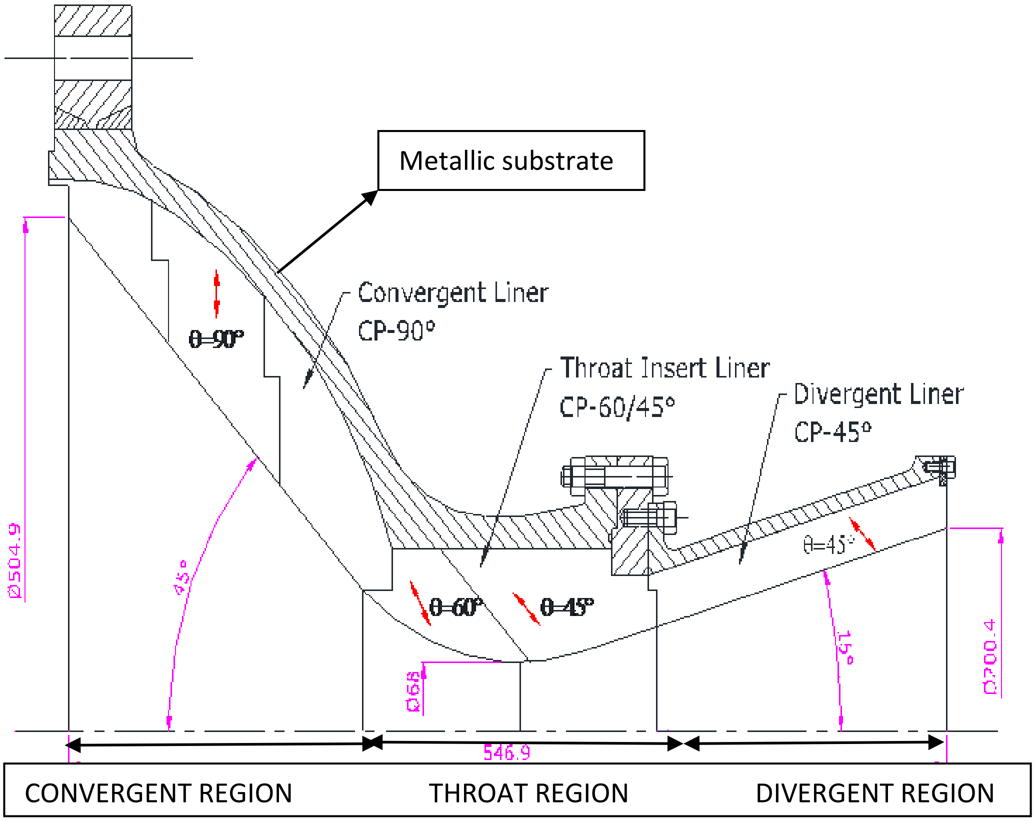


Figure 4.8: Test simulation motor nozzle showing different ply orientations

Figure 4.8 shows a typical convergent divergent test simulation motor nozzle showing the different ply orientations. Different types of ply orientation were experimented at different regions of the nozzle. Figure 4.9 explains the concept of ply angle (θ) with respect to the nozzle flow direction. Figure 4.10 and 4.11 explains the concept of ply orientation parallel to the flow (θ=0°) and ply orientation perpendicular to the flow (θ=90°) respectively to the direction of flow in a rocket motor nozzle.

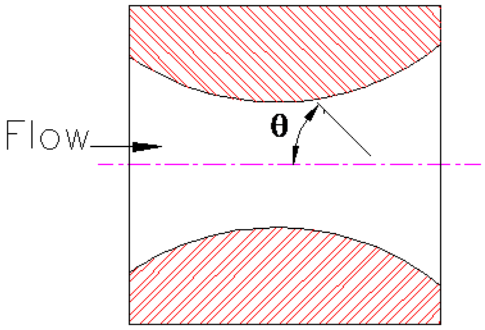


Figure 4.9: Ablative liner with ply orientation at an angle θ° to the flow

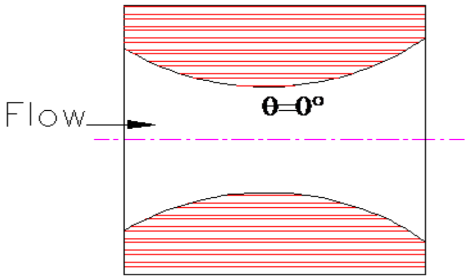


Figure 4.10: Ablative liner with ply orientation at an angle 0° (parallel) to the flow

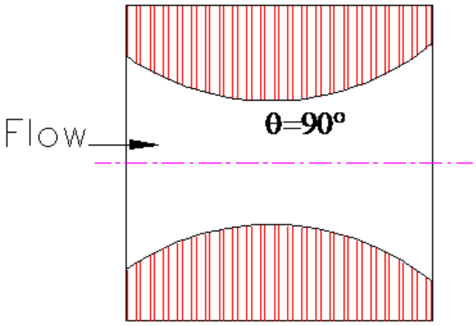


Figure 4.11: Ablative liner with ply orientation at an angle 90° (perpendicular) to the flow

Fibre architecture refers to the pattern in which the fibres are oriented in a prepreg ply. In a prepreg roll, fibres are aligned in the warp and weft regions as shown in Figure 4.12. There are two methods of cutting the prepreg plies for moulding or tape winding. While cutting the prepreg plies according to the patterns developed, it is obvious that a random combination of warp and fill fibres will be present in any prepreg ply. This may neither be uniform nor be repeatable. However, this type of fabric architecture is widely employed due to its process simplicity and ease of fabrication. So at any longitudinal or radial cross section of an ablative composite product, the number of fibres in the section may vary from place to place. This can possibly lead to variations in mechanical and thermal properties of the composite. Such a possible nonuniformity can lead to unpredictable and inferior performance of the ablative during its service conditions in a nozzle. This factor was chosen for more detailed investigations.

However, in the case of in the second method, the prepreg plies are cut at an angle of 45° to the axis of the fabric as shown in Figure 4.13. In this case the tapes are bias-cut and the tapes are further formed by differential stretching by the operator manually or using a series of taper rollers in the tape winding machine. This type of process calls for high degree of skill on the part of the operator and is more process intensive than the first method. Theoretically, such an arrangement of tape cutting results in more uniform distribution of fibres along the circumference of the cross-section of the product. More uniform fibre distribution can lead to uniform and improved properties and performance. Hence, this promising aspect was chosen for detailed experiments and evaluation.

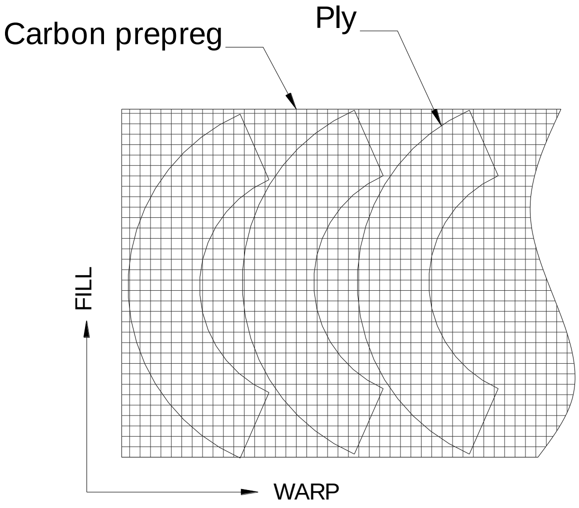


Figure 4.12: Carbon and Silica fabric architecture showing warp and weft fibres and plies cut as per the patterns required

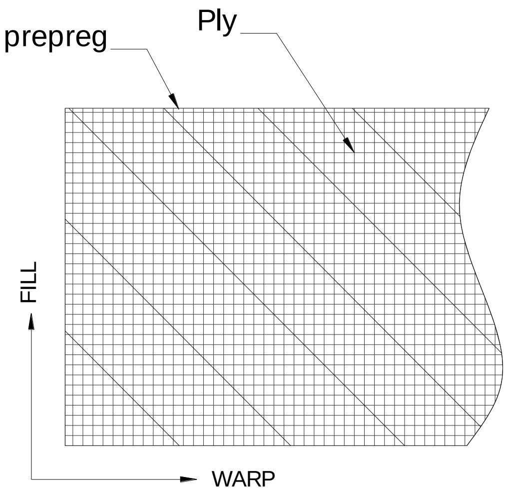


Figure 4.13: Carbon and Silica fabric architecture showing warp and weft fibres and plies cut at an angle of 45° to the edge of the fabric

Figure 4.14 depicts the fibre architecture in a plane of the ablative liner from the aft end during winding pattern cut tapes. It is evident that in a single prepreg ply, the distribution of fibres in the warp and fill directions vary from section to section. In a typical ablative liner, three such individual plies are used to complete one circumference forming a plane. Thus in any plane, it is observed that a random pattern of warp and fill combination can exist. Similarly, when many such layers are building up to complete the liner layup, more nonuniformity along the height of the liner can naturally be expected. This concept was selected for further studies.

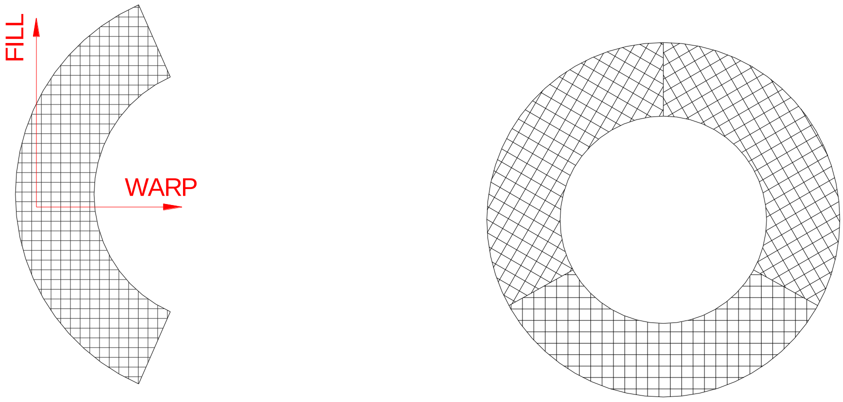


Figure 4.14: Fibre architecture in a plane of the ablative liner during winding pattern cut tapes

In figure 4.15, where plies are cut at 45° to the edge of the fabric, a sort of quasi-isotropic pattern exist around the circumference. To investigate whether such a pattern leads to a more uniform and improved set of mechanical properties more experiments were planned.

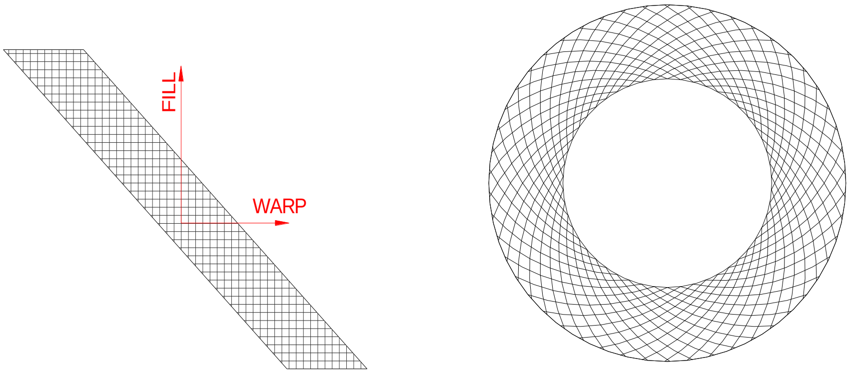


Figure 4.15: Fibre architecture in a plane of the ablative liner during winding bias-cut tapes

Thus the following two important parameters are selected for further in-depth study.

1. Direction of orientation of the fibres of the prepreg (ply orientation) to the direction of hot gas fow in a nozzle (or the nozzle axis) and
2. Fibre architecture i.e., pattern of fibre alignment and distribution within the ablative at a given cross-section-
    a. Normal stacked pattern-where fibres are aligned at random across the circumference
    b. Fibres aligned uniformly across the circumference; this is achieved by ply cutting at a biased angle of 45° and differential stretching of the ply to form the tape.

4.6 Curing (polymerisation) of the prepreg layup

The prepreg which is moulded on the mandrel is to be cured to achieve the mechanical and thermal properties of the ablative. This was achieved by controlled chemical reactions in a vessel under temperature, pressure and vacuum. The liner was enclosed in a rubber bag and is placed in a reaction vessel called hydroclave. Vacuum lines were connected to this impermeable bag to suck out the volatile matter evolved during the condensation polymerisation reaction of the phenolic resin. Water was used as the pressurization medium in a hydroclave.

Figure 4.16 shows a schematic of the wound prepreg with bleeder, breather and vacuum bag assembled for curing. Sealant was used to ensure positive sealing at all the interfaces. Vacuum hoses were connected to the prepreg assembly through leak-tight vacuum ports which communicate through a vacuum manifold to a vacuum suction pump.

The prepreg was wound over a mandrel and was covered with 7 layers of bleeder and breather materials. The function of the bleeder material is to absorb the excess resin in the prepreg which is squeezed out during the polymerisation process due to pressure application. The breather material allows the evolving volatile matter to escape freely to the vacuum suction lines. Entrapment of volatiles during curing can lead to defects like delaminations in the product.

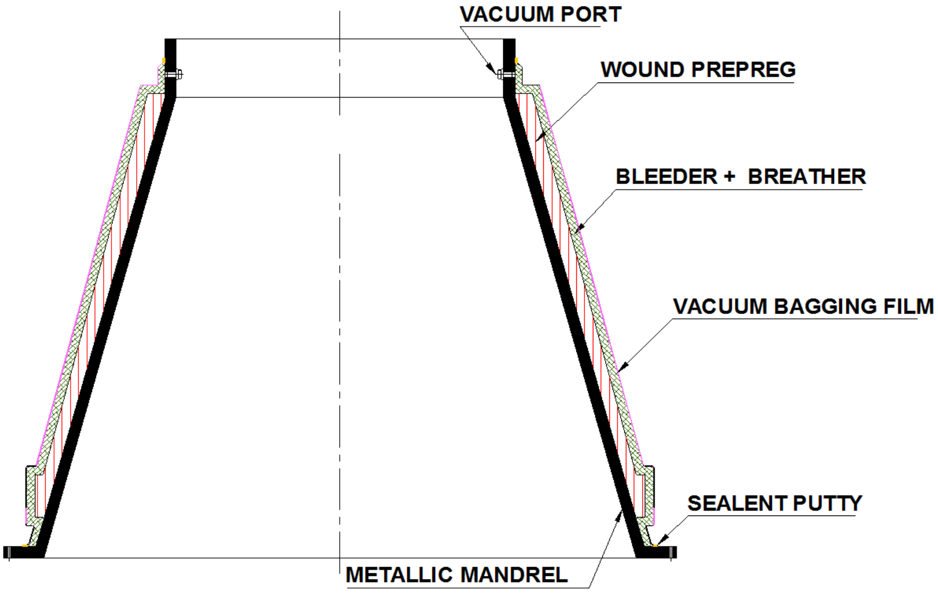


Figure 4.16: Schematic showing the wound prepreg with curing accessories

Figure 4.17 shows the curing set up inside the hydroclave. The product with the bleeder, breather, vacuum bag and vacuum hoses were placed in the pressure vessel. Vacuum hoses were connected through a resin trap to a high capacity vacuum pump. Separate heating, cooling and circulation circuits are operational for water inside the hydroclave. Heating of water was achieved through hot thermic oil circulated through pipes inside the hydroclave. Pressurisation of water was done through circulation pumps. The product can be heated upto 200°C and can be pressurized upto 70 bar pressure in a hydroclave. Cooling water circulation lines in the vessel ensure controlled cooling of the product during the cooling phase.

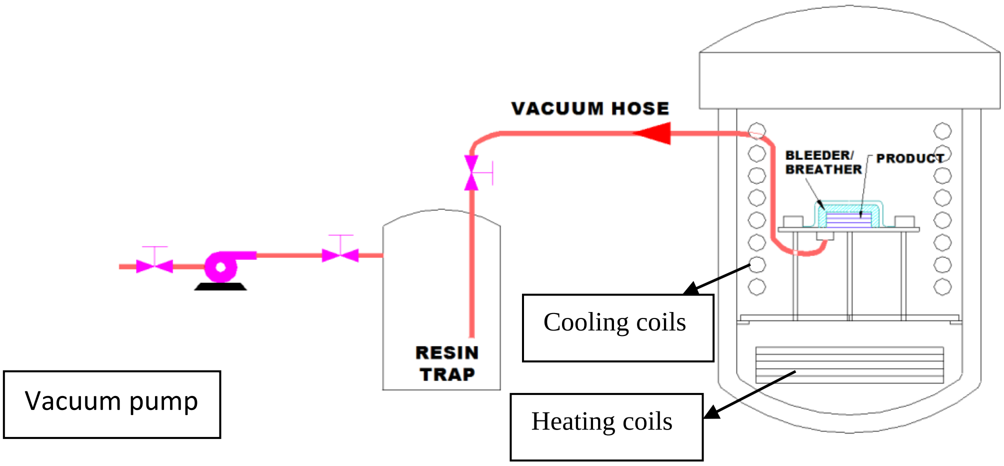


Figure 4.17: Curing setup for an ablative liner in a hydroclave

The curing cycle followed included a heating regime with simultaneous pressure application. After reaching the final cure temperature, it was soaked for 3 hours to ensure the completion of uniform curing. After soaking depressurization and cooling was done. During the entire curing cycle, vacuum lines were connected to the product to ensure that all the evolved volatile matter was removed efficiently to avoid entrapped volatiles leading to delaminations. The typical cure cycle followed for curing a standard ablative nozzle liner is shown in Figure 4.18.

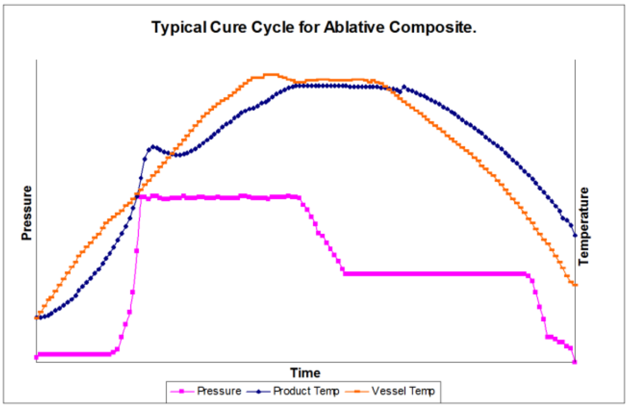


Figure 4.18: Typical curing cycle for an ablative liner in a hydroclave

The major process parameters monitored during the curing stage are

1. Curing temperature
2. Curing pressure
3. Heating rate and cooling rate
4. Vacuum levels
5. Soaking temperature and duration

Of these parameters, the curing temperature and curing pressure is considered as the most important and decisive parameters. The properties are expected to be dictated by the cure temperature and pressure. The degree of completion of reaction is directly related to the cure temperature while the cure pressure has a bearing on the level of consolidation and densification of the final product. Heating rate and cooling rate are also important from the quality point of view. A rapid heating cycle may lead to the building up of thermal stresses in the product leading to delaminations. Similarly a quicker cooling cycle may not allow all the stresses to get relieved. However, these are not found to be very sensitive from the property point of view for further evaluation. A heating rate of 4 to 10°C per hour is generally employed. Higher heating rates are allowed initially till around 85°C per hour, and then it is limited to around 7°C per hour till the maximum pressure application. Maximum pressure was applied around 115°C and rate of heating was kept around 4°C per hour. After the maximum pressure is applied, the liner is heated to the soaking temperature of 155°C, after which it was cooled gradually. Initially a low cooling rate of 4°C per hour was employed till around 130°C. Thereafter, a higher cooling rate of 7°C per hour was allowed till 90°C. Then, a higher cooling was allowed till ambient temperature.

The maximum temperature of curing which is also the soaking temperature is determined by the chemistry of the phenolic resin. Once the resin is chosen, the maximum cure temperature and the soaking temperature are determined. The soaking duration largely depends on the size of the product. A soaking duration of 3 hours is given for standard products. Hence, the cure temperature and cure pressure were chosen for sensitivity studies for this stage of processing.

Once the curing is completed the ablative product is fully processed. What remain are secondary operations like machining which is done to obtain the desired size, shape and configuration of the product. Machining is also a very critical operation in the realization cycle of an ablative. Unlike conventional metallic machining where material removal is in the form of chips, material removal is in the form of fine powder for composites. So, coolants cannot be used. Dust collection suction systems are used to collect the powder which also acts as a cooling mechanism for the tool. Poly crystalline Diamond (PCD) tools were used to machine the ablatives to make specimens for property evaluation. Since standard cutting parameters are available for feed, speed and depth of cut for ablative machining, further investigations were not planned. However, it was observed that the direction of cutting is very important for specimen preparation. Machining against the layup direction itself had led to the initiation of delaminations. As the mechanical and thermal properties are highly sensitive to the orientation, dimensional tolerances and geometric requirements, sufficient care was taken for machining the cured composite and for specimen preparation. Though effect of coolants as well as of contaminants like oil was attempted, the same was discontinued as there was no significant quantifiable degradation is properties and performance. Some studies on the thermal aspects during machining of ablatives have already been reported [85-87]. Hence, further investigations were not pursued.

4.7 Effect of temperature and time

An effort was also made to study the effect of temperature on the critical properties of ablatives. Since the phenolic resin plays an important role in the performance of the composite, properties were likely to be affected by the effect of heat on the composite. To study this, evaluation of properties at ambient temperature and at different higher temperatures is essential. Hence, the dependence of properties on temperature was investigated.

In some instances, the ablative composite may not be put into the service conditions as soon as it is processed. An idea about the possible deterioration of properties, if any, with the passage of time shall provide valuable insight for quality and reliability assessment. Hence, some ageing studies were initiated to understand how the mechanical properties vary with the passage of time for specimens stored under standard conditions. For this specimens prepared for the investigations were labeled and stored properly. Evaluation was repeated every six months.

After conducting a detailed study on the processing aspects of ablatives and a detailed characterization study on the reinforcements, resins and prepreg, the critical parameters were identified and earmarked for further investigations. The details of the investigative studies done on these selected parameters are explained in the next chapter.

CHAPTER 5

SENSITIVITY STUDIES ON THE CRITICAL PARAMETERS AFFECTING THE ABLATIVE PERFORMANCE

After a detailed study of the raw materials and the process sequence for realizing ablative composite products, the following critical parameters were selected for further in depth investigations.

5.1 Parameters selected for sensitivity studies

1. Constituent raw materials
    - 1.1 Reinforcements
        - 1.1.1 Carbon Fabric
            - Carbon content
            - Sodium content
            - Tensile breaking strength
        - 1.1.2 Silica Fabric
            - Tensile breaking strength
    - 1.2 Matrix Resins
        - Viscosity
        - Degree of advancement (point of trouble)
        - Solid content
        - Specific gravity
        - Phenol and formalin content
2. Prepreg parameters- Resin content (%)
3. Fabric ply orientation to the direction of flow
4. Fibre architecture in the ply; fibre alignment and distribution
5. Cure temperature
6. Cure pressure
7. Effect of temperature on properties
8. Effect of ageing on properties

Having selected the critical process and raw material parameters, the important thermal and mechanical properties which directly affect the functional performance of an ablative composite were enlisted. For studying critically each parameter, the other parameters were kept constant at a standard range.

5.2 Properties evaluated for the studies

1. Density or specific gravity: Density is the fundamental property of any composite. This gives an indication of the process quality and shall serve as a basic check point for reference. Though density may not be a very crucial property from the functional point of view, it serves as a base reference for comparison. The values of density ensure that the process followed by and large results in the production of a composite with the normal levels of compaction and consolidation. Basically, all mechanical properties are directly linked to the compaction of the composite during processing. Hence, density was selected as the basic reference for comparison.

2. Interlaminar Shear Strength (ILSS): Among the mechanical properties, ILSS is the most critical property for this type of composites. In most cases, the predominant failure mode is by shear in the interlaminar region between two plies of the ablative composite as this is the weakest. Several failures, especially in the throat region have been observed due to failure in interlaminar shear. Hence, this critical property was selected for comparison.

Tensile loads are not significant during the service conditions of ablative composites as these are predominantly under pressure and compressive loads due to the high temperature, high pressure gas flows through the internal surfaces of the rocket nozzles and the external surfaces of the reentry vehicles. So, compressive strength and compressive modulus has been evaluated for comparison.

3. Compressive Strength (CS) (along the ply direction and across the ply direction): The ablative composites, during the functional operation, are subjected to internal compressive loads by the pressure of the hot gas flowing through the

nozzles. Hence, this is an important functional requirement for ablatives. There is a significant difference in the strength along the ply and across the ply directions. Hence, evaluation was done using specimens made in both the directions.

4. Compressive Modulus (CM) (along the ply direction and across the ply direction): The stiffness properties assume great significance in critical launch vehicle components like throat inserts where a predominant failure mode is due to lack of stiffness in the compression mode. Here also, evaluation was done in both the ply directions to understand the difference in the behavior.

5. Heat of ablation is the most defining property of the ablative. It is the amount of hear required to ablate unit mass of the composite. Hence, it serves as a real yardstick for comparison. This cardinal property was evaluated for all the comparison studies.

6. Specific heat is a basic thermal property which defines the thermal behaviour of any material. This property was also evaluated for comparison in the perturbation studies.

7. Thermal conductivity (along the ply direction and across the ply direction) is a direction sensitive property and hence was evaluated in both along the ply and across the ply directions. It determines the heat transfer characteristics of the material and hence was chosen for comparison studies.

8. Erosion rate (along the ply direction and across the ply direction) is the most important functional characteristic of the ablative composite as it denotes the rate at which the material erodes when subjected to the service conditions. This also being a direction dependent property was evaluated in both along the ply and across the ply directions.

The studies were broadly divided in two phases. In the first phase, laminates were synthesized with carbon phenolic and silica phenolic ablative materials. A standard process for fabrication of ablative laminate was followed in which the chosen parameter for the perturbation studies alone was varied in a controlled manner by keeping all other parameters constant. Composite laminates were used for the sensitivity studies of the following parameters.

a) Raw material parameters in carbon and silica reinforcements (like carbon content, sodium content, breaking strength)

b) Properties of the matrix phenolic resin

c) Wet resin content (WRC) in the CP and SP prepreg

d) Cure temperature

e) Cure pressure

The parameters which can be varied and studied effectively in the laminate level were studied in the laminate level itself and those parameters which can be simulated only in the full liner level were studied by making ablative liners. Processing of ablative liners was more involved in terms of time, cost and effort. Hence, only the most essential parameters only were studied at the liner level. In this case, specimens were prepared from ablative liners processed on metallic mandrels and cured in a hydroclave. For the sensitivity studies of the following parameters, this approach was used.

a) Fabric ply orientation to the direction of flow

b) Fibre architecture in the ply - fibre alignment and distribution

The other two selected parameters

a) Effect of temperature on properties and

b) Effect of ageing on properties

which were not related to the route in which the ablative composite was processed were studied on the specimens made both in the ablative laminate route and in the ablative liner route. For studying the effect of temperature on the properties of ablatives, specimens were subjected to different temperatures and the effect of temperature on properties was studied. Similarly, a set of specimens from each laminate and liner was set aside initially and was kept under controlled storage conditions. Periodically, specimens were drawn from this stock every six months and were evaluated for the same properties.

5.3 Processing of the laminates

Two different types of laminates were processed, one with carbon fabric and the second one with silica fabric as the reinforcement material. Phenolic resin was the matrix material for both types of laminates. The basic process for both types of laminates was similar except for the number of layers of each type of laminate and the curing cycle. These differences were necessitated by the difference in thickness of the carbon and silica fabrics and due to the difference in thermal conductivity of the two fibres. The thickness of each carbon phenolic prepreg ply is approximately 0.35 to 0.40 mm while the corresponding thickness of silica phenolic prepreg ply is approximately 0.65 to 0.70 mm. Since, laminates of the same thickness of approximately 40 mm were to be made, the number of plies used to process each laminate was varied. 100 plies were used for carbon phenolic laminates while 60 plies were used for silica phenolic laminates. Similarly, since carbon fibres are better conductors than silica fibres, carbon phenolic laminate processing can have a faster heating and cooling rate than corresponding silica phenolic laminates.

The fabric was impregnated using phenolic resin with the following properties.

1. Specific gravity : 1.14
2. Viscosity : 240 cP
3. Degree of advancement (point of trouble): 7.8 ml of water
4. Total solid content: 63%
5. Free phenol content: 4.5%
6. Free formalin content: 2%

After impregnation, the volatile content was maintained between 5 to 7% and the wet resin content is maintained between 40 to 50%. The degree of advancement of the resin in the prepreg, (CI) was maintained between 23 to 27 ml of water so as to ensure easy flow of resin and good processablity. The impregnated prepreg was stored at 4°C till it was taken out for cutting the plies. This was essential to ensure that the resin in the prepreg does not advance to a level of solidification. The prepreg was made in long rolls of approximately 50 m length and 1 m width. Figure 5.1 shows the realized carbon phenolic prepreg. Polythene sheets were used as a release agent while rolling the prepreg into rolls. Figure 5.2 shows the silica phenolic prepreg which was realized for preparing the laminates.

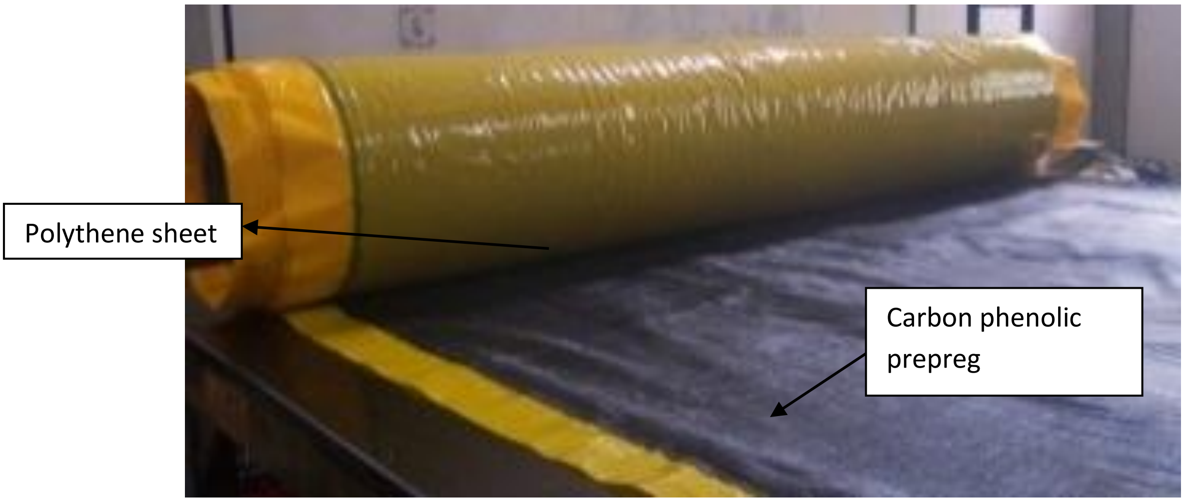


Figure 5.1: Carbon phenolic prepreg

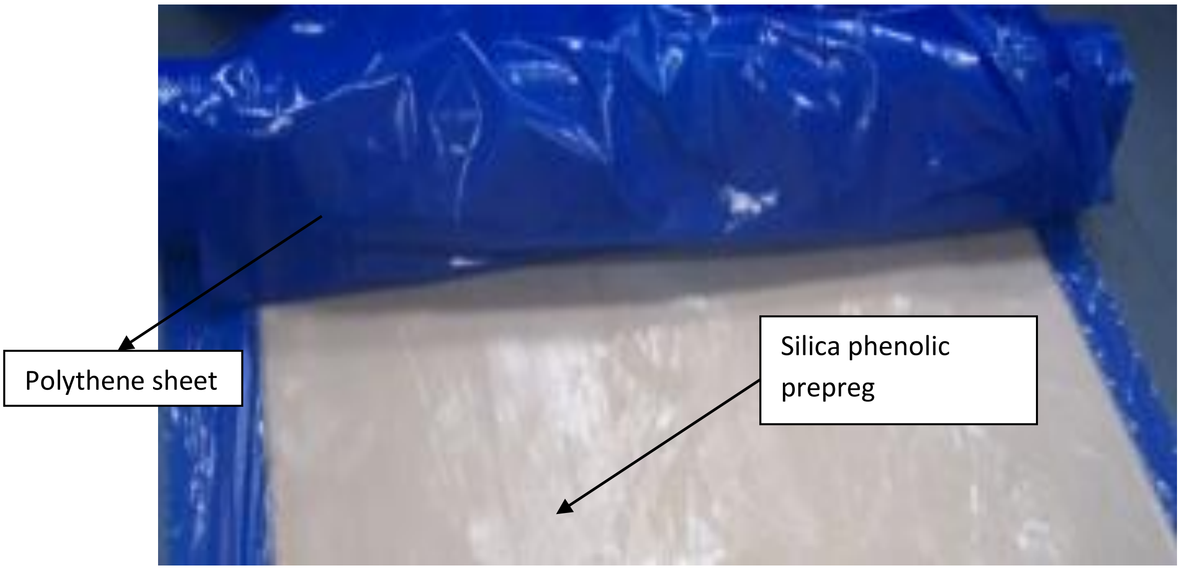


Figure 5.2: Silica phenolic prepreg

The roll was unrolled and placed on a clean work table and plies of 500 mm length and 400 mm width were cut using a metallic template. Figure 5.3 shows a schematic showing how the plies were cut from a prepreg roll using a template. The dimensions were measured and confirmed.

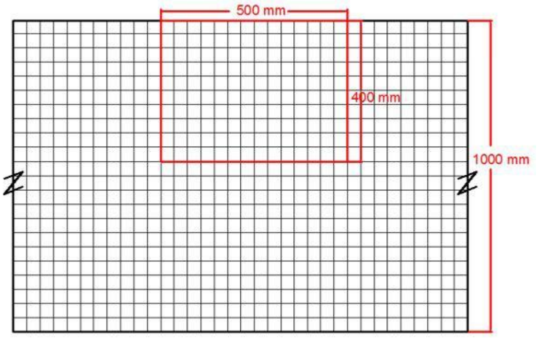


Figure 5.3: Schematic indicating cutting of plies from the prepreg roll

5.3.1 Processing of carbon phenolic laminates

100 plies each of approximately 0.35 to 0.40 mm thickness were made and stacked one on top of another to build a wet laminate of 38 to 40 mm thickness. Adequate care was taken to ensure that the edges were aligned perfectly. Irregular edges in the laminae can lead to nonuniform resin accumulation at the edges eventually causing quality problems. After laying up each lamina, a soft roller was manually used to squeeze out the entrapped air and to achieve good uniform compaction and consolidation in the wet layup condition. Release films, bleeder and breather materials were positioned on both sides of the laminates and the wet layup was completed.

After completing the layup, the laminate was loaded in a 250Ton (T) hydraulic press with pressure application and heating facilities (Figure 5.4). The press had provisions to measure the temperature of the platens as well as the temperature of the product laminate through ‘K’ type thermocouples embedded in the middle of the laminate. The top and bottom platens had heating facilities for controlled heat input. Pressure was applied hydraulically and the load on the laminate was closely controlled so that the pressure acting on the laminate can be precisely varied, controlled and recorded. Load was applied on the laminate gradually with simultaneous heating of the platens at the following heating rate.

Figure 5.4 Hydraulic Press setup for curing of laminates.

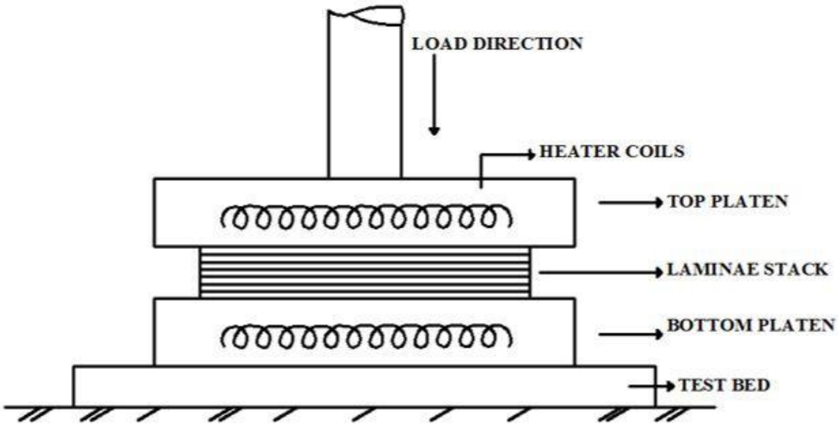


Figure 5.5 Schematic showing the curing setup.

Figure 5.5 shows the schematic representation of how the prepreg stacked into a laminate is positioned between the top and the bottom platens of the hydraulic press. Both the platens were equipped with heater coils which heats the laminate during the curing. The heating cycle was firmed up considering different heating rates in four different regimes as follows:

- 12°C/hour from ambient condition to 70°C
- 10°C/hour from 70°C to 100°C
- 8°C/hour from 100°C to 140°C
- 6°C/hour from 140°C to 155°C

Initially, a higher heating rate of 12°C/hour was applied as there are little volatiles generated in this phase of curing till about 70°C. As temperature increases beyond 70°C, the generation of volatile matter like water vapour, carbon dioxide and carbon monoxide begins. Hence the rate of heating was reduced to 10°C/hour so that enough time was available for the escape of volatile matter. This rate of heating was continued till 100°C. Beyond 100°C, when the rate of the reaction and the consequently the rate of evolution of volatiles further increased, the heating rate was further reduced to 8°C/hour so that more effective removal of volatile matter was ensured. This was the most critical phase in the curing of the ablative laminate since the maximum pressure application was planned around 115°C. Maximum pressure application temperature was very crucial since early application of pressure could lead to squeezing out of the entire resin; and if the pressure was applied late, there shall not be any effect on the consolidation of the laminate since the resin would have already attained a gelled state. The rate of heating was continued till around 140°C. The maximum cure temperature of this phenolic resin as specified by the manufacturer is 155°C. So a heating rate of 6°C/hour was maintained from 140°C to 155°C.

The load was simultaneously applied on the laminate in steps with the rise in product temperature. Initially, a nominal load of 8T was applied on the laminate to start with. It was gradually increased with temperature. Table 5.1 shows the temperature-load cycle applied for curing the ablative laminate till the maximum load application point of 115°C. Thereafter, the load was maintained constant at 133T and heating was continued till 155°C at a heating rate of 6°C/hour.

At 155°C, the product laminate was soaked for 3 hours to enable uniform and complete curing of the ablative laminate. The soaking ensured that the polymerisation reaction was completed all through the thickness of the laminate uniformly.

Table 5.1: Temperature-load application chart for curing of carbon phenolic laminates in heating cycle

Temperature(°C)	Load(T)		Temperature(°C)	Load(T)
30	8		94	41
40	8		95	43
50	8		96	45
60	8		97	47
70	8		98	49
71	9		99	51
74	10		100	53
76	10		101	57
79	11		102	61
81	14		103	65
82	16		104	69
83	18		105	73
84	20		106	78
85	22		107	82
86	24		108	86
87	27		109	90
88	29		110	94
89	31		111	100
90	33		112	106
91	35		113	112
92	37		114	125
93	39		115	133

After soaking, the following cooling cycle was followed:

- 6°C/hour from 155°C to 140°C
- 8°C/hour from 140°C to 100°C
- 10°C/hour from 100°C to 70°C
- Beyond 70°C, heating is discontinued and the laminate is allowed to cool naturally to ambient temperature.

The temperature-load cycle followed for the cooling cycle was as follows. The load of 133T which was maintained during soaking is held constant till around 125°C. Then the load is reduced in steps gradually so that the effective pressure on the laminate is reduced.

Table 5.2: Temperature-load application chart for curing of carbon phenolic laminates in cooling cycle

Temperature(°C)	Load(T)		Temperature(°C)	Load(T)
125	133		106	78
124	131		105	74
123	129		104	70
122	127		103	67
121	125		102	63
120	122		101	60
119	119		100	56
118	116		99	53
117	113		98	49
116	110		97	45
115	107		96	42
114	104		95	38
113	101		94	35
112	98		93	31
111	95		92	28
110	92		91	24
109	88		90	20
108	85		89	16
107	81		88	12

Beyond 88°C, the load was reduced to zero and is allowed to cool naturally in ambient air till room temperature. After processing the laminate, it is taken out of the hydraulic press and the dimensions of the laminate were measured.

- Height of the laminate before curing: 38 to 40 mm
- No of laminae used: 100
- Height of laminate after curing: 30 mm

The edges were trimmed using a circular band saw and the surface was polished with an emery paper to remove the accumulated excess resin. This was done as a pre-requisite for nondestructive evaluation.

Figure 5.6: Carbon phenolic laminates after processing and trimming of edges.

5.3.2 Processing of silica phenolic laminates

The silica phenolic laminate was also processed in a similar route but with some obvious changes due to the difference in individual thickness of plies as well as the thermal behavior of the constituent fibres. The silica phenolic prepreg was unrolled and placed on a clean work table and plies were cut using a metallic template. The dimensions were measured and confirmed. 60 plies each of approximately 0.70 mm thickness were made and stacked one on top of another to build a wet laminate of 40 to 42 mm thickness.

Since silica phenolic has lesser conductivity than carbon phenolic, minor modifications were done in the heating and cooling cycles. A slower heating cycle was necessary for silica phenolic laminate processing to ensure that all parts of the laminate reach the uniform temperature and complete cure is ensured for the composite. To avoid undesirable thermal stresses during the cooling regime, the cooling cycle was also deliberately made slower than that of the carbon phenolic. The same pressure application pattern was followed for both laminates. The heating cycle followed was as follows:

- 10°C/hour from ambient condition to 70°C
- 8°C/hour from 70°C to 100°C
- 6°C /hour from 100°C to 140°C
- 4°C/hour from 140°C to 155°C

Initially, a heating rate of 10°C/hour was applied for this laminate as compared to 12°C/hour given for the CP laminate. Very little volatiles were generated in this phase of curing till about 70°C. As temperature increases beyond 70°C, the rate of heating is reduced to 8°C/hour and this rate of heating is continued till 100°C. Beyond 100°C, more volatile evolution occurs and hence the heating rate is further reduced to 6°C/hour so that more effective removal of volatile matter is ensured. This is the most critical phase in the curing of the ablative laminate since the maximum pressure application is planned around 115°C. The maximum pressure application is done around this temperature and hence this is a very crucial phase in the processing. The rate of heating at 6°C/hour was continued till around 140°C and thereafter the laminate was heated at 4°C/hour till the maximum cure temperature of 155°C was attained.

The load is simultaneously applied on the laminate in steps with the rise in product temperature in the same pattern as was done for the CP laminates as shown in Table 5.1. The compaction started with 8T load and was gradually increased with temperature till the temperature in the laminate reached the maximum load application point of 115°C. Thereafter, the load was maintained constant at 133T and heating is continued till 155°C at a rate of 4°C/hour. In order to ensure the complete and uniform polymerisation in the laminate, soaking was done at 155°C for 3 hours.

After soaking, the following cooling cycle was followed:

- 4°C/hour from 155°C to 140°C
- 6°C /hour from 140°C to 100°C
- 8°C/hour from 100°C to 70°C
- Beyond 70°C, heating is discontinued and the laminate is allowed to cool naturally to ambient temperature.

The temperature-load cycle shown in Table 5.2 was followed for the cooling cycle of silica phenolic laminates also. The load of 133T which was maintained during soaking is held constant till around 125°C. Then the load is reduced in steps gradually so that the effective pressure on the laminate is reduced. Once sufficient consolidation and rigidisation of the laminate happens during polymerisation, the load was reduced.

Beyond 88°C, the load was reduced to zero and is allowed to cool naturally in ambient air till room temperature. After processing the laminate, it is taken out of the hydraulic press and the dimensions of the laminate were measured.

- Height of the laminate before curing: 40 to 42 mm
- No of laminae used: 60
- Height of laminate after curing: 31 to 32 mm

The edges were trimmed using a circular band saw and the surface was polished with an emery paper to remove the accumulated excess resin and to enable smooth and error-free nondestructive evaluation. The photos of the silica phenolic laminates in the as moulded condition and after the trimming and polishing stage are shown in Figure 5.7.

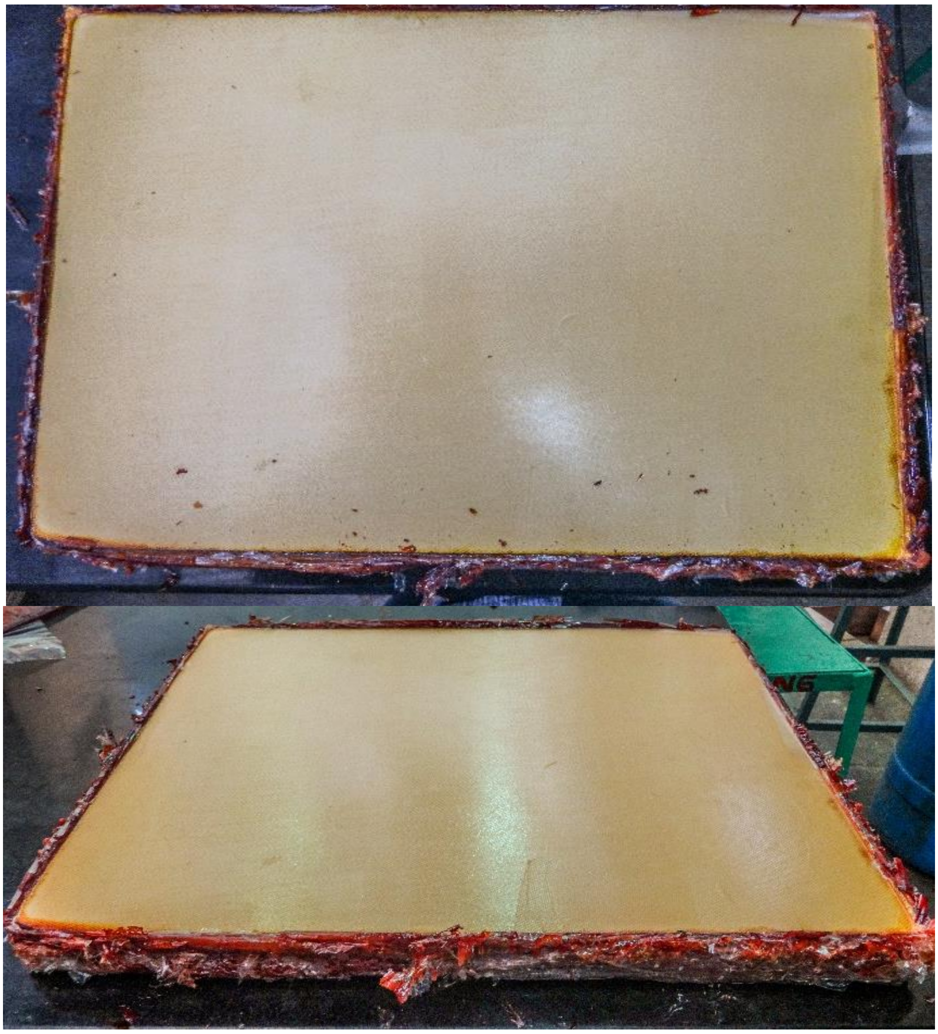


Figure 5.7: Silica phenolic laminate after processing and trimming of edges.

5.4 Nondestructive examination of the laminates

The laminate was inspected visually for any defects like cracks, edge deformations, open delaminations, lack of material, protrusions, porous regions, foreign particle inclusions and colour changes. Alcohol wipe test (AWT) was performed on the laminate after the visual inspection. A flint free cloth soaked in laboratory grade ethyl alcohol was used to wipe the surfaces of the laminate. The evaporation pattern of the surface was closely watched. In areas where defects like delaminations, porosity and other surface defects are present, the alcohol takes more time to evaporate. In this case, there were no defects observed. Tap test using a plastic mallet was also carried out over the entire surface of the laminate to rule out the possibility of any internal defects.

After confirming that there are no visual defects, the laminate was subjected to ultrasonic inspection. Very short ultrasonic pulse-waves with frequencies ranging from 0.1-15 MHz were transmitted into materials to detect internal flaws or to characterize materials. Two different methods of ultrasonic inspection were used for checking the integrity of the laminates.

1. Pulse-echo mode

2. Through transmission (attenuation) mode

The flaw detector used was a DRYSCAN 410D equipment.

Figure 5.8: Signal pattern on a DRYSCAN 410 D Ultrasonic flaw detector

A 24 mm diameter test probe was used to scan the entire surface of the laminate. Transmission-Reception mode with the following parameters was used for testing.

Velocity = 3000 m/s

Gain = 65 to 75 db

Frequency = 1 MHz

After setting the above parameters in the detector, the transmission and receiver probes were positioned on the opposite faces of the laminates and minor fine tuning of the parameters were done to get a beat pattern of 100% full screen height (FSH) on the detector screen as shown in Figure 5.8 . A threshold value of 20% of FSH was set for defect detection and the equipment would give an alarm as the signal falls below this threshold limit. A calibration standard specimen with delaminations was used to identify defective laminate signals.

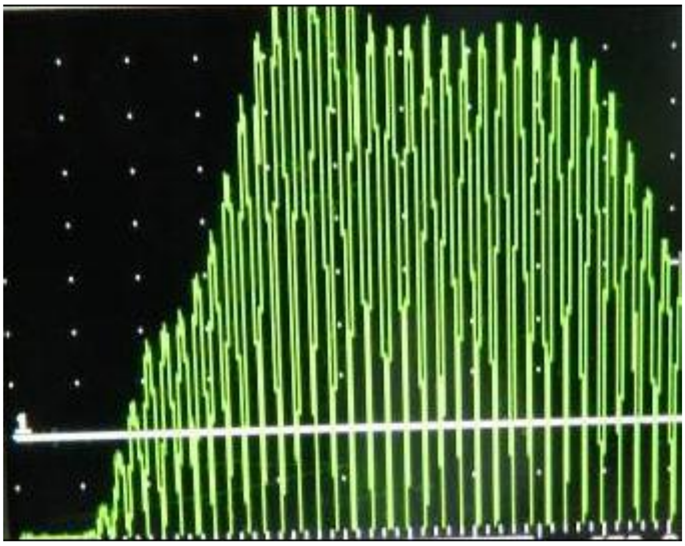


Figure 5.9: Normal signal pattern of laminates

In laminates without any defects a normal signal pattern as shown in Figure 5.9 was observed. In laminates where defects like delaminations were present, a signal pattern shown in Figure 5.10 was observed. Here there was a significant drop in the amplitude of the signal. Such laminates were not used for property evaluation.

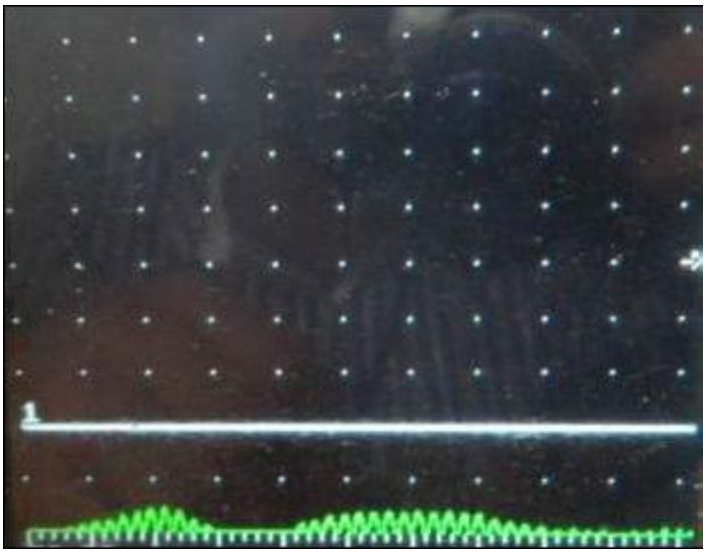


Figure 5.10 Signal pattern of laminates with defects

The laminate was subjected to 100% ultrasonic inspection. After confirming that there are no defects in the laminate during processing, the laminate was cut using a circular band saw for preparation of specimens.

5.5 Fabrication of specimens and characterization techniques

From the laminate, long rectangular blocks were initially cut using the circular band saw. These blocks were machined to the required dimensions in a milling machine or a turning lathe depending on the size and shape. A vacuum suction device was used as the dust collector to remove the carbon phenolic dust generated during the machining. A PCD tool was used for turning operations.

a) Density evaluation

Density is a fundamental property of the composite which gives a primary idea about the compactness, porosity and completeness of curing. From the rectangular blocks cut from the laminate, 25mm cubes were cut for evaluation of density. Density was evaluated as per ASTM D792-13 standard. Since the material had some inherent porosity, calculation of density by measuring the mass and volume can lead to errors. Hence, Archimedes principle was used to evaluate the density. The composite sample was first weighed in air in an analytical balance of accuracy 0.001g. The sample was then suspended by means of a weightless string from the hook in the balance. The 500 ml beaker filled with distilled water to sufficient height was placed on the platform kept over the pan. The sample was freely suspended in water, immersed fully without touching the sides of the beaker. The weight of the sample in water was taken. Density was evaluated for five specimens and consistent values were obtained.

b) Interlaminar shear strength (ILSS)

ILSS is the most critical functional property of ablative composites. It denotes the resistance to shearing at the interlaminar surfaces between two adjacent plies. Generally, ILSS is measured by 3 point bending test or double shear test. For ablative composites, double shear test is widely used.

Specimens of size 20 mm long, 9 mm wide and 5 mm thick were cut from the laminates. The direction of the plies in the specimen is shown in Figure 5.11.

The dimensions of the specimens were measured using a vernier caliper and pairs of specimens were selected to ensure uniform loading.

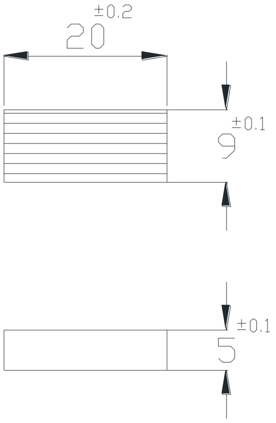


Figure 5.11: Interlaminar shear strength specimen

Two specimens of identical dimensions were placed in the fixture shown in Figure 5.12 below and subjected to shear between the two adjacent layers. The specimens were placed in the fixture in such a way that the layers are parallel to the direction of the piston displacement. The specimens with the fixture were loaded in an UTM and the ram speed was maintained 1mm/minute. The load was transmitted through the piston to the specimens. Specimen was loaded till failure. The design of the fixture ensured that the failure of the specimen occurred due to shear and not because of bending. ILSS was tested for 10 specimens and the strength was calculated.

Figure 5.12: Test setup for the evaluation of interlaminar shear strength

c) Compressive strength evaluation

Compressive strength is another important mechanical property of ablative composites. It is the capacity of the material to resist the change in the reduction of its size due to various compressive loads acting on it. Since the ablative composite has directional properties, compressive strength and compressive modulus is evaluated in both along the ply as well as across the ply directions.

From the rectangular blocks cut from the laminates, 8mm diameter and 16mm long specimens were machined in a centre lathe after ensuring the directions of the plies. After machining, the sample thickness and diameter were measured using a calibrated vernier calipers and the cross sectional area was measured from it. In Figure 5.13, the first specimen shows the plies aligned parallel to the axis of the specimen. The load application in the UTM was also along this axis along the plies. This test gave the compressive strength along the plies. In the second specimen, the plies were aligned perpendicular to the axis of the specimen and the specimen is used to evaluate the compressive strength across the plies of the composite. The specimens were loaded in the compressive strength testing fixture shown in Figure 5.14, in the UTM and loaded axially.

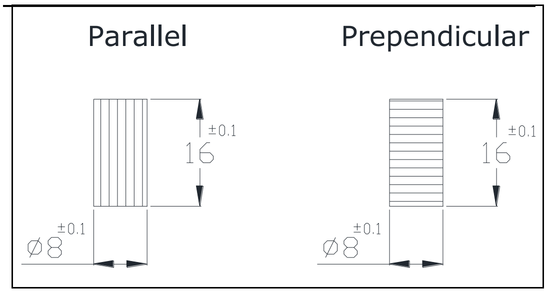


Figure 5.13: Specimens for the evaluation of compressive strength

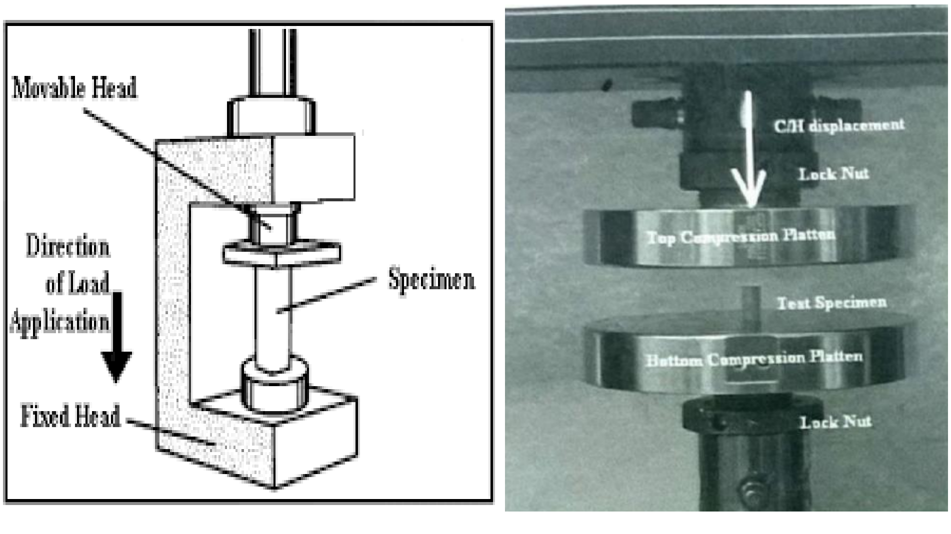


Figure 5.14: Test setup for the evaluation of compressive strength

Figures 5.15 and 5.16 explains the loading pattern on the parallel and perpendicular oriented specimens respectively.

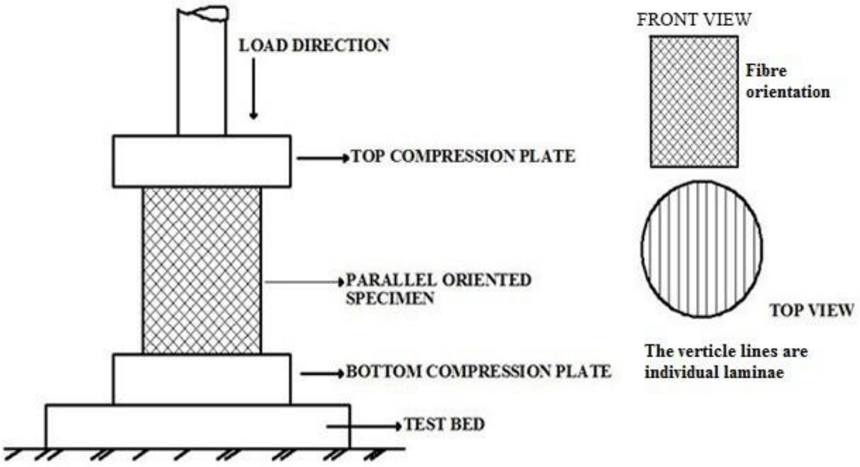


Figure 5.15: Schematic showing the loading pattern for compressive strength (parallel) specimens

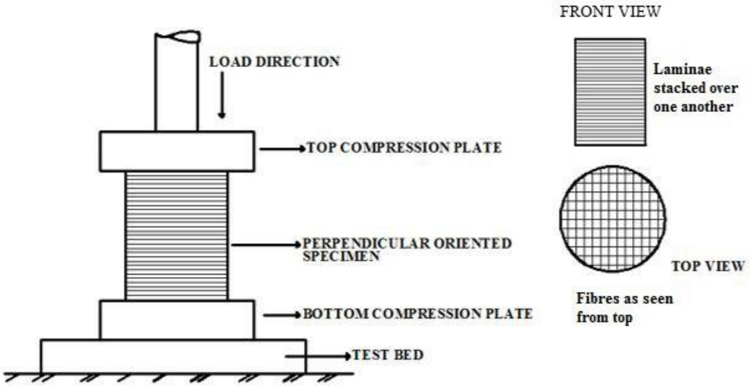


Figure: 5.16 Schematic showing the loading pattern for compressive strength (perpendicular) specimens

Compressive Strength was tested for 10 specimens and the values computed.

d) Compressive modulus evaluation

Similar to the compressive strength, compressive modulus is also sensitive to the ply direction in the specimen. Hence, specimens were made in the parallel as well as the perpendicular directions to the ply directions. The compressive modulus of a material gives the ratio of the compressive stress applied to a material compared to the resulting compression.

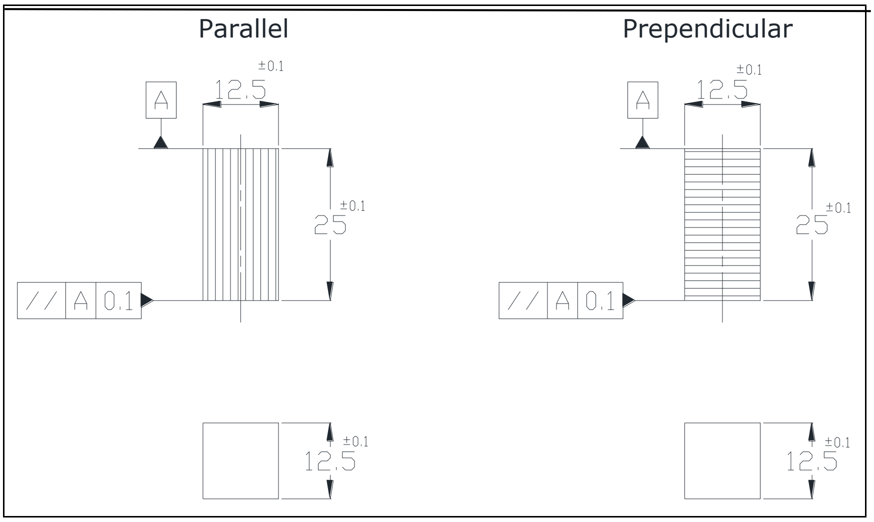


Figure 5.17: Parallel and Perpendicular specimens for the evaluation of compressive modulus

The specimens of size 25mm height x 12.5mm length x 12.5mm width (Figure 5.17) based on ASTM standards were machined and dimensions verified. The cross sectional area of the specimens was computed based on the actual measured dimensions. 5 specimens of each ply orientation were made and tested and the average values are reported.

Compressive modulus was measured by loading a specimen in an UTM on the bottom compression plate. Axial compressive load was applied parallel to the axis of the specimens at a ram speed of 1 mm/min. A strain gauge was used to measure the strain produced in the specimen.

The specimen for compressive modulus was made in a cuboidal configuration to enable the attachment of strain gauges. Ideally a cylindrical specimen would be used to avoid stress concentration effects at the edges. In order the rule out the concerns regarding the stress concentration effects on the specimen due to the cuboidal shape, a few experiments were repeated with video extensometer instead of strain gauge. In these tests, the strain measurement was done by using a video extensometer. A video extensometer is a device that is capable of performing stress/strain measurements by capturing continuous images of the specimen during test, using a frame grabber or a digital video camera attached to a PC. The specimen was marked with special markers using a reflective paint. The extensometer detects these black and white dots and assigns values to them. The pixel distance between these markers in the captured image were constantly tracked in the captured video, while the specimen was undergoing the test. This pixel distance was measured in real time and mapped against a calibration value to give a direct strain measurement, and to control the testing machine in strain control. The cylindrical test specimens used for this test were subjected to an axial compressive load parallel to their axes till failure. The video extensometer was zoomed at the specimen and the markers are set in the software between which the strain measurement was needed. The ram speed was maintained at 1mm/min. The faces of the specimens were ensured to be parallel to each other. It was confirmed that the effect of stress concentration was very negligible in the overall results of the tests. The average of five tests was reported for both the parallel and perpendicular directions.

e) Thermal properties: Heat of ablation and erosion rate

Heat of ablation and rate of erosion are the important thermal properties of any ablative polymer composite. It denotes the amount of heat required to ablate unit mass of the material. Ablation being a sacrificial phenomenon, material is lost from the parent composite during the function of the ablative. This can be due to mechanical erosion due particle impingement, thermal erosion due to the high temperature, pressure and shear forces due to the high velocity hot gases, chemical erosion, vapourisation and evaporation. This is basically measured by estimating the mass loss of the specimen after the test. A plasma arc generator was used to generate the heat flux required for the test. (Figure 5.18)

Specimens of 10 mm diameter and 20 mm length were machined from the laminates for testing the heat of ablation and erosion rates. The specimen was mounted in a specimen holder which is made of the same material as that of the specimen. This was done to avoid differential expansion of the specimen with respect to the specimen holder. The holder was also machined to the same orientation as that to the specimen.

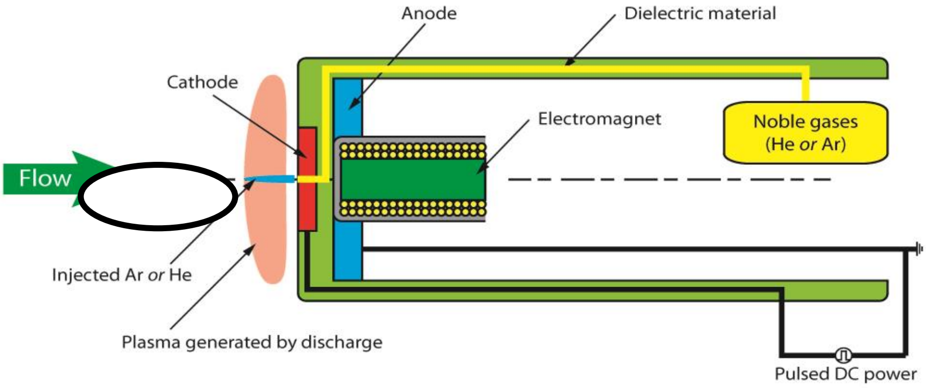


Figure 5.18: Schematic of a Plasma Arc Generator

The specimen was held in front of the nozzle of the arc plasma generator and the distance from the nozzle to the exposed edge of the specimen is calibrated based upon the required heat flux. Argon was used as the inert gas in the enclosure. The heat flux was maintained at 750 W/cm^2 for the test duration of 15 seconds. After the test, the mass of the tested specimen was measured again and the mass loss was calculated.

Heat of ablation = Heat energy applied on the specimen / Mass loss. (5.1)

The depth of the eroded surface is measured and the rate of ablation is given as,

$$\text{Erosion rate} = (L_2 - L_1) / t \tag{5.2}$$

where, L_2= length of the specimen after the test (mm)

L_1 = length of the specimen before the test (mm)&

t= duration of the test (s)

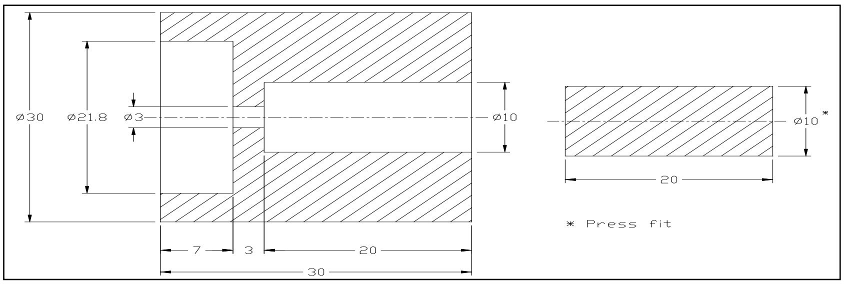


Figure 5.19: Ablation test specimen and the specimen holder

Since heat of ablation is a material property and is not dependent on the direction of the plies, general specimens were used for characterization. But as erosion rate is highly influenced by the direction of the plies, this parameter was evaluated in both along and across the ply directions.

f) Specific heat and thermal conductivity

Specific heat and thermal conductivity are two other important thermal properties of ablative composites. These were evaluated using the Laser Flash Apparatus (Figure 5.20). The specimens were of 15mm diameter and uniform thickness of 2mm (Figure 5.21).

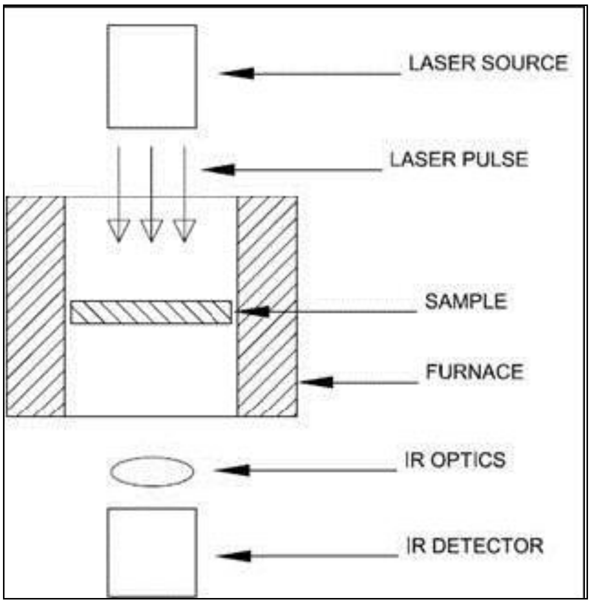


Figure 5.20: Schematic of a Laser Flash Apparatus

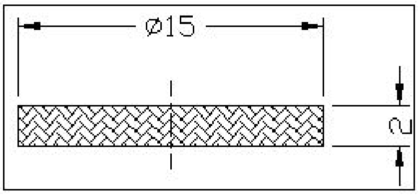


Figure 5.21: Specimen for thermal conductivity measurements

A thin disc of a solid material when subjected to an instantaneous pulse of heat energy on one face, will distribute this energy throughout its body. From the recorded data of the resulting transient temperature rise at the back face of the sample, thermal diffusivity can be deduced. It is assumed that the heat pulse is instantaneous and the sample is perfectly insulated from the environment. Under this ideal condition, the one-dimensional transient heat conduction equation can be solved to obtain the following result.

$$\alpha = 0.1388\, d^2 / t_{50} \qquad (5.3)$$

where d = thickness of the sample (m)

α = thermal diffusivity (m^2/s)

t_{50}= time taken by sample back wall temperature to reach 50% of the maximum temperature

Thermal diffusivity (α), Specific heat (C) and thermal conductivity (k) and density **(**ρ**)** of a solid material are related by the following equation

$$\alpha = k/\rho C. \qquad (5.4)$$

Density was measured from the mass and volume of the sample. From measured values of thermal diffusivity, specific heat and density, thermal conductivity was calculated as.

$$k = \rho C \alpha \qquad (5.5)$$

Specific heat was determined by a comparison method. For specific heat measurements, since the method was a comparative one, both the standard sample and test sample were sprayed with fine graphite powder coating to maintain identical emissivity for better accuracy of specific heat measurements.

The apparatus was first calibrated with a reference sample for the energy absorbed from the laser pulse. From the temperature rise data the energy absorbed is calculated as,

$$Q = (mC\Delta T) \qquad (5.6)$$

where,

m= sample mass

C= specific heat

ΔT= back wall temperature rise.

Then the test sample was subjected to the same laser pulse.

The temperature rise of the test sample due to the laser pulse was measured subsequently, the specific heat of the test sample was obtained from the following equation.

$$(mC\Delta T)_s = Q = (mC\Delta T)_t \qquad (5.7)$$

The subscript 's' stands for the standard sample and subscript 't' for the test sample.

The specific heat of the test sample was calculated as,

$$C_t = (mC\Delta T)_s / (m\Delta T)_t \qquad (5.8)$$

The standard sample and the test specimens are of materials having same order of diffusivity and nearly the same thickness for better accuracy and specific heat measurements. Vespel-0465 and Thermographite have been used as the reference specimens for specific heat measurements.

Since specific heat is a material property and is not dependent on the direction of the plies random specimens were used for characterization while thermal conductivity being a highly a directional property it was evaluated in both along and across the ply directions.

5.6 Sensitivity studies -Phase 1-Laminate level studies

5.6.1 Carbon content in carbon fabric reinforcement

As explained in chapter 3, carbon fabric was fully characterized for all the properties. The maximum and minimum average carbon content varied between 93 and 98%. Fabric rolls with the extreme values 93% and 98% of carbon content were selected and two laminates were processed with phenolic resin from the same batch with same properties, one with prepreg having an average carbon content of 93% and the second with prepreg having an average carbon content of 98% to represent both the extremes of the spectrum of carbon content. Specimens for all the mechanical and thermal properties were prepared from these two laminates and tested under identical conditions. The results were tabulated and compared.

5.6.2 Sodium content in carbon fabric reinforcement

From previous studies, it was noted that sodium content, a significant unwanted ingredient in the carbon fabric reinforcement can be a major contributor which increases the erosion rate of the carbon phenolic ablative during its functional performance. Hence, from the characterized carbon fabric, rolls having a sodium content of 320 ppm and 940 ppm were selected to represent the minimum and maximum levels. Laminates were made with these rolls of fabric as per the standard process keeping all the other process conditions identical. After making the laminates, specimens for the thermomechanical properties were fabricated and tested.

5.6.3 Tensile breaking strength of the carbon fabric reinforcement

The tensile breaking strength of the carbon fabric is a major property which contributes to the strength properties of the ablative composite. It was observed in the characterization studies that there are wide variations in breaking strength values in the available carbon fabric. Hence, two sets of carbon fabric representing the extremes of the available range were selected. The first set had carbon fabric rolls with lower breaking strength ranging from 30 kg per inch width to 35 kg per inch width. The second set of fabric had higher breaking strength of almost thrice the value of the first set, 90 kg per inch width to 105 kg per inch width. Two laminates were processed with these two sets and the thermomechanical properties evaluated from the specimens made from them.

5.6.4 Tensile breaking strength of the silica fabric reinforcement

Similar exercise was done for the silica fabric also. In this case, the values of the breaking strength varied between 25 kg per inch width to 90 kg per inch width. Two laminates were processed, one with lower breaking strength and the other with higher breaking strength for comparative evaluation. All the thermal and mechanical properties were evaluated from the specimens made from the two laminates.

5.6.5 Resin properties

As explained in chapter 3, phenol formaldehyde resin was used for the processing of carbon phenolic and silica phenolic ablative composites. The important properties of the phenolic resin which were expected to have a bearing on the properties of the ablative composites are

1. Viscosity at 30°C, (cP/Pa.s)
2. Specific gravity at 30°C
3. Total solid content at 170°C for ½ hr. (%)
4. Volatile content (%)
5. Free phenol (%)
6. Free formalin (%)
7. Point of trouble at 0.863 Sp.gr/10ml.of resin at 30°C

After detailed literature survey and some pilot experiments it was clear that it was difficult to isolate each property and conduct perturbation studies on the resin. The reason for this behaviour was the fact that the fundamental properties of a phenolic resin system are highly interdependent and perturbing one property will make changes on many other properties. Hence, it was decided to study two different phenolic resin combinations, which were commercially available, which had different properties of viscosity, advancement and phenol-formalin ratio. The basic properties of the two resin systems are given in Table 5.3.

Table 5.3: Basic properties of the two phenolic resin systems

No.	Property	Resin 1	Resin 2
1	Specific gravity at 30°C	1.12-1.16	1.18-1.20
2	Viscosity (cP)	150-300	400-600
3	Degree of advancement @ 30°C(ml of water)	6- 10	13- 16
4	Solids content, % at 170 deg C for 30 minutes	60-65	72- 75
5	Free phenol, %	3 -6	18-22
6	Free formaldehyde, %	1-3	0.2- 0.5

Keeping the reinforcement and process parameters identical, two laminates were processed with each of these resin systems. From these two laminates, specimens for thermal and mechanical property evaluation were made and tested. The results were tabulated and compared.

5.6.6 Resin content in the prepreg

Wet resin content, which is the indication of the resin content and the volatile content in the prepreg, is a very important factor affecting the properties and performance of the ablative composites. Laminates were made with different resin contents for both carbon phenolic and silica phenolic by adjusting the amount of resin absorbed by the fabric reinforcement during impregnation. This was achieved by adjusting the gap between the squeeze rollers in the impregnation plant during the processing. The excess resin was squeezed out to maintain the desired resin content in the prepreg. For carbon phenolic prepreg, four different batches were impregnated with an average resin content of 35 to 40%, 40 to 45%, 45 to 50% and 50 to 55%. For silica phenolic prepreg also, four different batches were impregnated with an average resin content of 30 to 35%, 35 to 40%, 40 to 45% and 45 to 50%. During impregnation, online pickup samples were taken and tested for resin content and the process parameters adjusted for fine tuning the process. After impregnation and before processing three different samples from different random locations were tested from each batch to confirm that the resin content is within the intended range. Four laminates each were processed for carbon phenolic and silica phenolic and detailed nondestructive testing was done. Unlike, the earlier laminates which did not have major defects after processing, a few of these laminates had significant observations. A portion of some laminates had to be cut and removed due to defects like delaminations and specimens were machined from the remaining region. After specimen preparation and acceptance by NDT again, property evaluation was completed for all the thermal and mechanical properties. The results were tabulated and compared.

5.6.7 Cure Temperature

The cure temperature of the ablative composite is a very critical factor which decides the integrity and quality of the composite. It also has a significant influence on deciding the mechanical and thermal properties of the ablative. Cure temperature is the maximum temperature in the curing cycle and at this temperature, the composite is soaked for 3 hours to enable complete uniform polymerisation. The ablative composite was first taken through a heating cycle at the rate of 6 to 8°C/hr till 115°C. The pressure is also gradually increased from ambient conditions. At 110 to 115°C, the maximum pressure is applied and then held constant. Then the temperature is increased in a controlled manner at the same rate till the maximum cure temperature.

To assess the extent of the influence of the cure temperature on the properties of the ablatives, composite liners were processed at different maximum cure temperatures of 135°C, 155°C and 175°C. The experiments were carried out for both carbon phenolic as well as for silica phenolic composites. In these cases, all the other curing parameters like cure pressure, vacuum, heating rate and cooling rate were maintained constant and only the cure temperature was altered. The cure pressure was maintained at 40bar and vacuum was maintained effectively throughout the cure cycle to ensure that all the evolved volatiles were removed. An effective heating rate of 6 to 8°C/hr was maintained during the heating regime of the curing cycle and the same cooling rate was maintained during the cooling regime. In a couple of cases of ineffective vacuum, the laminates had entrapped volatiles leading to voids and delaminations. These laminates were not processed further for specimen preparation. The composite liner blocks which were accepted after NDT were used for preparing specimens for thermal and mechanical property evaluation. The property evaluation was completed as per the standard test matrix for all the thermal and mechanical properties. The results were tabulated and compared.

5.6.8 Cure pressure

After the cure temperature, cure pressure is the next important characteristic parameter which influences the ablative composite properties. The pressure under which the ablative composite is cured decides the consolidation and the compaction of the liner. This in turn influences the density and the other mechanical and thermal properties. To understand the effect of cure pressure and to arrive at an optimum value, experiments with different cure pressures were conducted at 25 bar, 40 bar, 55 bar and 65 bar. Higher pressures could not be attempted due to facility limitations and safety concerns. Pressures lower than 25 bar resulted in very poor compaction. Laminates did not have sufficient compaction that the plies were observed to disintegrate during machining for specimen preparation. Experiments were conducted for both carbon phenolic as well as for silica phenolic composites. The maximum cure temperature was maintained constant at 150°C for all the experiments. The other curing parameters like vacuum, heating rate and cooling rate were maintained constant and only the cure pressure was altered. An effective heating rate of 6 to 8°C/hr was maintained during the heating regime of the curing cycle and the same cooling rate was maintained during the cooling regime. The composite liner blocks which were accepted after NDT were used for preparing specimens for thermal and mechanical property evaluation. The property evaluation was completed as per the standard test matrix for all the thermal and mechanical properties. The results were tabulated and compared.

5.7 Sensitivity studies - Ablative liner level

5.7.1 Studies on ply orientation to the flow direction in the nozzle

A series of experiments were done to study the effect of the direction of fibres in the reinforcements to the direction of the flow in the nozzle. Specimens were prepared with fibres oriented at different angles ranging from 90° to 0° to the nozzle flow. All the critical mechanical and thermal properties were evaluated. Simulation tests and evaluation of erosion and char advancement rate were also done.

The angle of the reinforcement fibres to the heat flux direction is a very critical factor influencing the functional performance of an ablative composite. For understanding the effect of the ply orientation to the flow direction, both the thermal and the structural aspects were considered. It is desirable to employ the optimum ply orientation at different sections of a rocket nozzle to achieve optimum performance. During the functioning of a rocket nozzle, the rate of erosion is the most important factor which is influenced by the ply orientation. Other thermal parameters like the heat of ablation and specific heat are essentially the properties of the material and are not significantly affected by the ply orientation. The effect of thermal conductivity is also embedded in the rate of erosion and hence erosion rate was compared for specimens of different orientation. In this study, the rate of erosion specimens of 10 mm diameter and 20mm length were machined from pressure cured liners processed using the same standard process. Specimens with different ply orientations starting from 0° (parallel to the direction of heat flux), 30°, 45°, 60° and 90° (perpendicular to the direction of heat flux) were machined and their dimensions measured using a vernier caliper.

As a standard material, silica phenolic was used for the tests. The tests were conducted in an arc jet facility in which high temperature plasma was generated. The facility primarily consists of a plasma generator and subsystems like power supply system, coolant supply system, gas supply system, data acquisition and control system. Argon was used as the stimulant gas for this series of tests. 100 W/cm^2 was chosen as the heat flux as this was the typical service conditions of silica phenolic liquid propulsion engine throats. Initially, a calibration was carried out for the plasma jet before the test. A water cooled Gardon heat flux gauge was used to measure the heat flux at different axial locations with respect to the nozzle exit. In order to avoid heating from the sides of the specimens and to ensure unidirectional heating during testing, a guard ring made of silica phenolic itself was used during the test.

The eroded surface after the test was carefully inspected and the mass loss and the eroded length were measured. The depth of char in the specimen was also measured carefully to evaluate the heat affected zone. Apart from the crucial ablative properties, mechanical property evaluation for density, compressive strength and modulus and interlaminar shear strength were evaluated as per standard procedures and the results compared to identify the best ply orientation.

In addition to the layered composites where the plies are oriented at different angles to the flow, there is another category of ablatives in which the prepreg is sized to small chops which are mixed with phenolic resin and are moulded to random fibre oriented composites. In such moulded composites, the plies are randomly oriented and a well defined angle of ply orientation cannot be specified. An effort was made to mould random fibre composites and specimens were made from these composites for evaluating thermal and mechanical properties. These properties were compared to similar properties evaluated from layered composites.

5.7.2 Studies on Fibre architecture

The effect of fibre orientation in the prepreg, which is one of the most critical factor influencing the properties and functional performance of ablatives was investigated by processing laminates through two different fibre architecture. A detailed study was attempted on how the fibre architecture affects the thermal and mechanical properties of ablative composites. At a particular cross-section of the ablative, the alignment and distribution of fibres in a prepreg ply can be tailored in two different patterns.

a) Normal stacked pattern-In this pattern, the fibres were aligned at random across the circumference. Figure 5.22 shows the scheme of cutting pattern plies from a roll of prepreg. In fibres in the warp and fill (weft) directions are shown in the sketch. The plies are cut using a standard template developed from the geometry of the mould. Figure 5.23 (a) shows the sketch of a cut ply. For a typical mandrel cross section of 2m diameter 3 plies were required to cover on full circumference of the mandrel. Figure 5.23 (b) depicts the anisotropy in the fibre architecture in a plane. Random orientation of warp and fill fibres are observed in any particular cross-section.

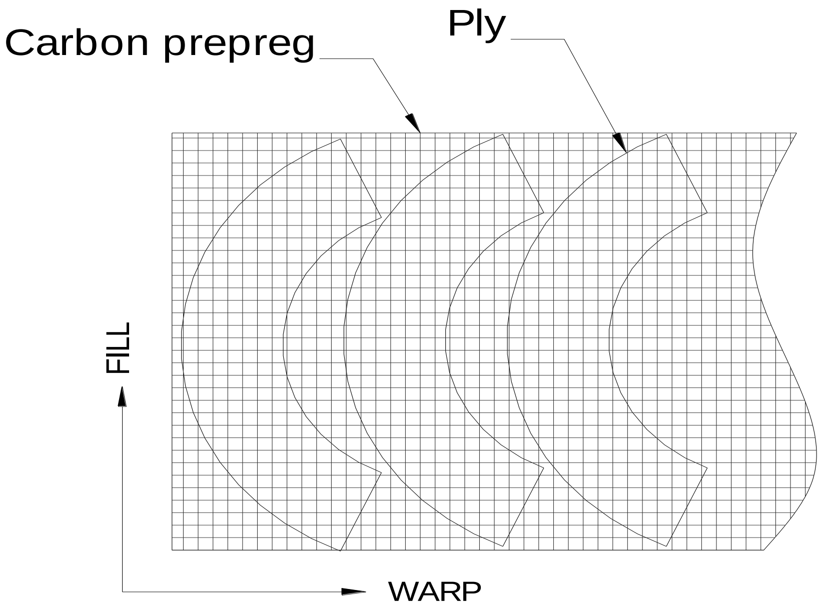
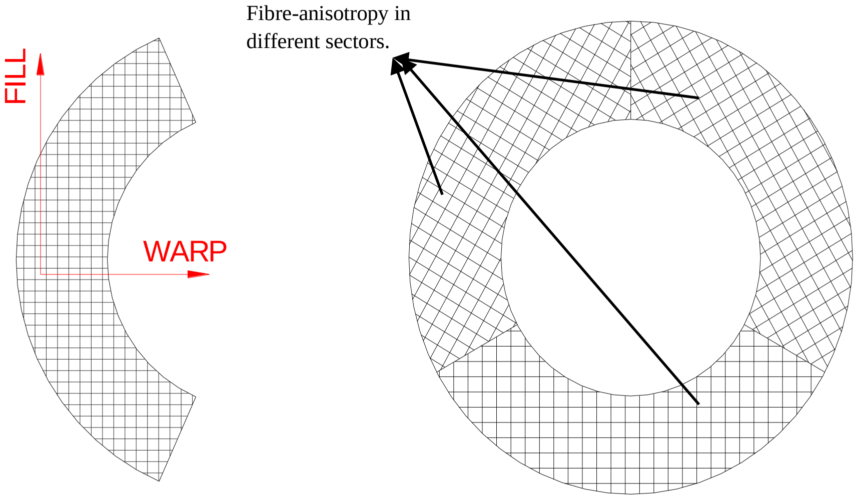


Figure 5.22: Schematic showing how plies are cut from a roll of prepreg



a) Single ply

b) Anisotropy around the circumference formed by 3 plies

Figure 5.23 Fibre architecture in a pattern cut tape system

2. Fibres aligned uniformly across the circumference, achieved by ply cutting at a biased angle of 45° (Figure. 5.24) and differential stretching of the ply to form the tape (Figure. 5.25). Here, a more or less quasi-isotropic distribution of fibres along the circumference is observed.

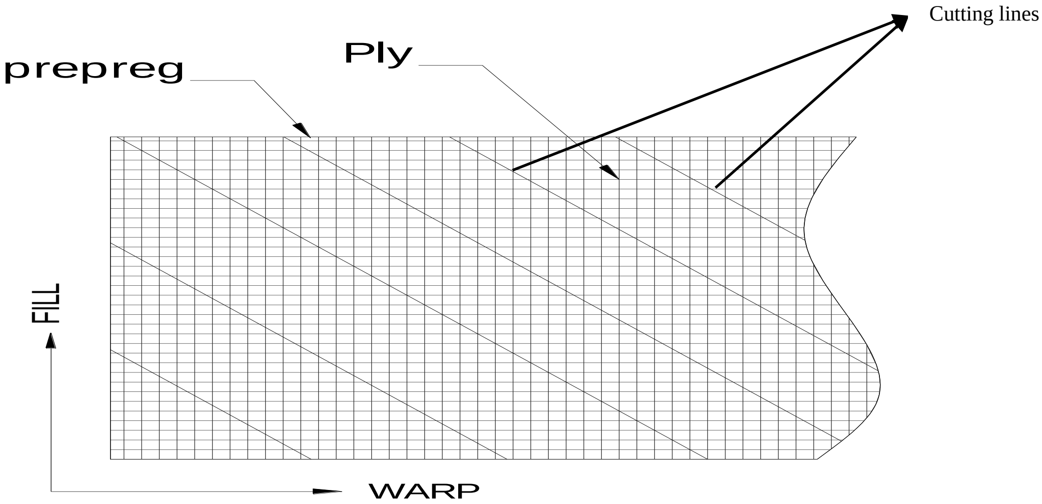
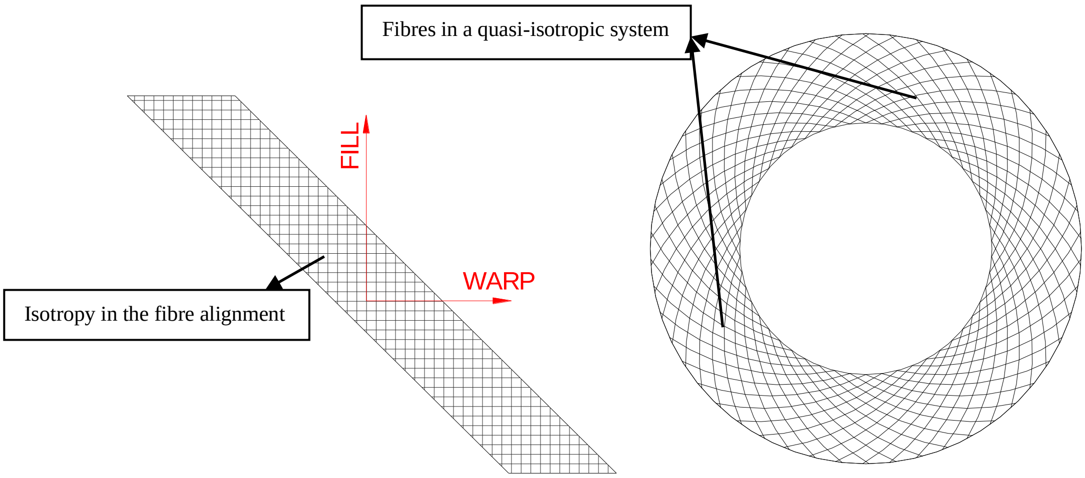


Figure 5.24: Schematic showing how plies are cut at an angle of 45° to the edge.



a) Single ply b) isotropy around the circumference formed by 3 plies

Figure 5.25 Fibre architecture in a bias angle pattern cut tape system (L2)

Comparison of mechanical and thermal properties of both the configurations was done. Ground test on simulation motors and evaluation of erosion and char advancement rate were also completed and the results were compared.

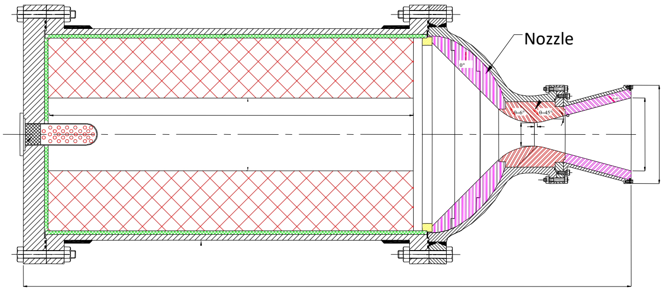


Figure 5.26: Schematic of a Test simulation Motor

A Test Simulation Motor (TSM) (Figure 5.26) using Hydroxyl-terminated Poly butadiene (HTPB) based solid propellant was used for the simulation studies. The ablative liners with different ply architecture were used in the nozzle of this motor and were subjected to identical test conditions. After the test, elaborate post test inspection and measurements were carried out. The pre test and the post test contour were mapped to understand the erosion pattern and to quantify the erosion. These measurements were done on a coordinate measuring machine (CMM). After mapping the post test contour, the extent of charring on the liner surfaces was examined in detail. Char was physically removed at 4 different equispaced locations; 90° apart around the circumference and the depth of the heat affected zone was measured using a vernier caliper. These values of erosion and char depth were tabulated and compared.

5.7.3 Effect of temperature on properties:

In order to investigate whether there is any substantial variation in the mechanical properties with increase in temperature, some limited investigations were done. Specimens prepared for the different tests were used for these studies also. The specimens were heat treated to different temperatures like 200°C, 400°C, 600°C, 800°C and 1000°C in an inert Argon atmosphere in a furnace. Then, they were subjected to mechanical property evaluation. Compressive strength and interlaminar shear strength were evaluated and compared at these different temperatures and the results were compared.

5.7.4 Effect of ageing on properties:

Specimens which were fabricated for the different investigations were stored in controlled conditions and were evaluated every six months to assess the property degradation, if any. Some representative properties were only evaluated as this was sufficient to understand the trends. Compressive strength and ILSS were chosen from the mechanical properties and specific heat, thermal conductivity and heat of ablation were selected from the mechanical properties. The results were tabulated and compared.

CHAPTER 6

RESULTS AND DISCUSSIONS

After a detailed study of the raw material properties and processing aspects, all the parameters which are likely to influence the thermal and mechanical properties of ablative composites and their functional performance were enlisted. From this large set of parameters, the most critical parameters were selected by literature survey, survey of processing techniques and collection of data from the processing laboratories. The raw material and process parameters selected for detailed investigations as explained in chapter 4 are listed below.

1. Carbon content in the carbon fabric reinforcement
2. Sodium content in the carbon fabric reinforcement
3. Breaking strength of the fibre in the carbon reinforcement
4. Breaking strength of the fibre in silica reinforcement
5. Matrix (resin) properties: viscosity, degree of advancement (point of trouble), specific gravity, solid content, phenol and formalin content.
6. Wet resin content in the carbon phenolic prepreg
7. Wet resin content in the silica phenolic prepreg
8. Fabric ply orientation to the direction of flow
9. Fibre architecture in the ply - fibre alignment and distribution
10. Cure temperature of carbon phenolic composite
11. Cure temperature of silica phenolic composite
12. Cure pressure of carbon phenolic composite
13. Cure pressure of silica phenolic composite
14. Effect of temperature on properties of ablative composites
15. Effect of storage on properties of ablative composites

For understanding the importance of each of the above parameters, standard laminates or liners were processed by varying each parameter in a controlled manner, keeping all the other process and raw material parameters same at the standard range.

For acceptance and qualification of ablative composites for aerospace applications, the characterization and testing were done with respect to the following thermal and mechanical properties. These properties give vital and comprehensive information regarding the quality of the composite as well as its functional merit.

1. Density (specific gravity)
2. Inter-laminar shear strength (ILSS)
3. Compressive Strength (CS) - (along the ply direction)
4. Compressive Strength (CS) - (across the ply direction)
5. Compressive Modulus (CM) - (along the ply direction)
6. Compressive Modulus (CM) - (across the ply direction)
7. Heat of ablation
8. Specific heat
9. Thermal conductivity- (along the ply direction)
10. Thermal conductivity- (across the ply direction)
11. Erosion rate- (along the ply direction)
12. Erosion rate- (across the ply direction)

All the specimens were fabricated and tested as per the standards being followed for aerospace applications. The results and inferences are summarized below. Standard units are used for all the tested values except in the case of special tests where the calibrated units of the test equipments are used. These units are mentioned at the respective places.

6.1 Parameters from the reinforcements

6.1.1 Carbon fibre reinforcement

a) Carbon content:

From the characterized values of the carbon content in the reinforcement, the minimum and maximum values were 93% and 98% respectively. These rolls were taken and laminates were processed using these fabrics. Specimens for thermal and mechanical properties were prepared and evaluation was completed. The results are tabulated below. Table 6.1 gives the summary of the thermal property evaluation done for the two laminates with carbon content 93% and 98%.

The difference in the carbon content in the two laminates was 5%. For this order of difference, there was no significant difference in density. The density of the laminates was observed to be of the same order and the difference was well within the normal dispersion levels. The density of the composite was determined by the density of the constituent materials and since they are the same, the effect of carbon content was negligible on density. However, the erosion rate was observed to be influenced by the difference in carbon content in the reinforcement. Erosion rate along the ply direction was observed to decrease by 18% with increase in carbon content from 93 to 98%. This trend was seen in both along and across the ply directions. However, across the ply direction, this effect is less pronounced as only a reduction of 7% was observed because the influence of resin was more than the reinforcement in this case. The resistance to erosion was found to improve with higher carbon content in the reinforcement since higher percentage of carbon provides more char strength and higher char retention.

Heat of ablation values exhibited significant dispersion. Average values of samples with higher carbon content showed an increase of 19% as compared to the samples with lower carbon content. This increase in the heat of ablation is attributed to the fact that more heat input was required to ablate unit mass of the ablative since more content of carbon needs more amount of heat input for ablation.

Thermal conductivity increased in both along the ply and across the ply directions with increase in carbon content. Along the ply direction, the average value increased from 1.07 W/mK to 1.32 W/mK, an increase of 12.5% whereas in across the ply direction, the corresponding average values increased from 0.64 W/mK to 0.825 W/mK, a significant increase of 29%. The increase in the thermal conductivity with increase in carbon content may be due to the direct contribution of carbon in enhancing the conductivity.

Specific heat did not change significantly with carbon content change. Wide dispersion was also observed in the test results. The values for the set with 93% carbon content varied from 989 to 1309 J/kgK whereas the set with 98% carbon content gave values in the range of 1089 to 1317 J/kgK. The values were in the similar range and the average values differ only by around 50 J/kgK. This indicates that specific heat being a bulk property is not influenced by the 5% change in the carbon content.

Table 6.1: Effect of carbon content on the thermal properties of carbon phenolic composite

Carbon Content, (%)	**93**	**98**
Density (g/cc)	1.420 - 1.451	1.440 - 1.456
Erosion rate- along ply (mm/s)	0.037 - 0 .039	0.030 - 0.032
Erosion rate- across ply (mm/s)	0.033 - 0.037	0.031 - 0.034
Heat of ablation (cal/g)	6749 - 7419	7623 - 9254
Thermal conductivity -along ply (W/mK)	1.03 - 1.11	1.30 - 1.34
Thermal conductivity-across ply (W/mK)	0.62 - 0.68	0.73 - 0.92
Specific heat (J/kg K)	989 - 1309	1089 - 1317

Table 6.2 gives the summary of the mechanical property evaluation done for the two laminates with carbon content 93% and 98%.

From the test results, it was clearly evident that the carbon content in the reinforcement directly influenced the mechanical properties of carbon phenolic laminates. The basic strength properties evaluated by compressive strength showed a clear dependence on the carbon content. Along the ply direction, the compressive strength increased by around 20% with an increase of 5% in carbon content in the reinforcement. The same behaviour was observed in samples made across the ply direction also. Since fibres are the major load bearing element in the composite, the strength values increased with the carbon content. This increase may be contributed by the strength of graphitized carbon fibres. Compressive modulus values also show a slight increase with increase in carbon content. Interlaminar shear strength was not showing much dependence on the carbon content; this may be due to the fact that this property is basically a resin-dominant property and depends less on the reinforcement properties.

Table 6.2: Effect of carbon content on the mechanical properties of carbon phenolic composite

Carbon Content, (%)	**93**	**98**
Compressive strength - along ply (MPa)	221.80 - 239.62	246.94 - 309.86
Compressive strength - across ply (MPa)	514.14 - 578.95	590.02 - 725.69
Compressive modulus - along ply (GPa)	12.83 - 13.39	13.08 - 14.38
Compressive modulus - across ply (GPa)	11.37 - 14.87	13.87 - 15.54
Interlaminar shear strength (MPa)	32.32 - 49.36	27.07 - 49.66

b) Sodium content:

The next parameter evaluated was the sodium content, an impurity element in the carbon fabric reinforcement. From the rolls which were characterized for the experimental studies, the values of sodium varied between 340 ppm to 940 ppm. Two sets of carbon fabric rolls, one with 340 ppm sodium content and the other with 940 ppm sodium content were used to process the carbon phenolic laminates. The test results of the thermal property characterisation are tabulated in Table 6.3 and the results of mechanical property evaluation are tabulated in Table 6.4.

From the experimental results it was observed that the sodium content in the carbon fabric significantly affected the thermal performance of the carbon phenolic composite. To understand the sensitivity of the ply direction, erosion tests were conducted in both along the ply and across the ply directions. When tested at a heat flux of 750 W/cm^2 for a cumulative duration of 15 seconds, the sample with 940 ppm of sodium content eroded at a much higher rate than the sample with the lower sodium content. An increase to the extent of 70% was observed in the case of specimens made along the ply direction and more than double the erosion rate was noticed in the case of specimens made across the ply direction. This indicated that the sodium was an undesirable impurity in the carbon fabric reinforcement and should be kept at the minimum possible level. This is in line with the published catalogue values of proprietary aerospace carbon fabrics where the sodium values are limited below 600 ppm. The absence of alkali content in the carbon fibre is the reason for its improved stability. The presence of sodium and potassium leads to catalytic oxidation causing increased erosion of the material. Correspondingly, heat of ablation values for specimens with higher sodium content were found to be lesser than the corresponding values for the lower sodium content samples. However, this difference was not very significant. Thermal conductivity values in both along the ply and across the ply directions also showed an increasing trend with increase in sodium content. This is in line with the increased erosion rates and this strengthens the conjecture that sodium is highly undesirable from the ablative performance point of view. As expected, density was not affected by the sodium percentage in the fabric as the absolute values are negligible.

Table 6.3: Effect of sodium content on the thermal properties of carbon phenolic composite

Sodium Content, ppm	**340**	**940**
Density (g/cc)	1.420 - 1.451	1.440 - 1.456
Erosion rate- along ply (mm/s) @750 W/cm^2, 15 s	0.017 - 0 .019	0.030 - 0.032
Erosion rate- across ply (mm/s) @750 W/cm^2, 15 s	0.013 - 0.017	0.031 - 0.034
Heat of ablation (cal/g) @750 W/cm^2, 15 s	7749 - 9419	7623 - 9254
Thermal conductivity - along ply (W/mK)	1.03 - 1.11	1.30 - 1.34
Thermal conductivity - across ply (W/mK)	0.62 - 0.68	0.73 - 0.92
Specific heat (J/kg.K)	1189 - 1309	1089 - 1317

Specimens were tested for various mechanical properties from laminates made with the extreme values of sodium content in the fabric. Though elaborate testing was done for compressive strength, compressive modulus and ILSS, no clear dependence could be established.

From the test results, it was observed that the mechanical properties were not very sensitive to sodium content in the carbon fabric. The difference in the property values can be attributed to the scatter or dispersion in the test values inherent in composite characterization tests. Sodium being a trace elemental impurity in the fabric is not expected to influence the strength values. The tested values of mechanical properties of carbon phenolic laminates with sodium content values of 340 ppm and 940 ppm are tabulated in Table 6.4

Table 6.4: Effect of sodium content on the mechanical properties of carbon phenolic composite

Sodium Content, ppm	**340**	**940**
Compressive strength - along ply (MPa)	221 - 238	204- 258
Compressive strength - across ply (MPa)	435-507	485- 610
Compressive modulus - along ply (GPa)	12.83 - 13.39	13.08 - 14.38
Compressive modulus - across ply (GPa)	11.37 - 11.87	11.87 - 13.54
Interlaminar shear strength (MPa)	32.32 - 49.36	27.07 - 49.66

c) Tensile breaking strength of the carbon fibres in the reinforcement:

During the characterization of the fabric, it was observed that the tensile breaking strength of the fibres was varying over a very large range. The values ranged from 30 kg/inch width to 105 kg/inch width (1.18 kg/mm to 4.13 kg/mm). (The equipment and the test fixtures are calibrated to measure tensile breaking strength of specimens of a standard width of 1 inch (25.4 mm) and the reading from the test rig is obtained in kg/inch width as per the standard followed globally by fabric manufacturers). A minimum breaking strength of the fibres was essential from the processing point of view so that it could withstand the tension during the impregnation process in the plant. If the minimum tensile strength was not available, the fabric was being stretched leading to nonuniform resin pickup during the impregnation process. In certain cases, physical tearing of fabric led to the stoppage of the impregnation itself. This was a highly undesirable observation. Hence, carbon fabric with breaking strength below 30 kg/inch width was not taken for the experiments. From the available characterized fabric, rolls were chosen from both the lower and higher ends of the available strength values. The lower segment had breaking strength values between 30 to 35 kg/inch width and the higher segment had values between 90 to 105 kg/inch. These fabrics were impregnated with phenolic resin and laminates were made. Thermal and mechanical properties were evaluated and results are summarized in Tables 6.5 and 6.6.Since breaking strength of the fibres in the fabric can affect only mechanical properties, density and other thermal properties like erosion rate, thermal conductivity and specific heat were not significantly affected by difference in the breaking strength of the fibres of the carbon fabric.

Table 6.5: Effect of tensile breaking strength of carbon fibres in the fabric on the thermal properties of carbon phenolic composite

Breaking strength, kg/inch width	**30-35**	**90-105**
Density (g/cc)	1.420 - 1.451	1.430 - 1.456
Erosion rate- along ply (mm/s) @750 W/cm^2, 15 s	0.03	0.03
Erosion rate- across ply (mm/s) @750 W/cm^2, 15 s	0.033 - 0.037	0.031 - 0.034
Heat of ablation (cal/g) @750 W/cm^2, 15 s	7050	7105
Thermal conductivity - along ply (W/mK)	1.03 - 1.11	1.13 - 1.24
Thermal conductivity - across ply (W/mK)	0.62 - 0.68	0.63 - 0.82
Specific heat (J/kg.K)	989 - 1309	1089 - 1317

However, a significant bearing on the mechanical properties were clearly visible. The compressive strength along the ply direction for the lower strength fabric varied from 181 to 208 MPa while the corresponding values for the higher strength fabric were about 70% higher in the range of 288 to 368 MPa. It was concluded that the higher tensile strength of the carbon fabric directly contributes to the higher strength values of the composites. Modulus values also showed a similar trend. In this case also, the interlaminar shear strength values were falling more or less in the similar band as seen in Table 6.6, the difference being less than 7%.

Table 6.6: Effect of tensile breaking strength of carbon fibres in the fabric on the mechanical properties of carbon phenolic composite

Breaking strength, kg/inch width	**30-35**	**90-105**
Compressive strength - along ply (MPa)	181-208	288-368
Compressive strength - across ply (MPa)	335-412	485-610
Compressive modulus - along ply (GPa)	12.83-13.39	13.08-14.38
Compressive modulus - across ply (GPa)	10.88-11.96	11.87-13.54
Interlaminar shear strength (MPa)	28.86-42.54	24.33-52.21

6.1.2 Silica fibre reinforcement

Tensile breaking strength of the silica fibre in the fabric:

As explained in chapter 5, tensile breaking strength of silica fibres in the fabric was the only parameter chosen for investigations for the silica fabric. When the silica fabric rolls were tested for their properties, it was observed that the tensile breaking strength varied in a significant range from around 25 kg/inch width to 90 kg/inch width. To study the effect of the tensile breaking strength, laminates were processed using two sets of fabric, the first one with lower breaking strength and the second one with higher breaking strength. Since the dispersion was quite high, the first laminate had fabric with breaking strength of 25 to 32 kg/inch width and the second one with breaking strength between 75 to 90 kg/inch width. The listed thermal and mechanical properties were evaluated and tabulated. Table 6.7 gives the thermal properties evaluated for the two laminates.

As is clearly evident from the Table 6.7, the tensile breaking strength of silica fabric did not contribute significantly to the thermal properties of the silica phenolic composite. Even silica fabric with about three times the tensile breaking strength was used; there was no significant change in the thermal properties evaluated. Hence, it was concluded that the tensile breaking strength does not affect the thermal properties since the fibre breaking strength contributes mainly to the strength properties of the composites and not to the ablative and thermal properties.

Table 6.7: Effect of tensile breaking strength of silica fibres in the fabric on the thermal properties of silica phenolic composite

Breaking strength, kg/inch width	**25-32**	**75-90**
Density (g/cc)	1.72 - 1.74	1. 73 - 1.74
Erosion rate- along ply (mm/s) @750 W/cm2, 15 s	0.028	0.030
Erosion rate- across ply (mm/s) @750 W/cm2, 15 s	0.023 - 0.024	0.021 - 0.024
Heat of ablation (cal/g) @750 W/cm2, 15 s	8243	8410
Thermal conductivity - along ply (W/mK)	0.57	0.59
Thermal conductivity - across ply (W/mK)	0.45	0.47
Specific heat (J/kg.K)	846	864

On the other hand, significant influence was noticed on the mechanical properties of the two laminates. The details are provided in Table 6.8

All the mechanical properties increased with an increase in breaking strength of the fibres in the silica fabric. As the tensile breaking strength increased from an average value of 28 kg/inch width in the first laminate to about 83 kg/inch width in the second laminate, the compressive strength in both the along the play and across the ply directions showed a clear increase. While the increase in the compressive strength along the ply direction was notably high (24%), the increase in the compressive strength across the ply direction (17%) too was considerable. Similarly, the compressive modulus along the ply direction was seen to be increasing from 9.65 GPa to 11.50 GPa, an increase of 19.2% and the compressive modulus across the ply direction increased from 10.05 GPa to 12.30

GPa, an increase of 22.42%. These observations helped to reach the conclusion that the tensile breaking strength of the silica fabric directly contributed to the strength and modulus properties of the silica phenolic composite. Since the reinforcement is the main load bearing component of the composite, the increase in the strength of the fibres in the fabric significantly contributed to the strength and stiffness of the composite. Fibres with higher breaking strength directly contributed to the strength properties of the laminate. However, for ILSS the average value increased from 21.6 MPa to 23.1 MPa only, an increase of around 6% only. Since ILSS was largely influenced by the resin as compared to the reinforcement this behavior was expected. The contribution of the fibre in resisting interlaminar shear was limited.

Table 6.8: Effect of tensile breaking strength of silica fibres in the fabric on the mechanical properties of silica phenolic composite

Breaking strength, kg/inch width	**25-32**	**75-90**
Compressive strength - along ply (MPa)	64.5-78.9	77.0-100.5
Compressive strength - across ply (MPa)	232.0-250.0	248.0-310.0
Compressive modulus - along ply (GPa)	9.65	11.5
Compressive modulus - across ply (GPa)	10.05	12.3
Interlaminar shear strength (MPa)	20.05-23.35	22.65-25.90

6.2 Parameters from the resin matrix

As explained in chapter 4, a thermosetting phenolic resin was used for the experiments. Since the defining properties of the resin like viscosity and degree of advancement are interdependent, perturbing one property will make changes on many other properties. So two different phenolic resin combinations (Resin 1 and Resin 2), with different characteristics were studied by processing carbon phenolic and silica phenolic ablative composites and evaluating their mechanical and thermal properties for comparison.

Resin 1 had got higher solid content, higher specific gravity and higher viscosity than Resin 2. The point of trouble for Resin 1 was around 13 to 16 ml of water while for Resin 2 it was around 6 to 8 ml of water only, which means that Resin 1 is less advanced than Resin 2. The free phenol in Resin 2 was kept low at around 6%, while in Resin 1 it was more than thrice that value. The free formaldehyde value on the other hand was kept low for Resin 1 while for Resin 2 it was more than double the value. Resin 1 was a virgin resin without any solvent. It had excess phenol present in the reactive mixture as a reactive diluent. In Resin 2, ethyl alcohol was added as a nonreactive diluent to reduce the concentration of reactive sites. This helped in increasing the shelf life and reducing the viscosity during impregnation. Due to the presence of nonreactive diluent, it appeared that Resin 2 is less advanced but actually it is more advanced as is obvious from the values of the point of trouble, which is a measure of advancement.

So the combined effect of the properties phenol content, formaldehyde content and total solid content was investigated. The effect of viscosity, degree of advancement and solids content were subjected to detailed investigations.

During the impregnation and processing trials, several important observations could be made. It was observed that the properties of the matrix were highly dependent on the time and temperature/storage conditions. As time of storage and ambient temperature increased, properties like viscosity and degree of advancement of the polymerisation changed significantly. Hence, the storage conditions and time are very important parameters which were to be closely monitored and controlled. Proper effective impregnation of the fabric with resin could be done for only certain bands of resin properties. Higher advancement beyond the values used in the experiments, namely, 6-10 ml of water for Resin 2 and 16 ml for Resin 1 posed difficulties during the process of impregnation. This was because the resin had already advanced more to the semi-cured stage causing hindrance to free flow and uniform wetting of the fabric. This was observed for both carbon and silica phenolic composites.

After the experiments, it was concluded that the optimum impregnation parameters for Resin 1 were

- Viscosity: 500-550 cP
- Point of trouble: 14-15 ml of water

And For Resin 2, the optimum parameters were

- Viscosity: 200-250 cP
- Point of trouble: 7-8 ml of water

Solid content and volatile content did not vary much with respect to time/temperature/storage conditions. As the reaction within the resin proceeded due to cross linking and polymerization, viscosity started building up and the degree of advancement also increased.

The results of experiments conducted on both carbon phenolic and silica phenolic laminates are tabulated below. Table 6.9 gives the variation in thermal properties of carbon phenolic laminates processed using both the resins.

It was observed that the density of the laminate processed using Resin 1 was slightly higher than that of the laminate processed using Resin 2. This may be due to the contribution of the resin since the reinforcement was the same; the specific gravity of Resin 1 is higher than that of Resin 2. The char yield and the char strength of the laminates processed using Resin 1 were found to be better than those of Resin2. In fact, the erosion rate along the ply direction was reduced by 34% and the erosion rate across the ply direction was found to be lesser by a significant 50%. This indicates significant improvement in the ablative performance of the resin with higher phenol-formaldehyde ratio and solid content. Correspondingly, the heat of ablation values for the specimens made using Resin1 was 8856 cal/g as compared to 6756 cal/g, an increase of 24%. As mentioned earlier, the excess phenol present in Resin 1, being a reactive diluent, takes part in subsequent reactions during curing as well as in the ablation process. The cyclic structure of benzene ring in phenol improves the char yield and char strength. Thermal conductivity values were falling more or less in the same band and no significant inference could be drawn from the tested data to indicate any superiority for either resin. Specific heat too, being a bulk material property, gave similar values for both the resin systems. From the processablity point of view, Resin 2 being less viscous was better to handle during the impregnation process.

Table 6.9: Variations in thermal properties of Carbon phenolic composites processed using Resin 1 and Resin 2

Phenolic Resin	**Resin** 1	**Resin** 2
Density (g/cc)	1.415- 1.456	1.386 - 1.411
Erosion rate- along ply (mm/s) @750 W/cm^2,15 s	0.015 - 0.022	0.027 - 0 .029
Erosion rate-across ply (mm/s) @750 W/cm^2,15 s	0.011 - 0.014	0.023 - 0.027
Heat of ablation (cal/g) @750 W/cm^2, 15 s	8856	6758
Thermal conductivity - along ply (W/mK)	1.21 - 1.26	1.17-1.26
Thermal conductivity - across ply (W/mK)	0.73 - 0.92	0.72-0.96
Specific heat (J/kg.K)	1321	1256

While analysing the test results of mechanical properties of carbon phenolic laminates (Table 6.10) processed using the two resin systems, it was observed that the compressive strength in both along the ply and across the ply for laminates processed using Resin 1 was higher than the corresponding values for laminates processed using Resin 2. Though there was significant dispersion in the tested values, the superiority of Resin 1 due to the presence of benzene ring in the backbone is reflected in the strength values of the laminates. The compressive strength values across the ply direction were observed to be higher since all the fibres in the fabric plies were available to share the compressive load whereas in the specimens where the load is applied along the ply, load sharing was done by the resin interface too. The increase in compressive strength values along the ply direction is 17.3% and the corresponding increase across the ply values is 25.6%.

Similar trend was observed in the tested values of compressive modulus also, though the extent was lower. The compressive modulus values were higher by 2.9% and 5.3% along the ply direction and across the ply directions respectively for specimens made using Resin 1 than those from Resin 2. Modulus is a derived quantity and it indicates the combined effect of stress and strain. If the change in elongation or strain is not very significant, then the resultant change may not be reflected in the modulus values.

Interlaminar shear strength being a resin dominant property showed significant sensitivity to the resin system. The values of ILSS improved by about 37% for Resin 1 as compared to the values of Resin 2. However, noticeable dispersion was also observed in the tested values of ILSS. This was attributed to specimen preparation related issues. However, the increasing trend for ILSS values for Resin 1 has been confirmed.

Table 6.10: Variations in mechanical properties of carbon phenolic composites processed using Resin 1 and Resin 2

Phenolic resin	**Resin 1**	**Resin 2**
Compressive strength - along ply (MPa)	235-297	199-241
Compressive strength - across ply (MPa)	475-623	369-449
Compressive modulus - along ply (GPa)	13.28-14.25	11.67-12.99
Compressive modulus - across ply (GPa)	11.65-12.56	11.37-11.87
Interlaminar shear strength (MPa)	27.07-43.21	19.85-24.65

Near similar observations were noticed in the test results of the experiments using the two resin systems on silica reinforcement also. All the thermal and mechanical properties were evaluated from the specimens fabricated from the laminates processed using silica fabric with Resin 1 and Resin 2. Table

6.11 gives the tested values of the thermal properties of silica phenolic composites processed using the two resin systems.

Table 6.11: Variations in thermal properties of Silica phenolic composites processed using Resin 1 and Resin 2

Phenolic resin	**Resin 1**	**Resin 2**
Density (g/cc)	1.70-1.76	1.69-1.71
Erosion rate- along ply (mm/s)	0.028	0.035
Erosion rate- across ply (mm/s)	0.021	0.030
Heat of ablation (cal/g)	9400	7150
Thermal conductivity - along ply (W/mK)	0.61	0.55
Thermal conductivity - across ply (W/mK)	0.51	0.47
Specific heat (J/kg.K)	1040	928

For silica phenolic laminates also, it was evident from Figures 6.1 to 6.3 that Resin 1 gave clearly superior thermal/ablative and mechanical properties than Resin 2.This may be due to the higher phenol to formaldehyde ratio in this resin, which yields higher and stronger char. The density increased from an average value of 1.70 g/cc to 1.73 g/cc. The erosion characteristics showed a marked superiority (Figure 6.1) for Resin 1 as the erosion rate under test conditions was 25% lesser than that of the Resin 2 system in the case of along the ply specimens. In similar lines to the observations noticed for carbon phenolic composites, erosion rate was 43% lesser in the across the ply direction for samples from Resin 1 system as compared to Resin 2 system. Thermal conductivity in both along and across the ply directions and specific heat values are compared in Figure 6.2 and were comparable for both the resin systems. These observations are in line with the observations made during the experiments on carbon phenolic composites. Hence, it was inferred that Resin 1 with higher viscosity, degree of advancement and phenol-formaldehyde ratio showed superior ablative characteristics as evident from lower erosion rates and higher values of heat of ablation.

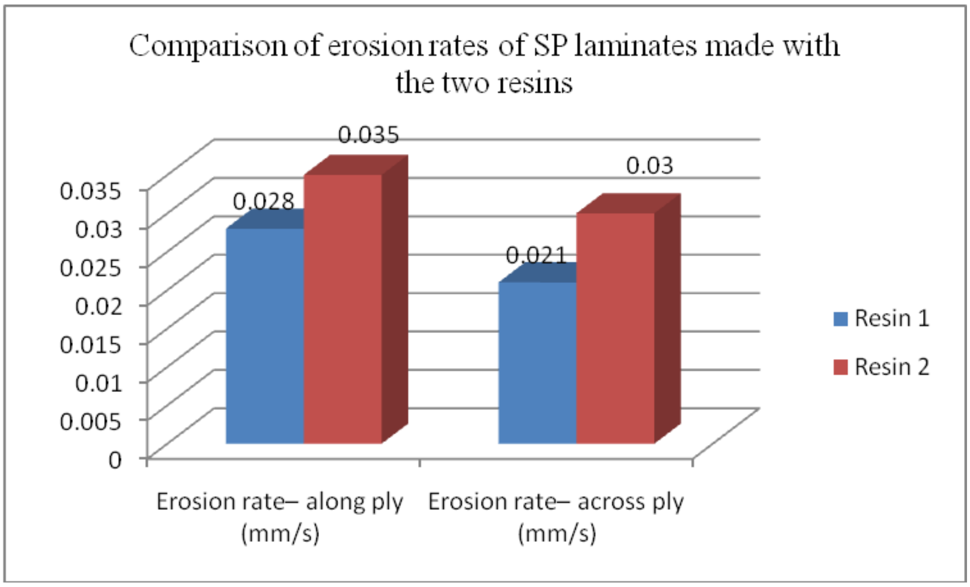


Figure 6.1: Comparison of erosion rates of Silica phenolic composites processed using Resin 1 and Resin 2

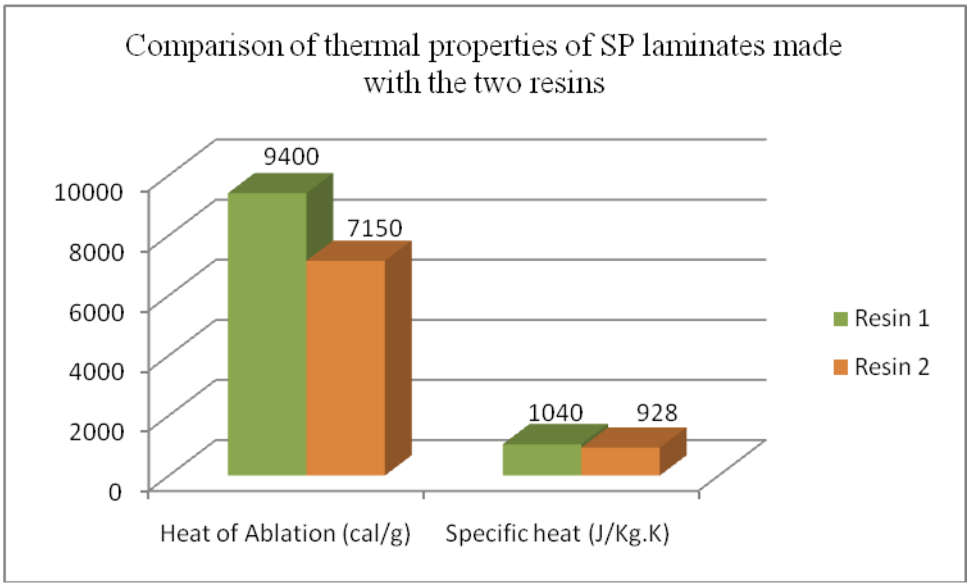


Figure 6.2: Comparison of thermal properties of Silica phenolic composites processed using Resin 1 and Resin 2

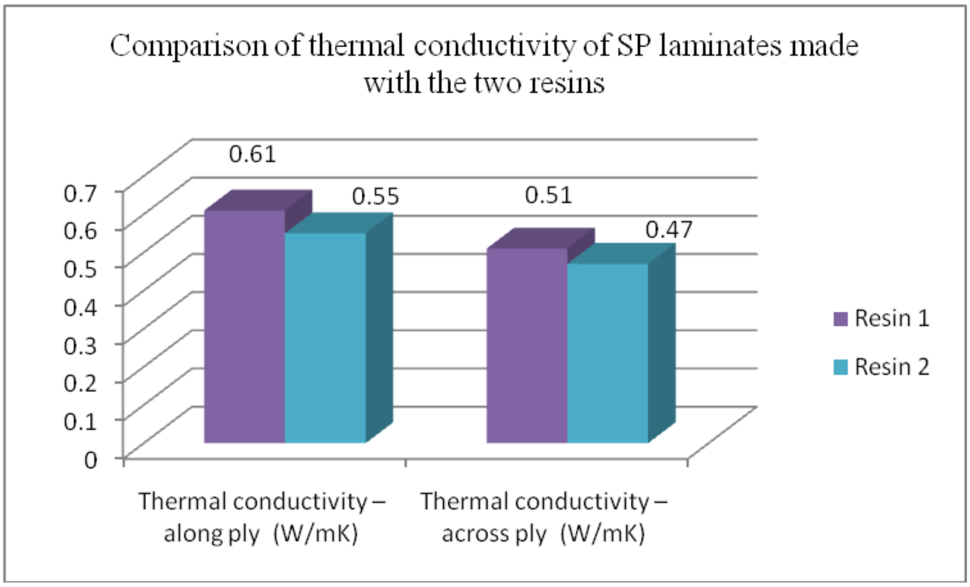


Figure 6.3: Comparison of thermal conductivity of Silica phenolic composites processed using Resin 1 and Resin 2

Table 6.12 tabulates the mechanical properties evaluated from laminates made from silica fabric impregnated with phenolic resin systems 1 and 2. Significant increase is seen in all the mechanical properties. The compressive strength along the ply direction increased from an average value of 68.4 MPa to 94.2 MPa, an increase of 27%. Corresponding increase of compressive strength across the ply direction was 24%. Similarly, compressive modulus also increased by 29% in the along ply direction and by 30% in the across the ply direction. ILSS improved by 31% for Resin system 1 over Resin system 2. (Figure 6.4 and Figure 6.5). Hence, it was concluded that for all the mechanical properties showed improved values in the Resin system 1. The optimum phenol-formaldehyde ratio has mainly contributed to the better properties of the ablative composite.

To conclude, both for carbon phenolic and for silica phenolic, irrespective of the fabric reinforcement used, Resin 1 with higher phenol-formaldehyde ratio, showed superior thermal/ablative as well as mechanical properties. However, from the processing point of view, Resin 2 being less viscous offered more convenience during impregnation.

Table 6.12: Variations in mechanical properties of Silica phenolic composites processed using Resin 1 and Resin 2

Phenolic resin	**Resin 1**	**Resin 2**
Compressive strength - along ply (MPa)	94.2	68.4
Compressive strength - across ply (MPa)	288	220
Compressive modulus - along ply (GPa)	10.9	7.75
Compressive modulus - across ply (GPa)	11.7	8.15
Interlaminar shear strength (MPa)	31.5	21.56

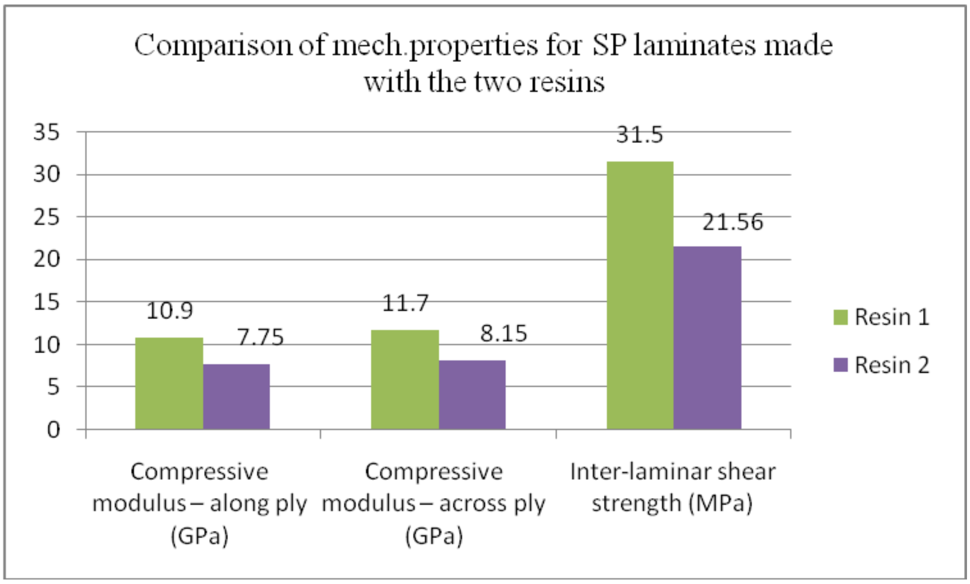


Figure 6.4: Comparison of compressive modulus and ILSS of Silica phenolic composites processed using Resin 1 and Resin 2

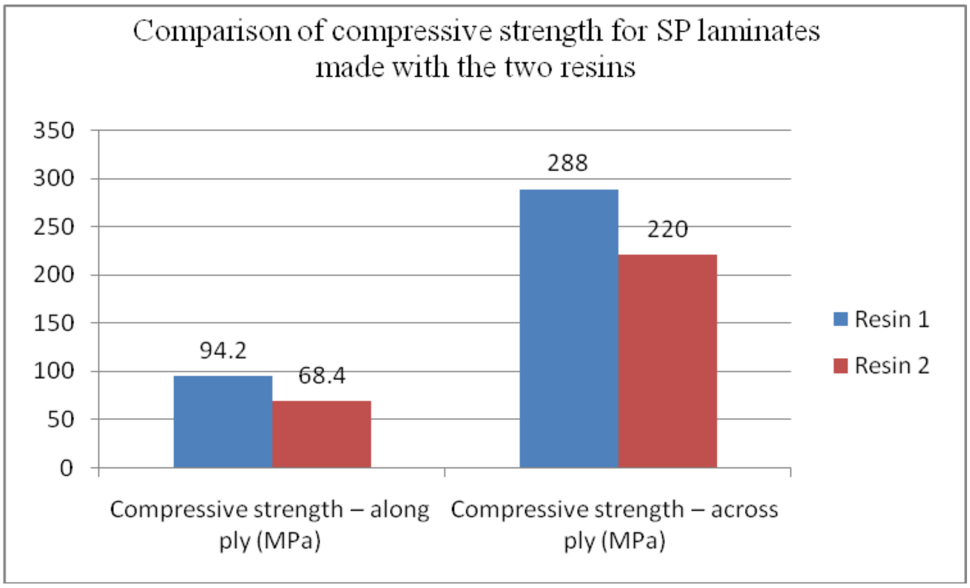


Figure 6.5: Comparison of compressive strength of Silica phenolic composites processed using Resin 1 and Resin 2

6.3 Prepreg parameters: Wet resin content

As explained in chapter 5, wet resin content was selected as the representative prepreg parameter for perturbation studies. Studies were carried out independently for both carbon phenolic and silica phenolic composites. Resin content is one important parameter which directly affects the quality of the composite. So in addition to the routine testing of thermal and mechanical properties, elaborate nondestructive evaluation was also carried out on the laminates prepared for the studies. The resin content in the prepreg has a very strong influence on the properties and performance of the ablative composite. On one hand, the percentage of resin in the prepreg also indicates the percentage of reinforcement in the composite. Reinforcement directly contributes to the strength and stiffness properties while the phenolic resin contributes to the ablative and thermal properties. Hence, the optimum resin content is critical from the functional point of view. Secondly, the amount of resin content in the prepreg has a direct correlation with the amount of resin in the final composite. Excess or scarcity of resin in the composite gives rise to defects in the composites. More resin leads to resin rich lines, resin patches and accumulated resin at the edges and corners. If less than optimum amount of resin is present, then more serious defects like resin lean lines and even delaminations can result. If sufficient amount of resin is not available for proper adhesion of adjacent layers, physical separation of plies may occur, leading to delaminated composite structures. Hence, elaborate nondestructive testing was done on all the laminates before preparation of specimens. From the visual, ultrasonic and radiographic inspection done on the composites, optimum resin content for the composites which would lead to composites without any structural defect was concluded.

6.3.1 Resin content in the carbon phenolic prepreg

Laminates were prepared using carbon phenolic prepreg with different wet resin content values. Since it was difficult to maintain the value of wet resin content in a laminate at a fixed value, prepregs with resin content within a variation of 5% were selected and used for a particular laminate. During impregnation of the reinforcement fabric with phenolic resin the variation in wet resin content generally varies in a band of 5 to 10% due to the inherent variations in the thickness of the fabric. Even by setting the squeeze rollers to the desired gap settings, due to the variations in the thickness of the fabric across the width, variation in resin pickup was inevitable.

To study the effect of resin content on thermal and mechanical properties of carbon phenolic, four sets of prepregs were prepared in the following wet resin content ranges. Values of resin content below 35% could not be used for laminate preparation since adequate resin was not available in the prepreg for satisfactory bonding between plies. The laminate was found to have separation of layers during the processing stage itself. Ultrasonic inspection also confirmed delaminations in laminates with resin content below 35%. On the higher side, when the resin content was increased beyond 55%, excess resin was found to be flowing on the prepreg at the prepregging stage itself. This led to severe handling and processing difficulties. Chances of unacceptable defects were very high if prepreg with resin content more than 55% was used. Hence, laminates were made from prepreg whose resin content was maintained in the following ranges.

i) 35% to 40 %

ii) 40% to 45%

iii) 45% to 50% and

iv) 50% to 55%

Laminates were prepared using each set of these prepregs and specimens were prepared for evaluating the thermal and mechanical properties. Table 6.13 shows the variations in thermal properties observed in the different ranges of resin contents.

Table 6.13: Variations in thermal properties of carbon phenolic composites processed at different resin content %

Prepreg parameters, WRC,%	**35 - 40**	**40- 45**	**45- 50**	**50 -55**
Density (g/cc)	1.44	1.421	1.407	1.388
Erosion rate- along ply (mm/s)	0.033	0.034	0.037	0.039
Erosion rate- across ply (mm/s)	0.031	0.033	0.033	0.035
Heat of ablation (cal/g)	8480	8510	8590	8580
Thermal conductivity ,along ply (W/mK)	1.03	1.07	1.11	1.11
Thermal conductivity ,across ply (W/mK)	0.73	0.77	0.80	0.81
Specific heat (J/kg.K)	1307	1245	1186	1274

A clear pattern in the behavior of erosion emerged from the results. As the resin content increased, the erosion rate also increased as seen in Figure 6.6. The resin in the composite charred when it was subjected to temperatures above the pyrolysis temperature. The presence of more resin in the composite may have led to more charring during the erosion test. This behavior was noticed to be similar for both along the ply and across the ply directions since the behavior of resin was the same in both cases. However, the difference in erosion rate was not very significant and may not really be very critical. The density of the laminates decreased with increase in the resin content as seen from Figure 6.7. This was because the resin has lesser density (1.10 to 1.20 g/cc) than the reinforcement (1.750 to 1.765 g/cc). Hence as the percentage of resin content increased, the density of the composite decreased. The decreasing trend was linear. The thermal conductivity in both the ply directions also remained more or less constant as observed from the test data.

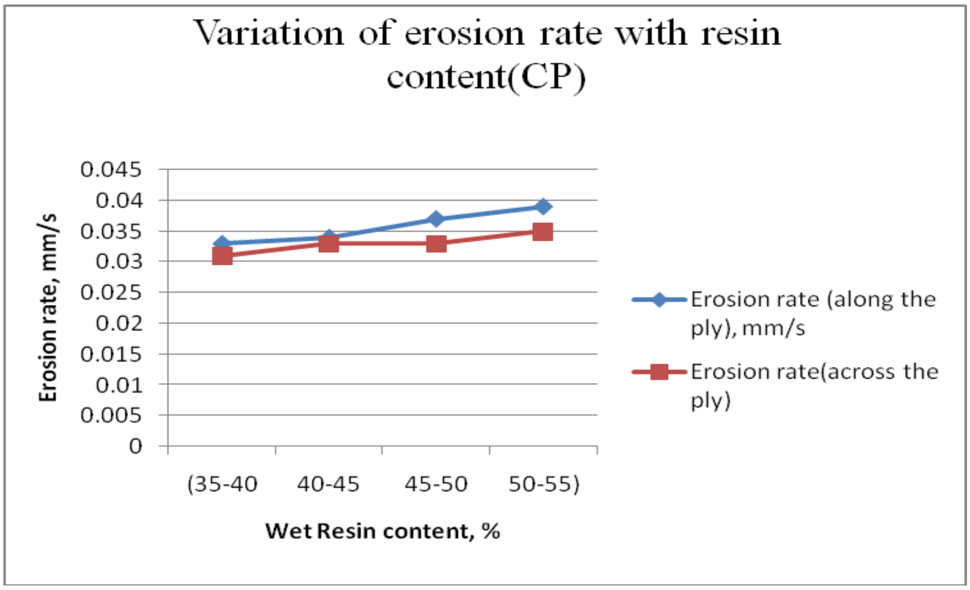


Figure 6.6: Variation of erosion rate with resin content in the CP prepreg

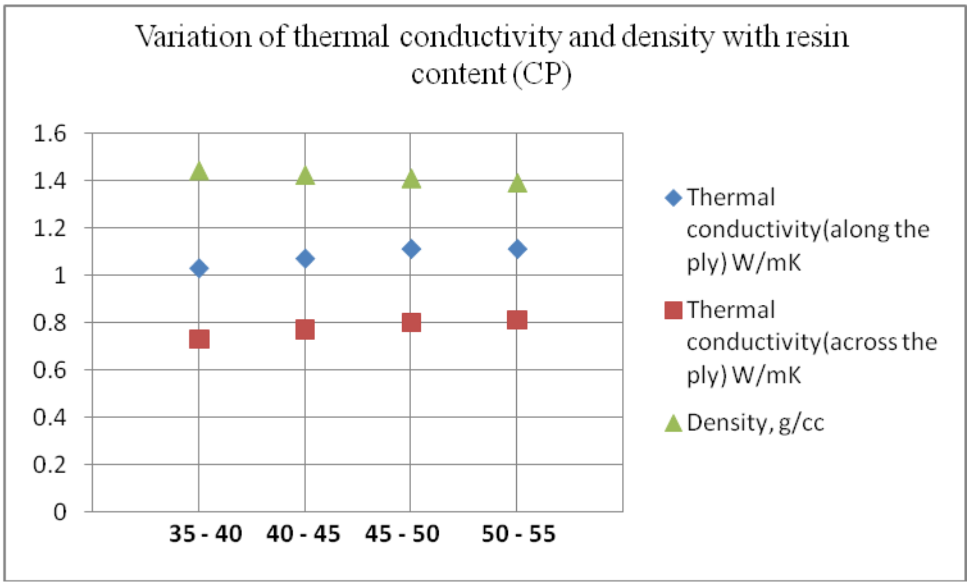


Figure 6.7: Variation of Density and thermal conductivity with resin content in the CP prepreg

The values of the heat of ablation evaluated for different ranges of resin contents too did not exhibit major differences as depicted in Figure 6.8. The values ranged from 8480 cal/g for the resin content band of 35 to 40% to 8580 cal/g for the resin content of 50 to 55%. These were well within the normal dispersion bounds. Similar observations were made in the case of specific heat also. In the specimen level, the amount of heat required for ablation did not vary much since the difference in resin content did not significantly alter the ablation characteristics of the composite. Hence it was concluded that these properties were not significantly affected by the changes in the resin content of carbon phenolic prepreg variations between 35 to 55%.

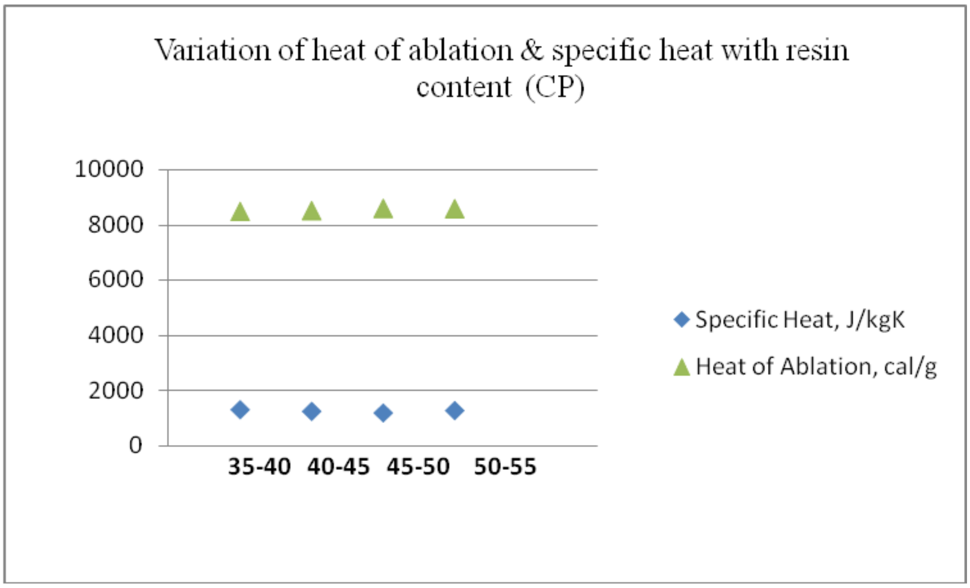


Figure 6.8: Variation of thermal properties (heat of ablation and specific heat) with resin content in the CP prepreg

However, interesting observations were made during the evaluation of mechanical properties from the carbon phenolic laminates. As seen in Table 6.14 and Figure 6.9, as the resin content in the prepreg increased, the mechanical properties showed a clear decreasing trend. For example, the average compressive strength along the ply direction was 310 MPa for resin content of 35 to 40%. It reduced to 247 MPa when the resin content was increased by 5%, further reduced to 224 MPa for the next 5% and to 207 MPa for the next 5% at 50 to 55% resin content. Similar reduction was seen in compressive strength across the ply direction also. Here, for 5% increase in resin content, 16% reduction was seen from 35-40% to 40-45% band. Further, 5% increase in resin content showed further reduction of 20% in strength properties. Similar trend was seen in the modulus properties also. Considerable reduction was noticed as the resin content was increased. However, a peculiar observation was noticed in the ILSS behavior. For the lowest resin band of 35-40%, the ILSS was 29.4 MPa. It increased by 20% as the resin content was increased by 5%. However, on further increasing the resin content by 5% to 45-50%, again a decreasing trend is seen. Substantial reduction of around 45% was noticed when the resin content was further increased to 50-55%. This led to the conclusion that ILSS does not follow the trend of the other mechanical properties like compressive strength and modulus. This is because ILSS is a resin dominant property; the interlaminar shear strength is achieved by the contribution of the resin adhesion to the adjacent plies. There seems to be an optimum resin content which provides the best interlaminar shear strength. For this carbon phenolic prepreg, from the test results, the optimum resin content band is 40% to 45% to achieve the best ILSS.

Table 6.14: Variations in mechanical properties of carbon phenolic composites processed at different resin content %

Prepreg parameters, WRC,%	**35 - 40**	**40- 45**	**45- 50**	**50 -55**
Compressive strength - along ply (MPa)	310	247	224	207
Compressive strength - across ply (MPa)	543	457	366	240
Compressive modulus - along ply (GPa)	14.3	13.2	12.1	11.7
Compressive modulus - along ply (GPa)	13.9	13.7	12.9	10.3
Interlaminar shear strength (MPa)	29.4	35.4	31.2	17.1

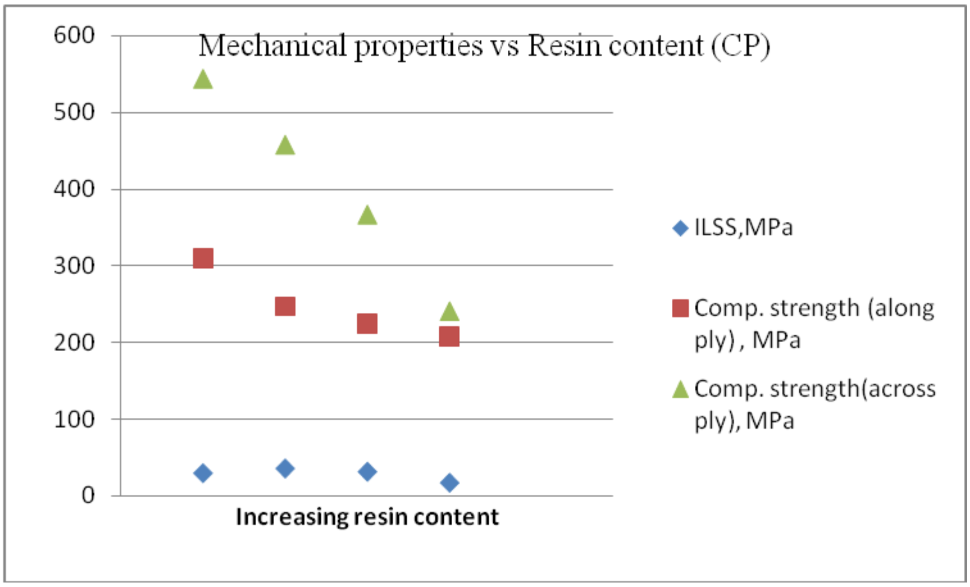


Figure 6.9: Variation of mechanical properties (CS and ILSS) with resin content in the CP prepreg

From the experimental results of carbon phenolic, it can be inferred that the thermal properties are generally not affected significantly by the variation in the resin content. However, the mechanical properties were affected by the variation in resin content. As the resin content in the prepreg increased, the compressive strength and compressive modulus in both along and across the ply directions were found to decrease. However for ILSS, the values were the maximum at an intermediate range of 40% to 45% and were seen to be lower at the other resin content ranges above and below this range. Considerable difference is magnitude was also noticed for ILSS. The other thermal and mechanical properties were also good for the resin content range of 40 to 45%. Hence, from the point of view of the properties, it was inferred that the resin content of 40 to 45 % is an optimum range for this type of carbon phenolic prepreg.

Nondestructive evaluation of the laminates was carried out using ultrasonic testing method. In the first laminate (35 to 40%), minor resin lean lines with nonuniform resin distribution were observed. These resin lean lines could be the initiating points for serious defects like delaminations and hence were not desirable. For the second and third laminates with resin contents in the 40-45%

and 45-50%, no defects were noticed and were found to be structurally integral with uniform resin distribution. For the fourth laminate with resin content between 50-55%, resin rich lines and resin accumulated patches were noticed due to the presence of higher resin in the composite. However, no delaminations were noticed. So it was concluded from NDT results that the resin content band between 40 and 50 % provided laminates without defects and with good structural integrity.

6.3.2 Resin content in the silica phenolic prepreg

Similar experiments and nondestructive evaluation were carried out using silica phenolic prepreg also. Laminates were prepared using silica phenolic prepreg with different wet resin content values in the following ranges. Unlike in the case of carbon phenolic, in the case of silica phenolic, laminate processed with a resin content of 30%-35% came out without any significant defects like delamination. However on the higher side, values of resin content above 50% led to excessive resin accumulation and nonuniform resin distribution. This difference in behavior was due to the difference in the wetting characteristics of the different types of reinforcement fabrics. Hence, the experiments were planned to be done on four laminates processed with the following bands of resin contents.

i) 30 % to 35%

ii) 35% to 40 %

iii) 40% to 45% and

iv) 45% to 50%

Laminates were prepared using each set of these prepregs and specimens were prepared for evaluating the thermal and mechanical properties. Table 6.15 shows the variations in thermal properties of specimens made from laminates of different resin contents.

From Table 6.15, it was inferred that that the thermal properties were not significantly affected by the changes made in the resin content of the silica phenolic prepreg also. In the same lines observed for carbon phenolic, the density for the laminate with the least resin content (30-35%) was the highest and the values kept on decreasing with increase in resin content. The erosion characteristics remained rather unaffected with only minor variations in the values when the resin content was altered in different bands. This behavior remained the same in both along and across the ply directions as seen from Figure 6.10. Figure 6.11 shows the comparison of heat of ablation and specific heat of specimens processed at different resin contents. Heat of ablation too remained in the same range for specimens made from the four different laminates. Thermal conductivity in both the directions also showed the same trend with all the values remaining in the same range as seen from Figure 6.12. Specific heat too was not found to be affected much by the change in resin content. As observed in the case of carbon phenolic laminates, it was observed that these properties were not significantly affected by the changes in the resin content of silica phenolic prepreg variations between 30 to 50%.

Table 6.15: Variations in thermal properties of SP composites processed at different resin content %

Prepreg parameters, WRC,%	**30-35**	**35 - 40**	**40- 45**	**45- 50**
Density (g/cc)	1.81	1.78	1.75	1.69
Erosion rate- along ply (mm/s)	0.027	0.028	0.029	0.029
Erosion rate- across ply (mm/s)	0.021	0.021	0.023	0.023
Heat of ablation (cal/g)	7850	7920	7890	7810
Thermal conductivity - along ply (W/mK)	0.61	0.60	0.59	0.54
Thermal conductivity - across ply (W/mK)	0.48	0.47	0.44	0.44
Specific heat (J/kg.K)	940	893	864	903

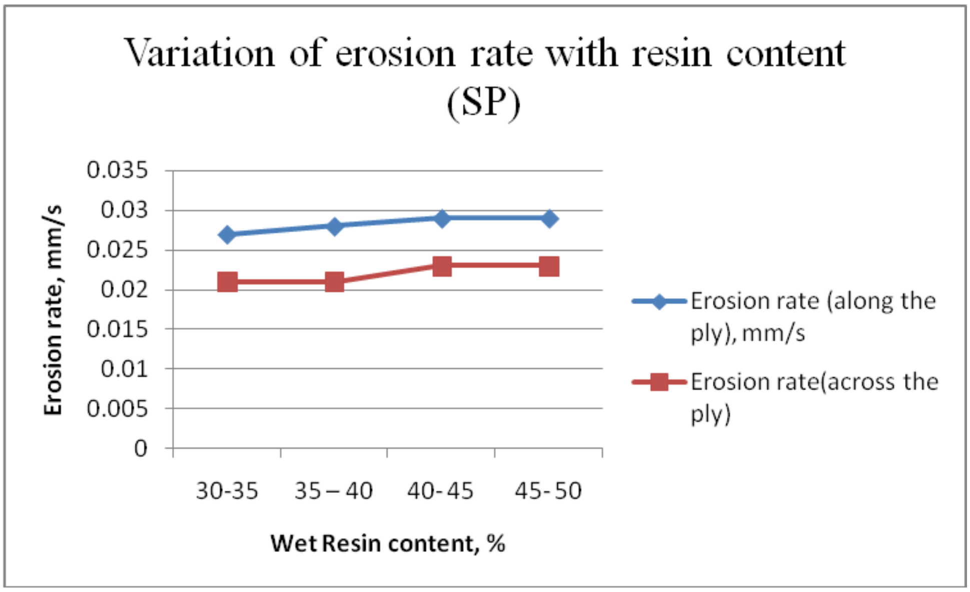


Figure 6.10: Variation of erosion rate with resin content in the SP prepreg

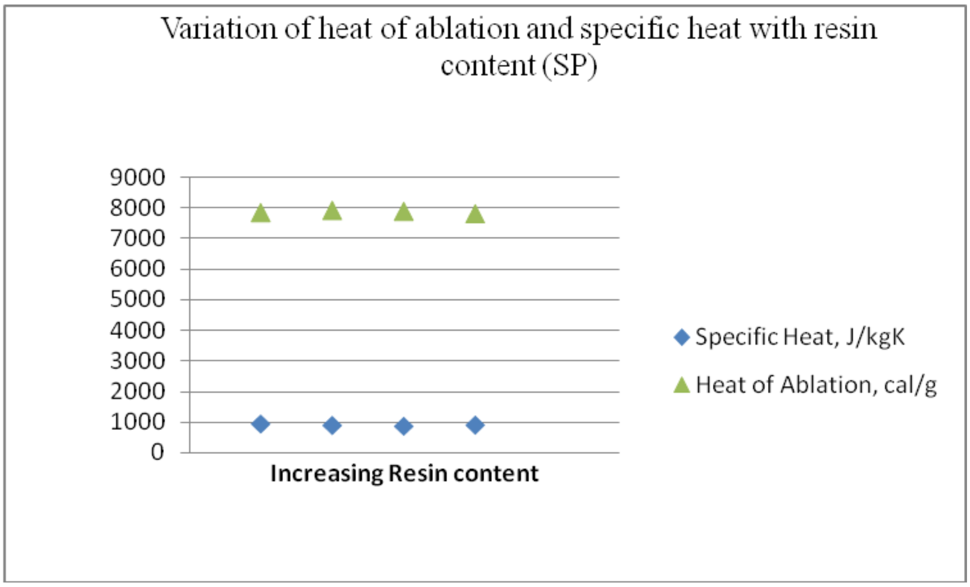


Figure 6.11: Variation of heat of ablation and specific heat with resin content in the SP prepreg

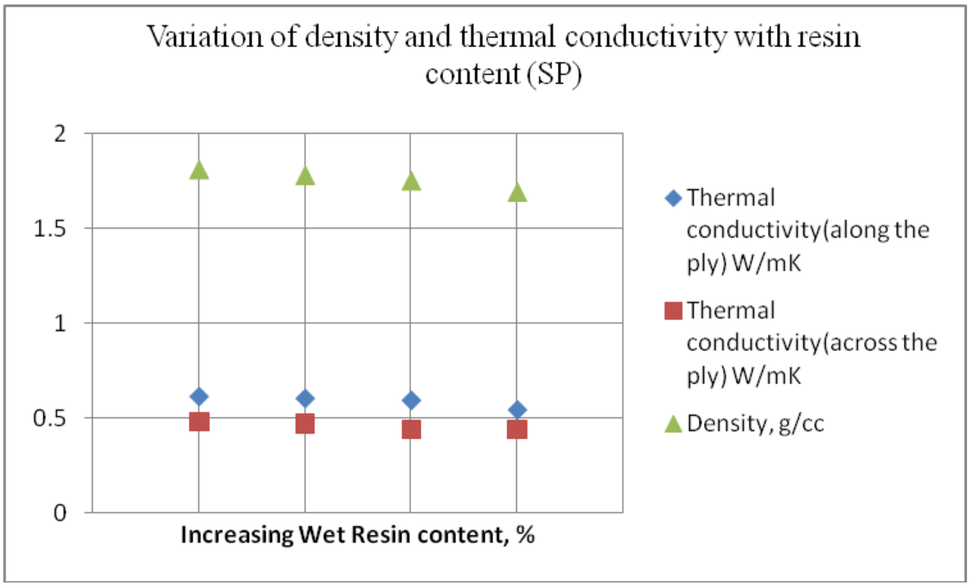


Figure 6.12: Variation of thermal conductivity and density with resin content in the SP prepreg

As far as the mechanical properties were concerned, it was observed that the changes in the values of the resin content affected the properties. The behavior was more or less similar to the trends observed for carbon phenolic laminates. The variations in the mechanical properties of silica phenolic laminates for different resin content values are tabulated in Table 6.16.

As the resin content in the prepreg increases, the compressive strength in both along and across the ply directions was found to decrease as seen from Figure 6.13. Though the decreasing trend was noticed with increase in the resin content values for compressive modulus also, the reduction was only marginal. It may be within the same dispersion range. However for ILSS, the values were the maximum at an intermediate range of 35% to 40% and were seen to be lower at the other resin content ranges above and below this range. These trends are depicted in Figure 6.14. The ILSS values were found to be optimum for 35 to 40 % and thereafter it was found to be decreasing. A lower resin content than the optimum causes insufficient bonding between the layers leading to lower ILSS. When the resin content is the optimum, good interlaminar shear resistance is exhibited by the composite. Thereafter, due to excess resin content, the resin accumulation and resin patches may lead to weaker interlaminar zones where the fibre content is lesser and the fibre to resin bond is nonuniform. These areas were prone to early failure leading to lower ILSS values.

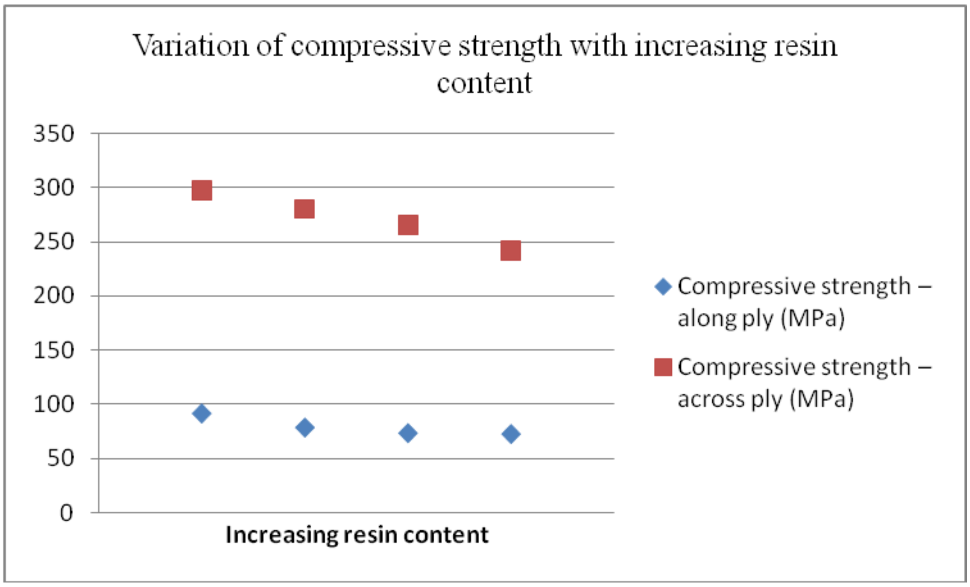


Figure 6.13: Variation of CS with resin content in the SP prepreg

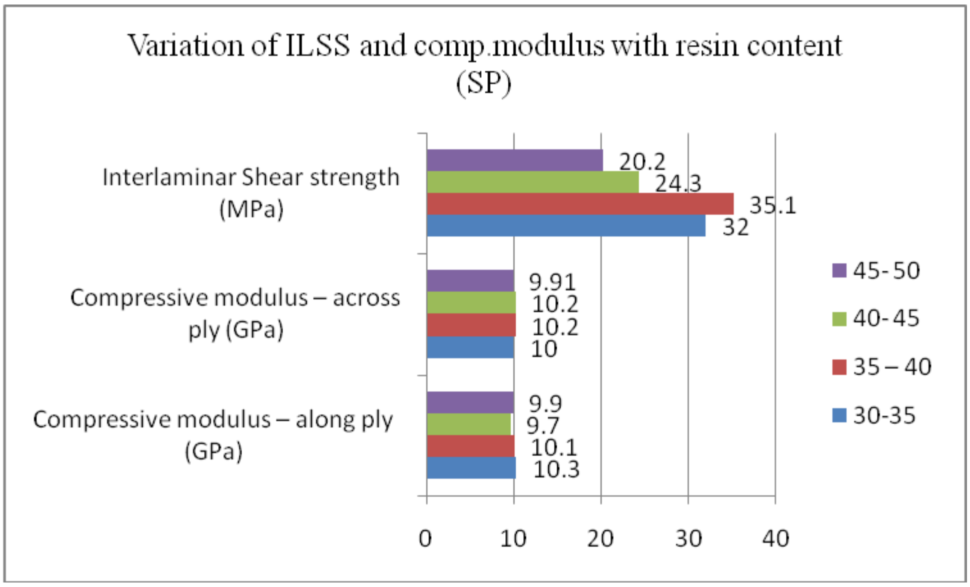


Figure 6.14: Variation of compressive modulus and ILSS with resin content in the SP prepreg

Considerable difference is magnitude was also noticed for ILSS. The other thermal and mechanical properties were also good for the resin content range of 35 to 40%. Hence, from the point of view of the properties, it was inferred that the resin content of 35 to 40 % is an optimum range for this type of silica phenolic prepreg. Higher resin content leads to the reduction in mechanical properties since the amount of fibre reinforcements reduces with increase in the resin content.

Table 6.16: Variations in mechanical properties of SP composites processed with different resin content %

Prepreg parameters, WRC,%	**30-35**	**35-40**	**40-45**	**45-50**
Compressive strength - along ply (MPa)	91.2	78.5	73.5	72.7
Compressive strength - across ply (MPa)	297	280	265	242
Compressive modulus - along ply (GPa)	10.3	10.1	9.7	9.9
Compressive modulus - across ply (GPa)	10	10.2	10.2	9.91
Interlaminar Shear strength (MPa)	32	35.1	24.3	20.2

Ultrasonic testing was also done on all the processed laminates. Laminates with resin content lower than 30% showed clear separation of plies as delaminations. In the laminate with resin content of 30 to 35% satisfactory bonding of layers were observed and no delaminations were present. But very minor resin lean lines were still observed. These resin lean lines could be the initiating points for serious defects like delaminations and hence are not desirable. For the second and third laminates with resin contents in the 35-40% and 40-45% range, structural integrity was confirmed in NDT. Uniform consolidation of plies with good resin distribution was noticed. For the fourth laminate with resin content between 45-50%, excessive resin rich lines and patches were noticed due to the presence of higher resin in the composite. However, clear delaminations were not noticed. So it was concluded from the NDT results that the resin content band between 35 and 45 % provided laminates without defects and with good structural integrity.

Hence, it was observed from the experimental results that both carbon phenolic and silica phenolic laminates exhibited similar characteristics. However, the optimum ranges of resin content for good mechanical properties were slightly different for the two types of reinforcements. The observations on the quality of the laminates as tested by ultrasonic testing were also considered while suggesting the optimum resin content values for the laminates. For carbon phenolic, the optimum resin content range for prepregs used for laminates with good properties and structural integrity is 40 to 50% and for silica phenolic the corresponding optimum range is between 35 and 40%. As the resin content increases, in general, the mechanical strength properties showed a decreasing trend. This was more pronounced in compressive properties and less sensitive in stiffness values. Thermal properties show a lesser dependence on resin content values. When the resin content values are below the optimum ranges, delaminations with physical separation of plies were noticed and when the resin content values were above the optimum range, resin rich lines/patches appeared causing nonuniformity and reduction in structural integrity. Figure 6.15 shows a typical silica phenolic ablative composite with delamination and resin lean lines due to lesser than optimum resin content values in the prepreg.

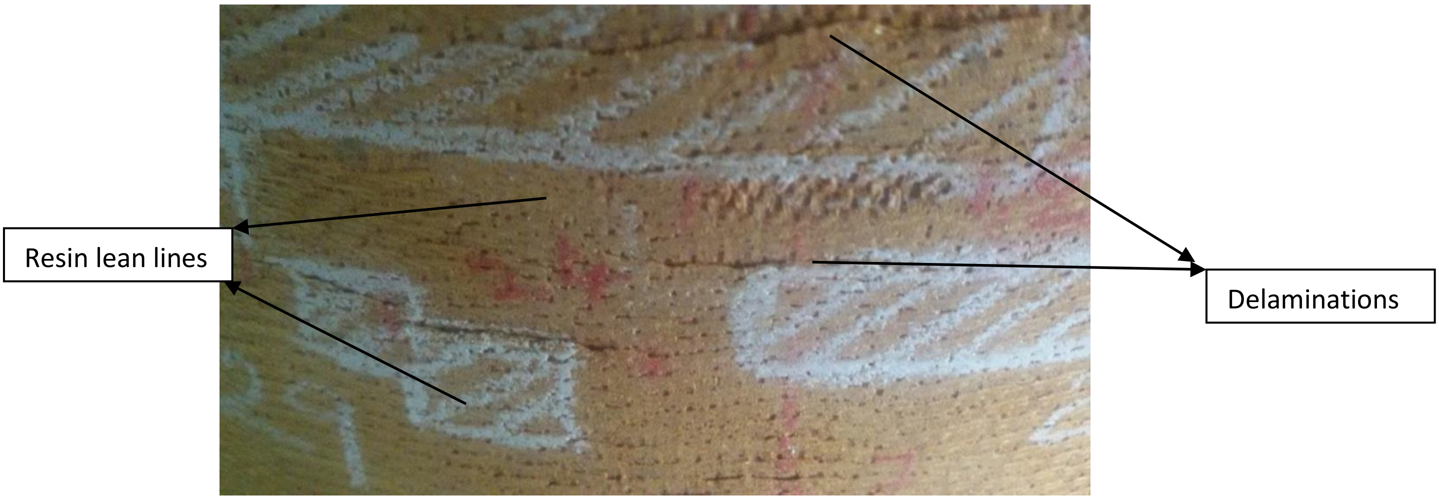


Figure 6.15: Delaminations and resin lean lines in SP composite

Though the matrix resin used is the same, the difference in the optimum resin content in the prepreg is attributed to the different wetting characteristics of the fabrics.

6.4 Cure temperature

Cure temperature of the ablative composite is one of the major process parameters which is strictly controlled and monitored during the processing of an ablative composite. It is expected to have a very significant influence on the mechanical and thermal properties of the ablative. To assess the extent of the influence of the cure temperature on the properties of the ablatives, composite liners were processed at three different cure temperatures of 135°C, 155°C and 180°C. In all the experiments, the composite was soaked at this cure temperature for three hours to ensure that uniform temperature is achieved in all zones of the composite and no thermal gradients existed in the laminate. The experiments were carried out separately for both carbon phenolic and for silica phenolic composites.

After screening out the defective areas in the laminates through nondestructive testing, specimens were prepared and mechanical and thermal properties were evaluated and compared. The observations and inferences from the experiments performed on silica phenolic laminates are discussed first. Table 6.17 gives the comparison of thermal properties achieved in silica phenolic laminates processed at the three selected cure temperatures of 135ºC, 150 ºC and 180 ºC. All the critical thermal properties like heat of ablation, specific heat and thermal conductivity were evaluated. The functional performance parameter of resistance to erosion too was measured for comparison. The erosion rate in both along and across the ply directions do not show much dependence on the cure temperature as all the values of the tested samples fall in the same band itself with minor variations as seen from Figure 6.16.

Table 6.17: Comparison of thermal properties of SP composites processed at different cure temperatures

Cure temperature,°C	**135**	**150**	**180**
Density (g/cc)	1.76	1.78	1.78
Erosion rate- along ply (mm/s)	0.030	0.028	0.029
Erosion rate- across ply (mm/s)	0.025	0.024	0.025
Heat of ablation (cal/g)	7600	8380	8400
Thermal conductivity - along ply (W/mK)	0.61	0.6	0.59
Thermal conductivity - across ply (W/mK)	0.48	0.47	0.44
Specific heat (J/kg.K)	998	1040	1037

The density evaluated from the three samples showed minor differences only (Figure 6.17). However, it was noticed that as the cure temperature was increased from 135ºC to 150 ºC, there was a minor increase in density whereas beyond 150ºC to 180 ºC, there was no further increase in density. From this observation, it was inferred that sufficient consolidation of the prepreg plies and curing has been completed at 150ºC itself and further increase of curing temperature does not improve the density.

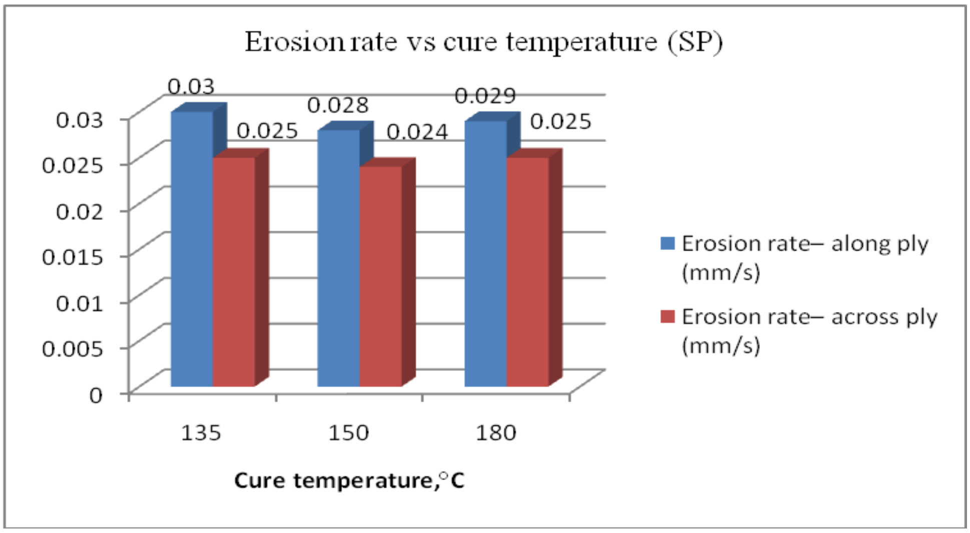


Figure 6.16: Erosion rate vs. cure temperature for SP composites

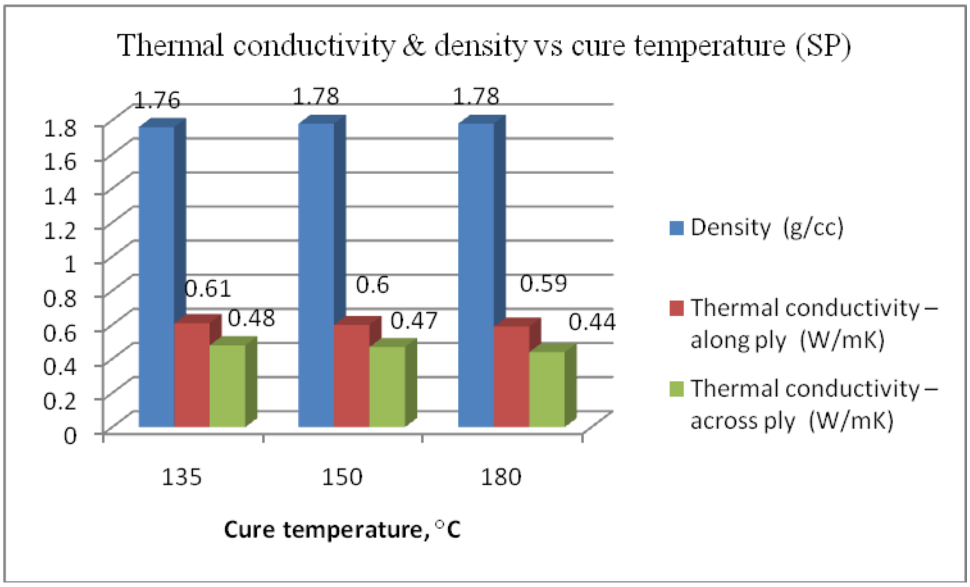


Figure 6.17: Density & thermal conductivity vs. cure temperature for SP composites

Similar observations were noted in the case of other thermal properties like specific heat, thermal conductivity and heat of ablation. The values obtained for samples cured at 150ºC showed marginally better values than the values of samples cured at 135ºC. But further improvement was not seen when the cure temperature was increased to 180ºC. These observations led to the inference that the cross-linking of polymers and thereby the curing is completed at 150ºC. Thus satisfactory thermal properties were built in the composite by curing at this temperature itself and further raising the cure temperature to 180ºC was not providing considerable improvement in the thermal properties of silica phenolic composites. The higher cure temperature also meant higher energy consumption, higher process cycle time and higher process cost. Hence, a cure temperature of 150ºC was providing satisfactory thermal properties and optimum process time and cost.

Similar observations were obtained from the comparison of mechanical properties evaluated from silica phenolic laminates cured at the different cure temperatures. Table 6.18 shows the comparison of mechanical properties.

Table 6.18: Comparison of mechanical properties of SP composites processed at different cure temperatures

Cure temperature,°C	**135**	**150**	**180**
Compressive strength - along ply (MPa)	75.2	107.5	97.2
Compressive strength - across ply (MPa)	252	307	295
Compressive modulus - along ply (GPa)	7.7	12.1	10.7
Compressive modulus - along ply (GPa)	6.6	10.7	10.0
Interlaminar shear strength (MPa)	23.75	35.72	32.20

The compressive strength along the ply direction increased by around 43% when the cure temperature was increased from 135ºC to 150ºC. This was a substantial increase but as the cure temperature was further increased to 180ºC, the strength values were observed to be reducing by 9%. The compressive strength across the ply direction also showed a similar trend of the value increasing from the cure temperature of 135ºC to 150ºC and then again reducing at 180ºC. These are depicted in Figure 6.18.

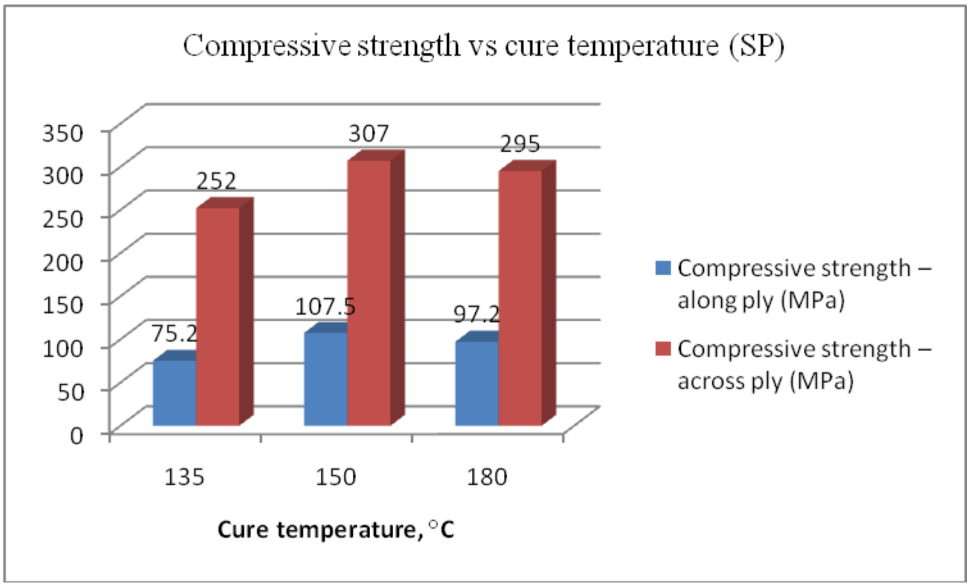


Figure 6.18: Compressive strength vs. cure temperature for SP composites

As seen from Figure 6.19, for compressive modulus, a cure temperature of 150ºC gave the best results. For ILSS, the values increased by almost 50% as the cure temperature was changed from 135ºC to 150ºC and further was found to decrease by about 10% as the cure temperature was further increased to 180ºC. So for all the mechanical properties the same behavior was observed. Hence, it was concluded that for this combination of silica phenolic composite, the optimum cure temperature is around 150ºC. This is the temperature at which complete cross-linking of polymers or polymerization reaction gets completed. This leads to the attainment of full strength for the composite. At temperatures below this optimum cure temperature, complete polymerization reaction does not take place and consequently, full strength properties are not achieved. On the other hand, once the composite is completely cured, further increasing the cure temperature appears to be detrimental to the properties as there is no further increase in the property values and even a slight reduction was observed in certain cases. The reduction can be attributed to the undesirable post curing wherein the resin get overcharred leading to the slight reduction in the strength values [118].

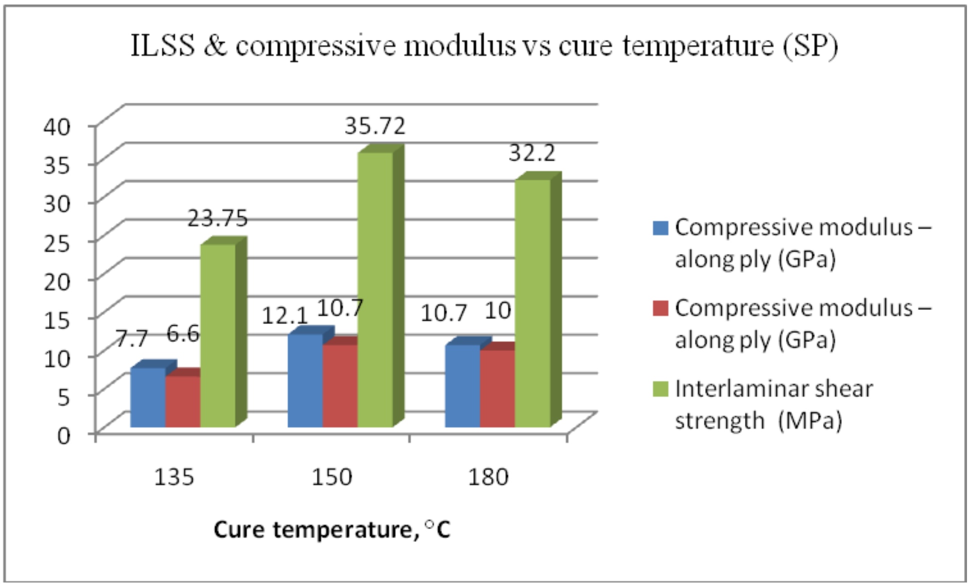


Figure 6.19: ILSS & Compressive modulus vs. cure temperature for SP composites

The same set of experiments was repeated by changing the reinforcement from silica to carbon using the same phenolic resin and following identical process parameters. Table 6.19 gives the comparison of thermal properties evaluated for carbon phenolic composite laminates process at the three different cure temperatures. Almost similar observations were obtained for carbon phenolic too.

Table 6.19: Comparison of thermal properties of CP composites processed at different cure temperatures

Cure temperature,°C	**135**	**150**	**180**
Density (g/cc)	1.39	1.41	1.41
Erosion rate- along ply (mm/s)	0.030	0.028	0.030
Erosion rate- across ply (mm/s)	0.025	0.021	0.022
Heat of ablation (cal/g)	8100	8680	8400
Thermal conductivity - along ply (W/mK)	1.03	1.13	1.07
Thermal conductivity - across ply (W/mK)	0.77	0.81	0.74
Specific heat (J/kg.K)	1268	1310	1290

The optimum cure temperature for carbon phenolic too was observed to be 150ºC where good thermal properties were obtained. Density values were the best for this temperature and the critical properties of erosion and heat of ablation did not seem to vary much with the cure temperatures. Mechanical properties were also evaluated and compared for carbon phenolic composites. The values of the mechanical properties of carbon phenolic composites are tabulated in Table 6.20.

Table 6.20: Comparison of mechanical properties of CP composites processed at different cure temperatures

Cure temperature,°C	**135**	**150**	**180**
Compressive strength - along ply (MPa)	210	297	290
Compressive strength - across ply (MPa)	458	522	498
Compressive modulus - along ply (GPa)	7.9	12.1	11.7
Compressive modulus - along ply (GPa)	7.2	11.7	10.5
Interlaminar shear strength (MPa)	23.4	33.7	31.7

As evident from Figure 6.20, for compressive strength, an increase of around 41% was noticed when the cure temperature was changed from 135ºC to 150ºC. Further, while increasing to 180ºC, there was a minor reduction in strength from 297 MPa to 290 MPa.

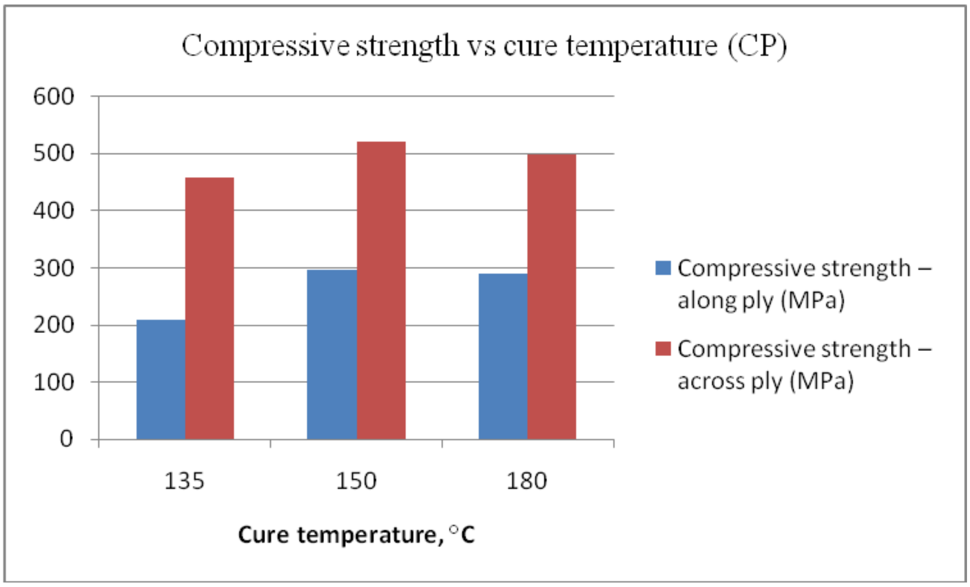


Figure 6.20: Compressive strength vs. cure temperature for CP composites

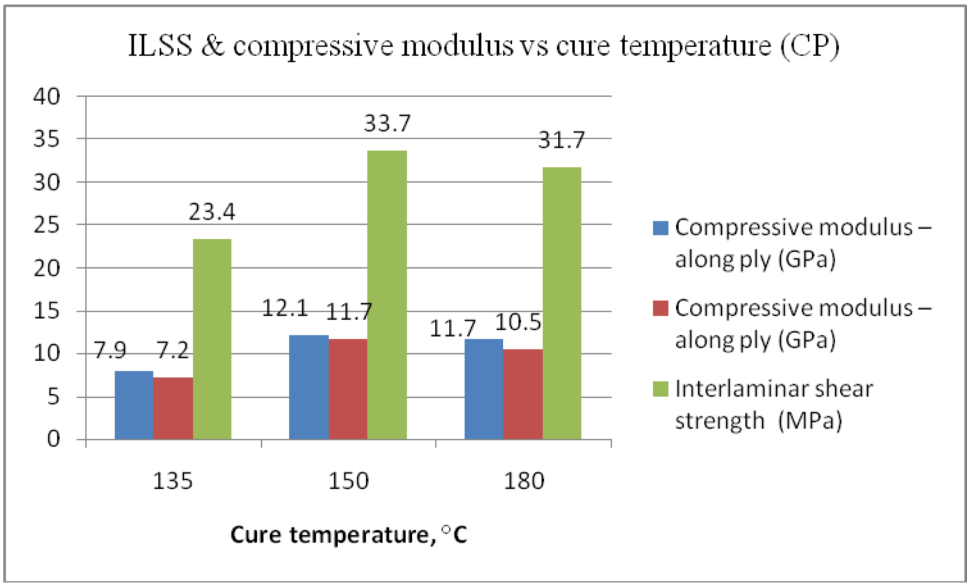


Figure 6.21: ILSS & Compressive modulus vs. cure temperature for CP composites

The stiffness property values too exhibited similar trend showing the best values at a cure temperature of 150ºC as seen from Figure 6.21. The ILSS values were improved by about 30% when the temperature of cure was increased from 135ºC to 150ºC.

For 180ºC, no major change was observed. Hence, for carbon phenolic composites also, a cure temperature of 150ºC was observed to be the optimum one as composites cured at this temperature exhibited good thermal and mechanical properties at lower process cost and time. The change in reinforcement had not affected the optimum cure temperature as the resin was the element which undergoes the chemical reactions of polymerization during curing.

6.5 Cure pressure

After determining the optimum cure temperature as 150ºC, investigations were carried out on the cure pressure for ablative composites. Cure pressure is an equally important process parameter which influences the ablative composite properties. It affects the consolidation and the compaction of the liner as reflected in the density. The other mechanical and thermal properties are also likely to be affected by this parameter. The experimental values of cure pressures were determined taking into consideration the facility limitations as well as process constraints. From the initial trials itself it was evident that lower values of cure pressures led to insufficient compaction. Such laminates had many defects like delaminations. Due to insufficient consolidation the plies of the laminate were disintegrating and physically separating during the machining of specimens. Hence, laminates with cure pressures less than 25 bar were not considered.

To understand the effect of cure pressure and to arrive at an optimum value, experiments with different cure pressures were conducted at 25 bar, 40 bar, 55 bar and 65 bar. Higher pressures could not be attempted due to facility limitations and safety concerns. Experiments were conducted for both carbon phenolic as well as for silica phenolic composites. The maximum cure temperature was maintained constant at 150°C for all the experiments. The other curing parameters like vacuum, heating rate and cooling rate were maintained constant and only the cure pressure was altered. Screening of the laminates using ultrasonic inspection to rule out defects was done. The property evaluation was completed as per the standard test matrix for all the thermal and mechanical properties. The results were tabulated and compared in Tables 6.21 to 6.24.

Table 6.21 gives the comparison of thermal properties achieved in silica phenolic laminates processed at the four selected cure pressures of 25 bar, 40 bar, 55 bar and 65 bar. As expected, the density of the composite increased with increase in curing pressure as higher pressure helped in compacting the layup more effectively. With increase in the cure pressure and better compaction, the thermal properties improved systematically and higher pressures gave superior performance. Better compaction led to better resistance to erosion and degradation of the ablative when exposed to heat flux.

Table 6.21: Comparison of thermal properties of SP composites processed at different cure pressures

Cure pressure, bar	**25**	**40**	**55**	**65**
Density (g/cc)	1.74	1.76	1.79	1.80
Erosion rate- along ply (mm/s)	0.035	0.033	0.028	0.028
Erosion rate- across ply (mm/s)	0.035	0.031	0.026	0.025
Heat of ablation (cal/g)	7850	8150	9120	9454
Thermal conductivity - along ply (W/mK)	0.59	0.60	0.61	0.61
Thermal conductivity - across ply (W/mK)	0.44	0.44	0.46	0.48
Specific heat (J/kg.K)	922.5	943	955	988

Table 6.22 is the tabulation of the comparison of mechanical properties achieved in silica phenolic laminates processed at the three selected cure pressures of 25 bar, 40 bar, 55 bar and 65 bar.

Table 6.22: Comparison of mechanical properties of SP composites processed at different cure pressures

Cure pressure, bar	**25***	**40**	**55**	**65**
Compressive strength - along ply (MPa)	181	204	287	304
Compressive strength - across ply (MPa)	590	645	725.69	764
Compressive modulus - along ply (MPa)	13.08	13.45	14.38	15.03
Compressive modulus - across ply (MPa)	12.87	13.02	15.54	17.23
Interlaminar shear strength (MPa)	27.41	33.54	49.66	56.35

*- delaminations were noticed.

In the experiments evaluating mechanical properties also, the effect of cure pressure was evident. As pressure increased, the compressive strength and modulus increased linearly (Figure 6.22).

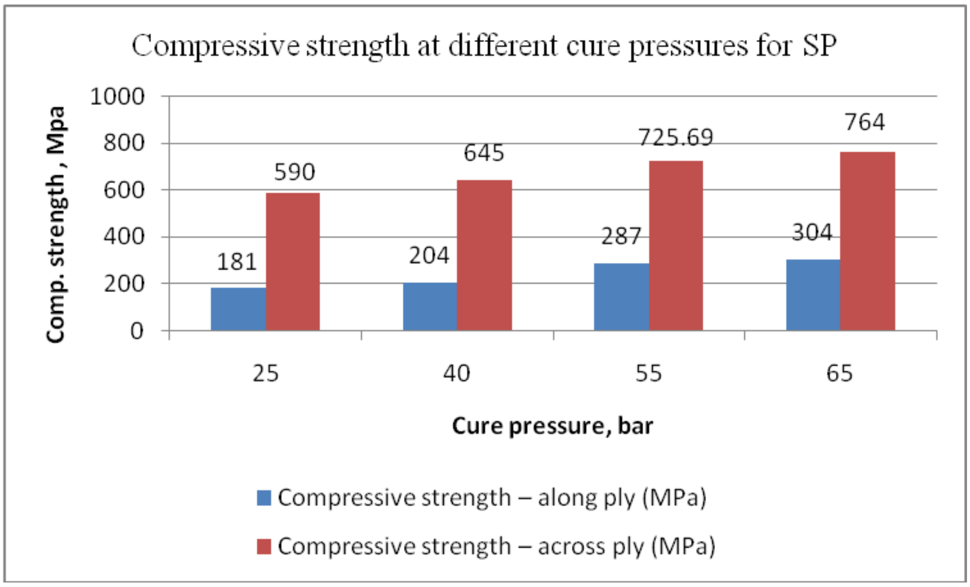


Figure 6.22: Compressive strength vs. cure pressure for SP composites

Another observation was the presence of delaminations in the specimens cured at 25 bar. This led to the conclusion that pressures less than 25 bar should be avoided for curing silica phenolic composites. Though the thermal properties were satisfactory, the presence of delaminations can lead to fatal failures during operations. Higher cure pressure guarantees good thermal and mechanical properties and thereby higher performance during the service conditions.

The experiments were repeated for carbon phenolic laminates also maintaining the similar conditions. Table 6.23 gives the comparison of thermal properties achieved in carbon phenolic laminates processed at the three selected cure pressures of 25 bar, 40 bar, 55 bar and 65 bar. All the thermal property values were tested and compared from specimens fabricated from laminates processed at the selected cure pressures keeping all other process parameters constant.

Table 6.23: Comparison of thermal properties of CP composites processed at different cure pressures

Cure pressure, bar	**25**	**40**	**55**	**65**
Density (g/cc)	1.38	1.41	1.42	1.45
Erosion rate- along ply (mm/s)	0.035	0.033	0.028	0.028
Erosion rate- across ply (mm/s)	0.035	0.031	0.026	0.025
Heat of ablation (cal/g)	7250	7600	9200	9254
Thermal conductivity - along ply (W/mK)	1.15	1.19	1.30	1.34
Thermal conductivity - across ply (W/mK)	0.48	0.47	0.73	0.92
Specific heat (J/kg.K)	940	1010	1037	1089

In the case of carbon phenolic too, similar behavior was noticed for thermal properties. Density systematically increased with increasing cure pressure. Resistance to erosion in both directions and heat of ablation too improved with increase in cure pressure. The mechanical property evaluation exercise also yielded similar results for carbon phenolic laminates. Table 6.24 is the tabulation of the comparison of mechanical properties achieved in carbon phenolic laminates processed at the three selected cure pressures of 25 bar, 40 bar, 55 bar and 65 bar.

Unlike in the case of silica phenolics, a cure pressure of 25 bar itself yielded composites of good structural integrity. There were no delaminations or resin lean lines in the laminates. When laminates were attempted to be cured at cure pressures less than 25 bar, defects like resin lean lines and delaminations were observed in Nondestructive testing. Hence, these laminates were screened out from further evaluation. From these results, it was inferred that a minimum cure pressure of 25 bar would be ideal for curing carbon phenolic laminates to achieve satisfactory thermal and mechanical properties.

From the Table 6.24, it is seen that the compressive strength in both along the ply and across the ply directions increased with increase in cure pressure. A consistent pattern of increase could be noticed from which it can be safely inferred that the cure pressure has a direct positive correlation with the strength properties irrespective of the orientation of the plies in the specimens (Figure 6.23). Though a similar increasing trend was seen in the stiffness properties also (Figure 6.24), the increase was not substantial. The ILSS was observed to have a strong dependence on the cure pressure. Significant increase was noticed in the tested values of ILSS with increase in cure pressure. The ILSS at a cure pressure of 65 bar was more than double than that of the corresponding value at 25 bar.

Table 6.24: Comparison of mechanical properties of CP composites processed at different cure pressures

Cure pressure, bar	**25**	**40**	**55**	**65**
Compressive strength - along ply (MPa)	267	297	310	323
Compressive strength - across ply (MPa)	489	522	549	601
Compressive modulus - along ply (GPa)	11.7	12.1	12.5	12.6
Compressive modulus - across ply (GPa)	11.5	11.7	11.9	12.1
Interlaminar shear strength (MPa)	20.4	33.7	40.8	51.4

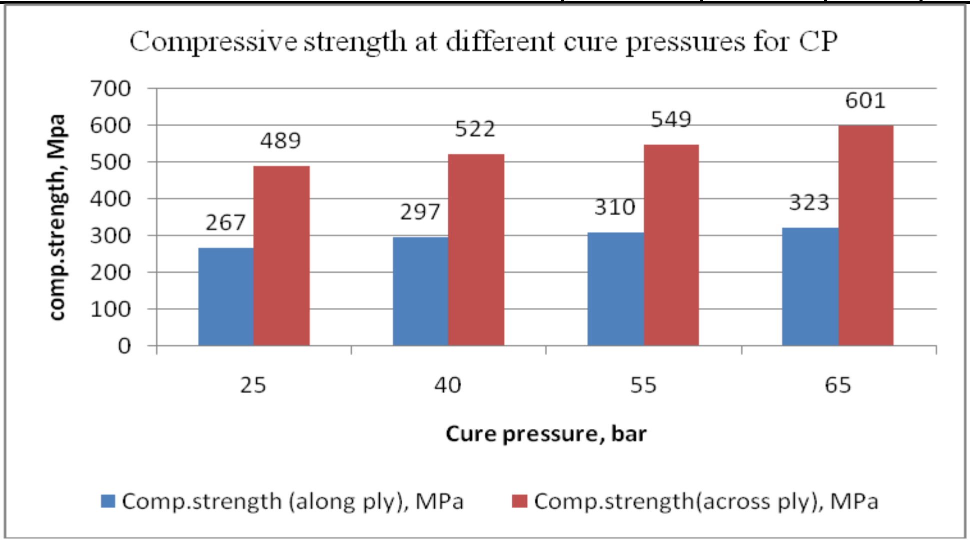


Figure 6.23: Compressive strength vs. cure pressure for CP composites

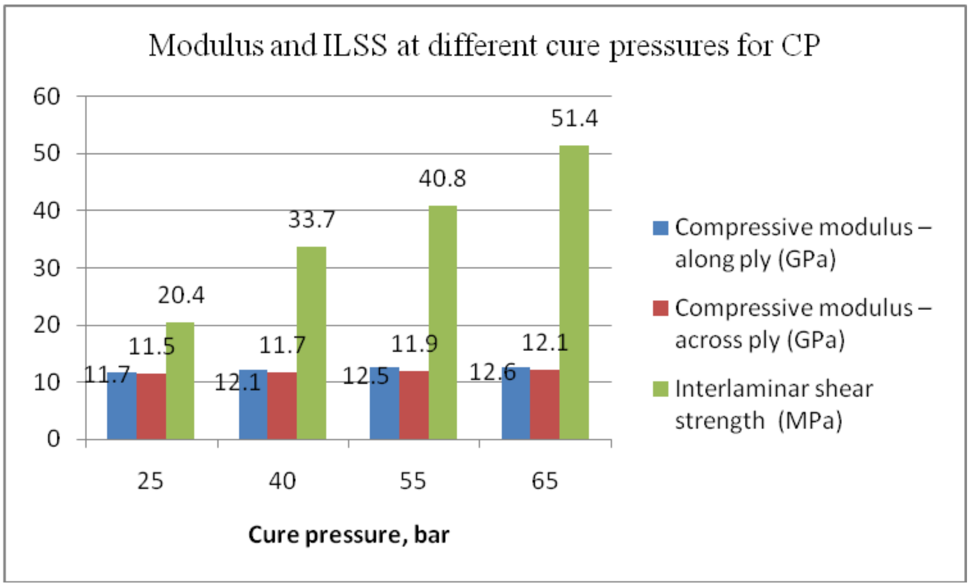


Figure 6.24: ILSS & Compressive modulus vs. cure pressure for CP composites

From the experimental results, it was concluded that the cure pressure for processing both carbon phenolic and silica phenolic composites directly influence the thermal as well as mechanical properties. For silica phenolic, cure pressures of 40 bar and above gave good results whereas for carbon phenolic, even cure pressures of 25 bar and above gave satisfactory results. This may be due to the difference in thickness of the plies and the difference in wetting characteristics of the fabrics. These observations are in line with the results obtained for cure modeling studies of Silica phenolic [118] where it was reported that a cure pressure of 35 to 40 bar could be the optimum pressure for polymerization. For carbon phenolic, being thinner and having better wetting characteristics with phenolic resins, the effective compaction was achieved at a relatively lower pressure than silica phenolic. This consolidation led to better structural integrity and better properties. Increase of cure pressure beyond 65 bar did not yield appreciable change in the properties. This is because once the resin is cured and the polymerization is completed, application of further pressure does not have any effect on consolidation or density.

6.6 Fabric ply orientation in an ablative liner to the direction of flow

During the functioning of a rocket nozzle, the rate of erosion is the most important factor influenced by the ply orientation. Other thermal parameters like the heat of ablation and specific heat are essentially the properties of the material and are not significantly affected by the ply orientation. The effect of thermal conductivity is also embedded in the rate of erosion and hence erosion rate was compared for specimens of different orientation to understand the influence of ply orientation on the performance of ablatives. A series of experiments were done to study the effect of the orientation of fibres in the reinforcements, to the direction of the flow in the nozzle, on the erosion behaviour of the composite. Fibres were oriented at different angles from 90° to 0° to the nozzle flow and resistance to erosion was assessed.

To understand the effect of ply orientation on the mechanical properties of the composite, compressive strength in both the along ply and across ply directions were evaluated and compared. Here, ILSS was not compared since ply orientation did not play any role in this property evaluation. The plies are always oriented in the same manner in the specimens for ILSS evaluation in order to ensure that the load is applied exactly along the interlaminar region. Density, being a material property, was also not expected to vary with ply orientation. All the specimens gave identical values. Table 6.25 gives the values of the erosion rates for specimens oriented at the five different ply orientations.

From the test data depicted in Figure 6.25, it was clear that when the plies are oriented at 0º to the heat flux, i.e., the plies are in line with the direction of the applied heat flux, the erosion was the minimum. As the ply angle with the direction of the heat flux increased the erosion was also increasing, though at a very small rate. However, the reverse trend was observed in the case of char advancement. When the heat affected length was measured after the test it was observed that the depth to which the composite was affected by the charring was the highest for the specimen in which the plies were oriented at 0º to the heat flux (parallel to the direction of the heat flux). The char affected zone progressively decreased with increase in the ply angle and this rate of decrease was much higher than the increase in erosion with the increase in ply angle. The char advancement was the minimum when the plies were oriented in a perpendicular direction to the direction of the heat flux. This was because the conductivity of the fibre was more than the conductivity of the phenolic resin. In the case when each ply was extending to the full length of the specimen, a clear conductive path was available for the heat flux through the length of the specimen. So the heat was quickly conducted along the length which led to faster char advancement to a greater depth. As the ply angle increases, this high conductive path length reduces leading to lesser char depth or char affected zone. At the perpendicular orientation, the heat has to travel between alternate regions of fabric and resin which provides the difficult path for the heat to conduct through the specimen. Hence, the char advancement rate was comparatively minimum in that case. Due to the relatively poor conduction heat transfer through the length, the heat got accumulated in the initial ply regions itself and this might have led to the higher disintegration of the composite material leading to comparatively higher erosion. For other ply angles, the heat conduction had improved and hence the erosion rate had reduced. However, the severity of this effect was seen to be minimal compared to the char advancement. Both erosion rate and char advancement rates are essential parameters in defining the ablative functional performance. Hence, it was concluded the extreme ply orientations were not the ideal choice for optimum performance, especially at the functionally critical zones of the nozzles.

Table 6.25: Variations in erosion rates of SP composites with different ply orientations to the direction of the flow.

Ply orientation ,°	**0**	**30**	**45**	**60**	**90**
Density,(g/cc)	1.75	1.75	1.75	1.75	1.75
Erosion rate,(mm/s)	0.027	0.029	0.031	0.031	0.033
Char advancement, (mm)	8.1	7.5	6.7	5.9	4.2

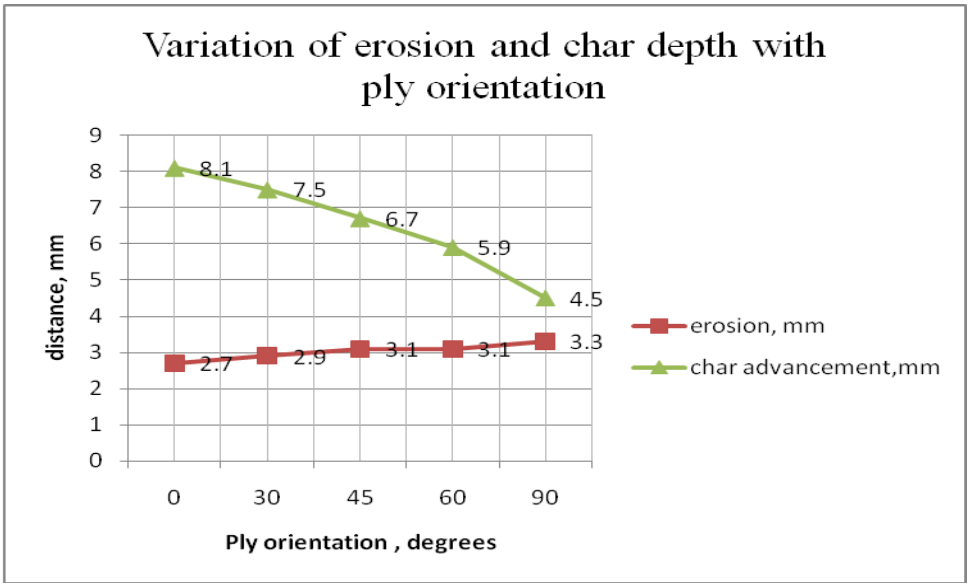


Figure 6.25: Variation of erosion and char depth for different ply orientations

Table 6.26: Variations in mechanical properties of SP composites with different ply orientations to the direction of the flow.

Ply orientation,°	**0**	**30**	**45**	**60**	**90**
Compressive strength - (MPa)	87.5	112	183	212	273

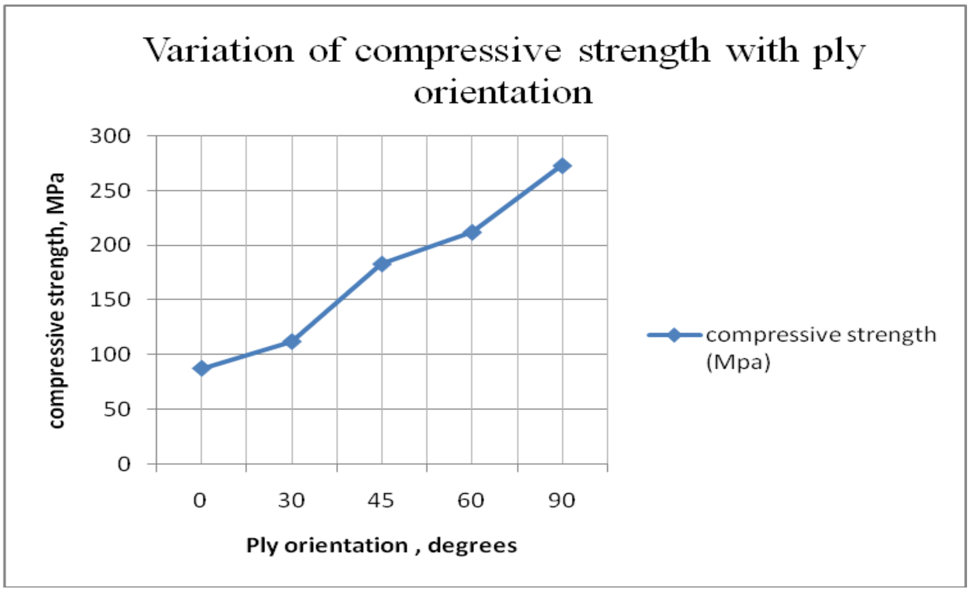


Figure 6.26: Variation of compressive strength for different ply orientations

From the test data, it was observed that the mechanical property of compressive strength was having a strong correlation with the ply orientation. When the plies were oriented parallel to the direction of application of the compressive load, it was observed that the strength values were as low as 87.5 MPa. It was observed that as the angle of ply orientation increased, the compressive strength also increased almost linearly as seen from Figure 6.3. The increasing trend was consistently seen in ply orientations of 30º, 45º, 60º and 90º. While the increase was around 109% at 45° ply orientation as compared to the parallel ply orientation, the increase was 212% from the base value for the perpendicular ply orientation.

On closer scrutiny of the failure patterns, some inferences were made. A wide difference was noticed between the strength values as the ply orientation changes from the parallel orientation to the perpendicular orientation. The variation is almost linear in nature as is evident from Figure 6.26. This can be explained considering the load carrying pattern of the plies when the specimen is subjected to the compressive load. The fibres fail due to micro buckling. It can be observed as the formation of kink bands on the failed surface of the tested specimen. On the other hand, the resin by itself will fail at a comparatively lower load. For an isotropic system of matrix under compressive load, the plane of maximum principle stress is at 45º. This failure line propagates upon increasing load and the composite fails. Interface failure occurs due to the bonding failure between the fibre and matrix. If in case any delaminations are present, it also leads to interface failure. In case of interface failure, the layers were torn apart.

In the perpendicular specimens, the plies behave like an integral system and take the load as a total composite. All the plies are participating in the load sharing and the failure has to happen due to crushing and this happens at a very high load only. It was difficult to correctly identify the start of a crack in the tested specimen. The initiation point was a minor void or a porous area where the stress concentration was high. There was no distinct pattern of failure as seen in the case of a parallel specimen. On the other hand, for a specimen with plies in the parallel orientation, the load is either taken by the fibre or the matrix. Though the fibre and the matrix participate in the load sharing, fibre takes most of the load while matrix just holds the fibres in place for effective load transfer. Three distinct types of failures were noted for the parallel specimens. The failure was either due to the failure of the fibre or the matrix or at the interface between the fibre and the matrix. The first type of fibre failure is the most desirable type where kink bands were formed over the fracture surface. When the matrix failed, a crack was seen in the specimen at an angle to the axis. This was the most common failure mode seen during the experiments, since matrix was the weaker element. The third mode of failure at the interface where the bond between the fabric and the matrix failed resulted in a physical separation of layers of the laminate causing a delamination. This mode was quite rare. Figure 6.27 is a schematic of a typical failed specimen of parallel oriented specimen and Figure 6.28 shows the failure pattern in a perpendicular specimen, which is a random explosive type of failure.

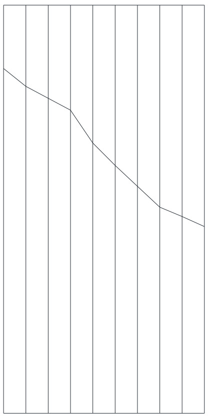


Figure 6.27 Tested specimen-parallel ply orientation

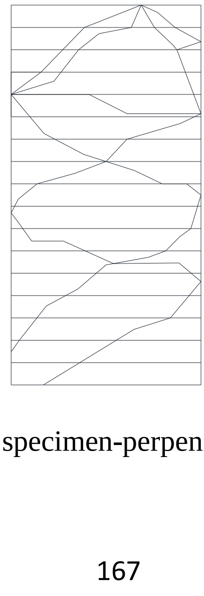


Figure 6.28 Tested specimen-perpendicular ply orientation

In addition, to the layered composites, random fibre moulded ablatives are also used in high temperature applications. These composites have been useful in reentry applications where in addition to high heat fluxes, flow velocities and shear forces also were important. While in layered composites, the prepreg plies were stacked one over the other and cured to form laminates, in random fibre oriented composites, the prepreg was sized to small chops which are mixed with phenolic resin and were moulded. In layered laminates, the fibres in the prepreg plies were systematically oriented in predefined directions. In random fibre oriented composites, the fibres in the prepreg chops were randomly oriented and hence a well defined angle of ply orientation cannot be specified. An effort was made to mould random fibre composites and specimens were made from these composites for evaluating thermal and mechanical properties. These properties were compared to the properties evaluated from layered composites.

In reentry applications, in addition to thermal properties mechanical properties of the ablative composite are equally important as it has to withstand the pressure loads as well as the shear loads of the high velocity flow. Compressive strength, ILSS and compressive modulus were evaluated. The results of the experiments are tabulated in Table 6.27.

Table 6.27: Comparison of mechanical properties of random fibre oriented composite and layered composite (CP)

	Parameter	**Random fibre composite**	**Layered laminate**
1	Density (g/cc)	1.456	1.350
2	Compressive strength -along ply (MPa)	390.02	224.42
3	Compressive strength -across ply (MPa)		353.98
4	Compressive modulus (MPa)	16.08	14.78
5	Flexural strength (MPa)	27.07	25.54

The average density values as measured using Archimedes's principle was found to be 1.350 g/cc for layered laminates and 1.46 g/cc for random fibre laminates. The increase in the density values could be attributed to the customized design of the moulds which enabled good consolidation at all regions of the composite for random fibre laminates. It is also well known that the density of the composite depends on fibre-resin proportion [density of carbon fibre = 2.1g/cc and density of phenolic resin = 1.2g/cc] and in the case of random fibre laminate, slender prepreg chops could occupy the intricate cavities and increase the fibre volume fraction for a given volume and thus simultaneously results in a near-net shape composite with higher density. The resin volume fraction in the composite was optimized by controlling the degree of advancement of the resin at the prepreg level itself. The inherent advantage of processing random fibre composites in a pre-designed mould is that the fibres fill the entire mould cavity and thus prevents unwanted resin accumulation near the edges.

In line with the increase in density, the compressive strength and modulus have also increased. The compressive strength for random fibre laminates was found to be 390 MPa, whereas for layered laminates it was observed to be 224 MPa and 354 MPa for along the ply and across ply respectively an increase of 42% and 9% respectively. The strength for layered laminates across the ply is higher than the strength along the ply for the reason that in the case of across the ply, the load is predominantly taken by the fibres and not by the resin. In the case of testing the layered laminate along the ply, the loads are predominantly acting on the resin and thereby results in premature failure. The increase in the strength for a random fibre laminate is a direct influence of the higher density. Compressive modulus values of random fibre oriented specimens also showed a similar increase of 8% over the layered composites specimens. ILSS for random fibre moulded composites does not have any significance and hence that parameter was avoided and instead flexural strength was evaluated. The flexural strength too improved by 6% and this is also a direct influence of the increased density of the random fibre laminates.

The crucial thermal and ablative properties were also evaluated and the results are tabulated in Table 6.28. The heat of ablation and erosion rate were measured after subjecting the specimen to a heat flux of 750 W/cm^2. The heat of ablation was found to be 8123 J/kg for random fibre composite, whereas the average value obtained for layered composites was 7119 J/kg. It is observed that the heat of ablation for random fibre composite is 14% higher than the layered composite. This increase can be attributed to higher fibre fraction (higher density) for random fibre composite. Heat of ablation refers to the amount of heat required to ablate unit mass of the composite. In the case of random fibre composite, there was effective consolidation leading to higher density of the composite. It is obvious that the composite having higher density would result in higher values of heat of ablation.

Specific heat and thermal conductivity were also evaluated. When compared to the layered laminates processed under vacuum, it is observed that the ablative properties of heat of ablation have improved by 14% and the erosion rate under standard conditions have been reduced by 8 %. This can be attributed to the better compaction of the laminate as evidenced by the higher density. In addition, the laminate is compacted uniformly due to the customized design of the near net shape mould. As expected there was no major change in specific heat since it is a bulk property.

Table 6.28: Comparison of thermal properties of Random fibre oriented composite and layered composite (CP)

	Parameter	**Random fibre composite**	**Layered laminate**
1	Heat of ablation @ 750 W/sq.cm (J/kg)	8123	7119
2	Thermal conductivity (W/mK)	0.56-0.77	0.81-0.99
3	Specific heat (J/kgK)	1329.4	1346.6
4	Erosion rate (mm/s)	0.037	0.040

To summarise, the results of the experiments with specimens fabricated with different ply orientation ranging from 0° to 90° to the flow direction and with random fibre moulded composites provided interesting inferences. The thermal and ablative properties were found to vary significantly with respect to the angle of the ply with respect to the flow. The erosion rate was the highest for parallel wound (0°) liners and the least for 90° liners. This is because for parallel wound liners, layer separation is occurring under shear flow while total ply retention in 90° ply is superior. However, on the other hand, the char advancement rate was the lowest for parallel wound (0°) liners and the highest for 90° liners as conductivity of fibres increased heat conduction rate. For the mechanical properties, the ply orientation of 90° gave the best compressive properties since the entire fibres were available to resist the load, while for the parallel oriented specimens the failure due to shear happened much earlier. This presented a need for a trade-off study with respect to the operating conditions.

For solid propellant motor nozzle liner applications, the ply orientations could be chosen as a trade-off between cost and performance. For critical regions like the throat and the convergent regions where high heat flux and pressure are encountered, a ply orientation of 45° to 60º would be more appropriate since this shall provide optimum results for both erosion and char resistance. In the divergent zones of the nozzle where the conditions of pressure and temperature are much benign, parallel orientation would be ideal. Here the required erosion resistance would be much less than the other regions of the nozzle. Further, this orientation would help to reduce the char advancement into the liner; hence a lesser thickness of the liner would be sufficient leading to savings in costs. For reentry applications involving large frictional heating and shear flows, a random fibre oriented composite shall be preferred over layered composites due to their better ablative as well as strength properties. Though the manufacturing of these are more labour intensive, the reliability provided by better char resistance and strength will compensate for the process difficulties.

6.7 Fibre architecture: distribution pattern of the fibres within a cross-section of the ply

Fibre architecture refers to the pattern in which the fibres are distributed or aligned in any cross-section of the ply during the prepreg tape winding or layup. The effect of fibre orientation in the prepreg, which is one of the most critical factor influencing the properties and functional performance of ablatives was investigated by processing laminates through two different types of fibre architecture.

1. Normal stacked pattern using plies cut using a pre-designed template(L1)

In this style, the prepreg plies were cut using a template from a roll of fabric as shown in Figure 6.29.

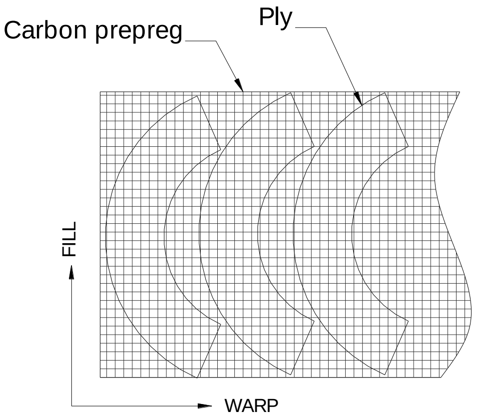


Figure 6.29: Layout for ply cutting for patterns

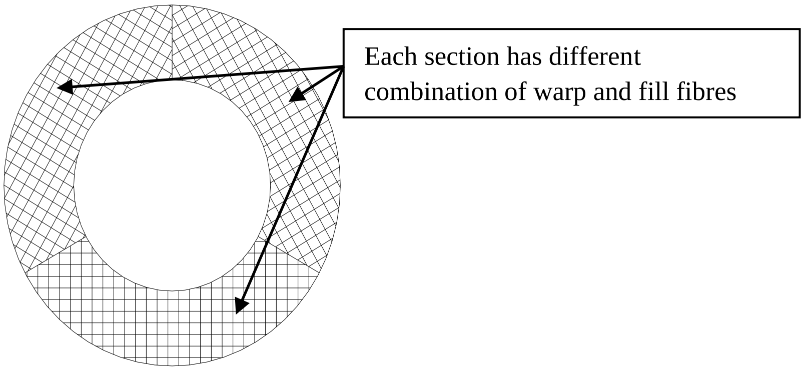


Figure 6.30: Fibre architecture in winding pattern cut tapes

The fibres in the warp and the fill direction were marked as shown in the figure. Figure 6.30 shows a single ply cut from the roll and the positioning of three such plies to form one full circumference of the cross-section of the liner. The fibres in the ply were observed to be aligned at random across the circumference. To cover one full circumference, three plies were required while processing a typical ablative liner of 1m diameter. When three different plies were placed in a plane the fibres in the warp and fill directions were aligned in different patterns as seen from the Figure 6.30. This pattern changed further for the next set of plies stacked over the first layer. So the fibre architecture in a plane is totally random and is not predicable. Further, the number of fibres in the warp and the fill directions were not the same and this leads to further loss of isotropy. However, this architecture was simple and less complicated from the processing point of view.

2. Fibres aligned uniformly across the circumference(L2)

This pattern of layup was achieved by ply-cutting at a biased angle of 45° as shown in Figure 6.31 and differential stretching of the ply to form the tape as shown in Figure 6.32. The plies were cut using a sharp knife using template aligned at 45° to the warp edge of the fabric roll. Then these tapes were formed to the required circumference of the mandrel for tape layup.

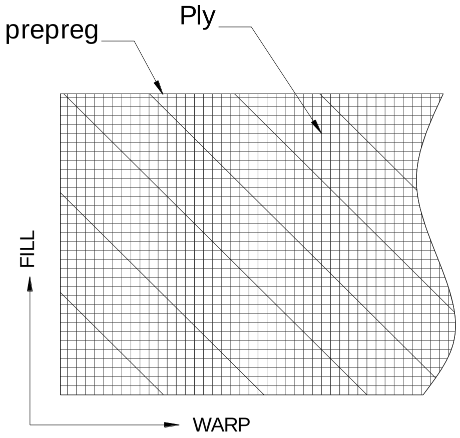
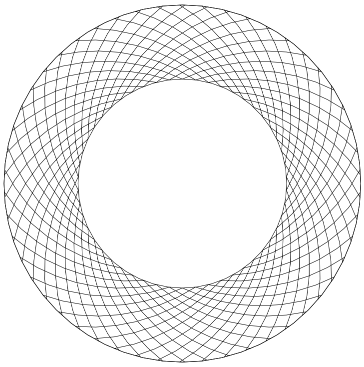


Figure.6.31: Layout for ply cutting for 45° bias tapes



Each section has almost similar combination of warp and fill fibres

Figure.6.32: Fibre architecture in winding bias-cut tapes

An ablative liner was processed on a metallic mandrel in each of the two configurations. From the liner, specimens were fabricated for thermal and mechanical property evaluation. Comparison of thermal and mechanical properties of both the configurations was done and the results are tabulated in Tables 6.29 and 6.30 respectively.

Table 6.29: Comparison of thermal properties of normal stacked pattern and 45° biased stacked liners

Parameter	**Normal stack pattern (L1)**	**45° biased pattern (L2)**
Density (g/cc)	1.416	1.427
Erosion rate- along ply (mm/s)	0.036	0.030
Erosion rate- across ply (mm/s)	0.033	0.029
Heat of ablation (cal/g)	7250	7600
Thermal conductivity - along ply (W/mK)	0.84	0.76
Thermal conductivity - across ply (W/mK)	0.71	0.64
Specific heat (J/kg.K)	1418	1384

From the tested data, it was observed that the density values did not show much difference, but the dispersion in the test results was much less in the biased pattern as compared to the normal pattern (Figure 6.33). This may be due to quasi-isotropy achieved in the biased style. The thermal properties, in general, as seen from Figure 6.34 were marginally superior in the case of composite (L2) in which the fibres were oriented at 45° to the selvedge when compared to the pattern-cut tapes (L1). The heat of ablation for L2 was observed to be about 5% higher than that of L1. It indicated that the ablation performance of the composite will be superior for the 45° biased pattern liner as compared to the normal random pattern liner. Similarly, thermal conductivity of L1 is about 10% higher compared to L2 for both the ply directions. This superior thermal and ablative performance of biased pattern may be attributed to the uniform distribution of the fibres. This helped in uniform distribution and faster dissipation of heat.

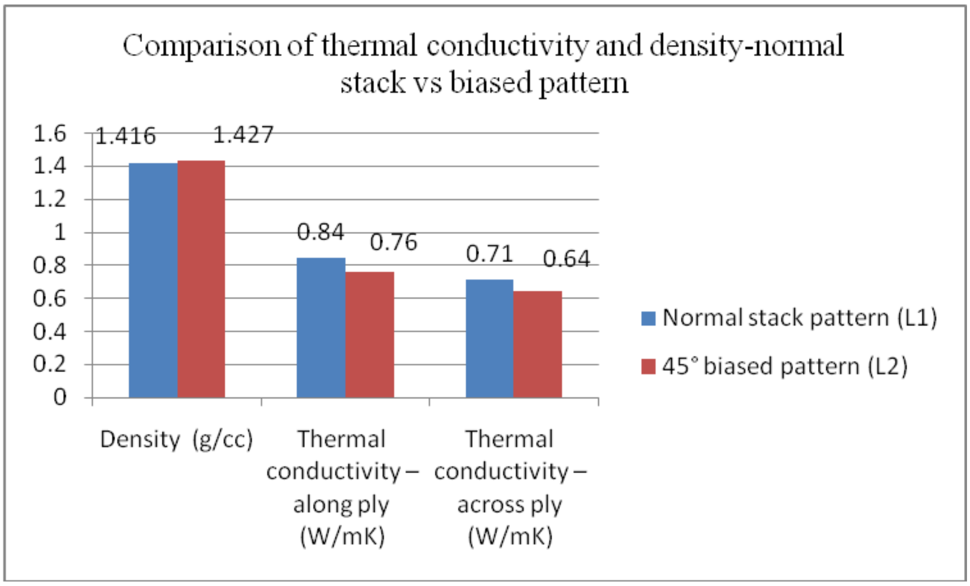


Figure.6.33: Comparison of density and thermal conductivity- normal stack vs. biased pattern

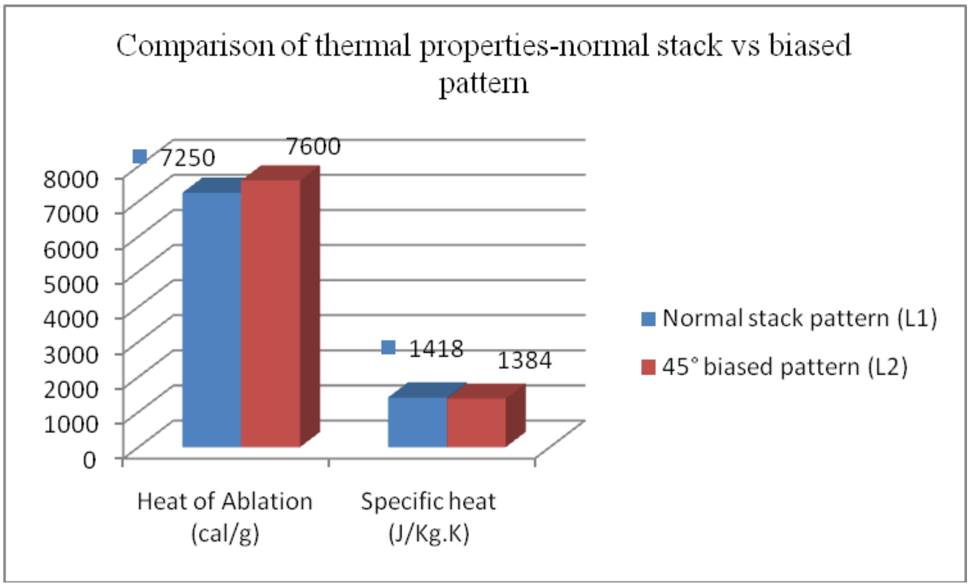


Figure.6.34: Comparison of thermal properties- normal stack vs. biased pattern

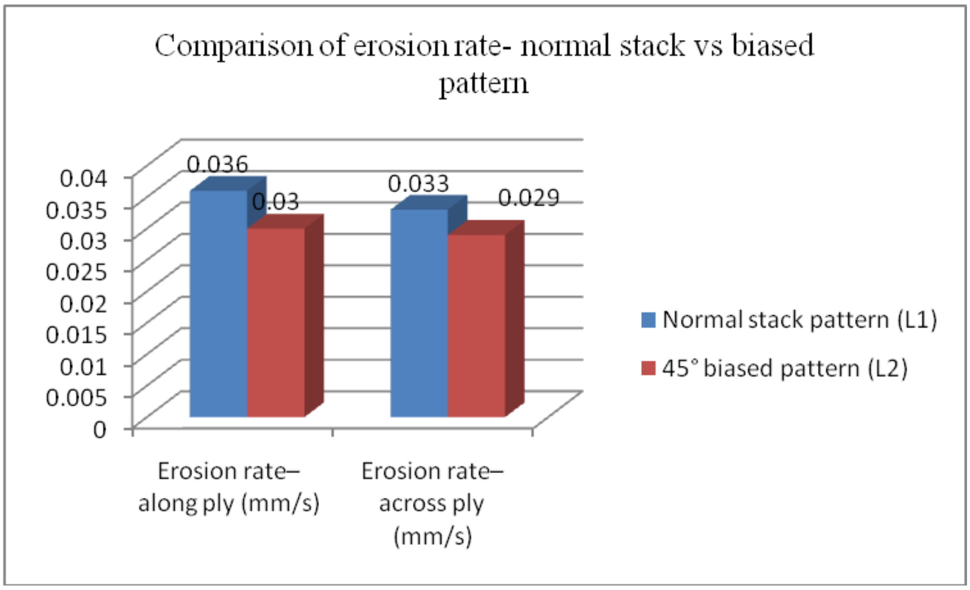


Figure.6.35: Comparison of erosion rates- normal stack vs. biased pattern

The resistance to erosion during the service conditions is considered as the most important characteristic feature of an ablative composite. The resistance to erosion for the liners constructed using the 45° biased pattern improved by over 16% along the ply direction and 12% across the ply direction respectively when compared to the liners constructed using the normal stack pattern. Hence, from the ablative performance point of view, the biased version offered significant gains as compared to the normal stacked pattern. The limited dispersion in the properties and the improvement in the absolute values rendered the biased version more effective. The quasi-isotropy exhibited due to the uniform distribution of fibres in the warp and in the fill directions is the major reason for the improvement.

The mechanical properties evaluated from the samples made from the liners processed in the two routes were also analysed.

When the results of the mechanical property evaluation were analysed, normal stack pattern samples gave values marginally better mechanical properties than the 45° biased pattern. The compressive strength values for the normal pattern were higher than that of the biased version in both the ply directions. Marginally higher ILSS was also observed. The stiffness property values also exhibited a similar trend with the normal pattern specimens showing higher values than the biased version. The random orientation of fibres in the specimens might be enhancing the strength properties by resisting the deformation due to the compressive loads. However, the dispersion among the tested values was lower for the biased specimens possibly due to the uniformity in the fibre alignment pattern. Wide dispersions were noticed for the mechanical properties of the normal pattern specimens.

Table 6.30: Comparison of mechanical properties of normal stacked pattern and 45° biased stacked liners

Parameter	**Normal stack pattern**	**45° biased pattern**
Compressive strength - along ply (MPa)	237.5	203.6
Compressive strength - across ply (MPa)	508.0	467.1
Compressive modulus - along ply (GPa)	12.98	11.15
Compressive modulus - across ply (GPa)	10.41	10.38
Interlaminar shear strength (MPa)	27.07	22.40

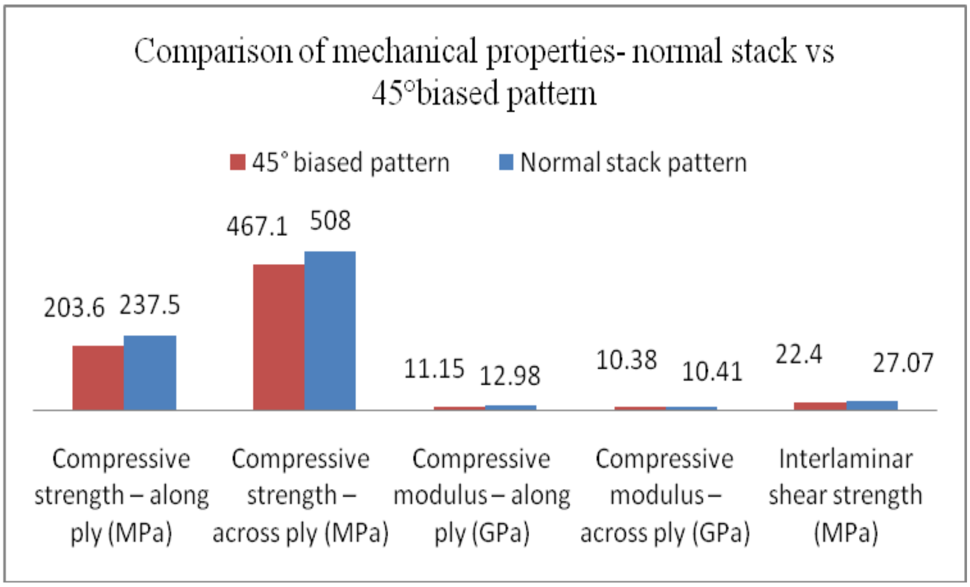


Figure.6.36: Comparison of mechanical properties-normal stack vs. biased pattern

Due to the conflicting observations in the thermal and mechanical test values, a confirmatory inference could not be reached regarding the choice of the fibre architecture. Hence, a subscale motor test was conducted with liners processed using both the fibre architecture.

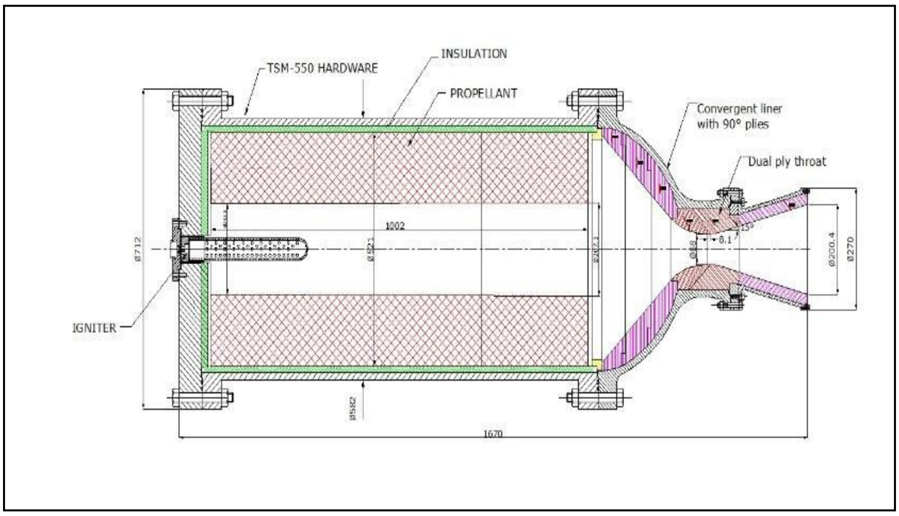


Figure.6.37: Test Simulation motor (TSM) used for studying the effect of fibre architecture

Figure 6.37 shows the schematic of the test simulation motor used for the experiments. Since the material of the ablative composite was the same and only the winding pattern changed both the liners showed erosion as well as charring. However, the extent of erosion and char were different.

When these laminates were subjected to simulation tests in test simulation motors shown in Figure 6.37, the angular-cut plies showed superior performance. This was confirmed by lesser and more uniform erosion of the ablative surface. The properties of the random fibre oriented liners were observed to have a larger dispersion due to the continuously varying fibre fractions at different sections. This leads to variations in properties along the length of the liner and along the circumference of a liner at a given plane. This is undesirable as the erosion behaviour becomes unpredictable and the performance of the ablative is affected. Figure 6.38 shows a comparison of the tested nozzle divergents which indicate lesser and uniform erosion for the angular-cut plies. Figure 6.38 (a) is the picture of the tested nozzle divergent inside surface of the normal stacked pattern liner which indicates an erosion pattern with variations. Irregular erosion was seen around the circumference and along the length of the liner. On the other hand, as seen from Figure 6.38 (b), the biased pattern liner showed a reasonably regular and uniform eroded internal divergent surface after the test.

(a)

(b)

Figure 6.38: Views of the divergent sections of the test nozzle after a simulation test

These observations clearly indicated the superiority of the biased scheme of fibre architecture. These observations were confirmed by physical measurements of the eroded surface. The depth to which the material has been eroded was computed by the difference between the pre-test and the post-test dimensions and is reported in Table 6.31. To capture the axial and circumferential variations in the erosion, the measurements were done at four equispaced locations, at 90° intervals, around the circumference and eight stations axially. The minimum and maximum values were tabulated. After erosion measurements, the depth of the heat affected zone as measured by the char depth was also done in the similar way and the results were tabulated.

Table 6.31: Comparison of erosion data and char depth data of the tested liner for the normal stacked pattern and the 45° biased stacked liners

	Normal stack pattern				45° biased pattern			
	Erosion (mm)		Char depth (mm)		Erosion (mm)		Char depth (mm)	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
1	10.3	13.7	14.3	17.5	8.6	9.1	13.9	14.0
2	14.5	18.6	19.0	23.4	11.2	12.0	15.4	15.9
3	17.4	23.6	22.5	28.9	16.5	17.1	18.2	18.8
4	20.9	24.7	26.5	28.1	16.5	17.1	18.2	18.8
5	19.9	20.2	20.3	24.1	15.6	16.3	19.1	19.6
6	12.5	15.7	16.0	18.1	8.5	9.1	12.1	13.3
7	9.6	12.3	12.3	15.7	7.9	8.2	9.9	10.2
8	7.2	8.7	10.2	11.7	4.5	6.0	6.3	7.0

Figure 6.39 and Figure 6.40 shows the erosion and char depth of normal stacked and 45° biased pattern. As seen in Figure 6.39, it was observed that the erosion of the normal stacked pattern liner were considerably more than the erosion at the corresponding stations for the 45° biased pattern liner.

Similar trend was noticed for the char depth data also. This was expected since the behaviour of erosion and charring is interdependent. The extent of erosion as well as char depth increased from the convergent region of the nozzle to the throat region due to the increase in the temperature, pressure and particle impingement from the hot gases flowing through the nozzle and thereafter is decreased from the throat region to the divergent region. In the divergent region towards the aft end of the nozzle, the pressures reached near ambient conditions and the temperatures too are benign.

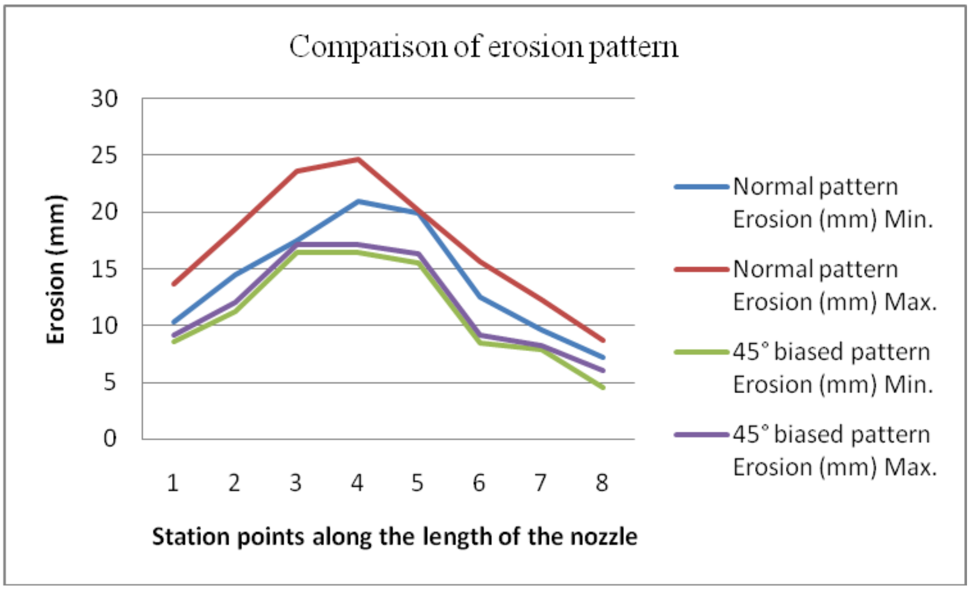


Figure 6.39: Comparison of erosion patterns of the normal stacked pattern and the 45° biased pattern liners

Almost at all the measurement stations, it was observed that the erosion as well as the char depth values was correspondingly higher for the normal stacked pattern liner as compared to the biased pattern liner. Another important observation was that the difference between the minimum and the maximum values at any particular station was much smaller for the biased stacked liner. This indicated that the erosion and the char depth were more uniform in this case around the circumference. This is very important since nonuniform erosion around the circumference can lead to pocketing erosion. This will make the ablative surface with undulations which can eventually cause thrust oscillations.

Thus, the effect of fibre orientation in the prepreg, which is one of the most critical factor influencing the properties and functional performance of ablatives has been investigated by processing laminates through two different fibre architectures. The laminate with fibres cut at 45° to the edge of the fabric showed marginally better thermal and ablative properties as compared to the laminate made using pattern-cut tapes. When these laminates were subjected to simulation tests, the angular-cut plies showed superior performance as evidenced by lesser and more uniform erosion of the ablative surface.

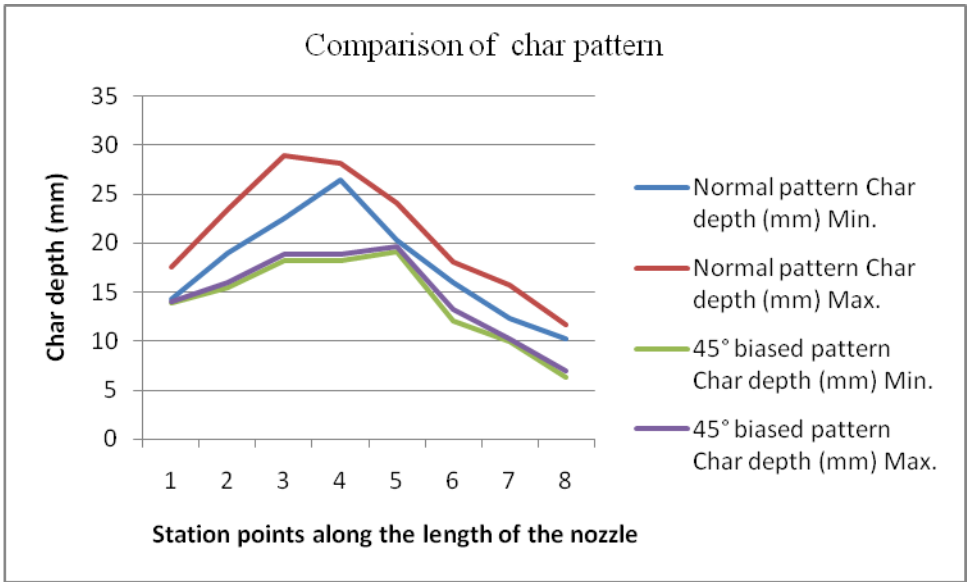


Figure 6.40: Comparison of char patterns of the normal stacked pattern and the 45° biased pattern liners

The properties of the random fibre oriented liners were observed to have a larger dispersion due to the continuously varying fibre fractions at different sections. This leads to variations in properties along the length of the liner and along the circumference of a liner at a given plane. This is undesirable as the erosion behaviour becomes unpredictable and the performance of the ablative is affected. However, this pattern shows comparable mechanical property values to the angular cut plies as the material is basically the same.

6.8. Effect of temperature on properties

To study the effect of temperature on the properties of ablative composites, silica phenolic was used for the study. The reinforcement fibres are not affected by the temperature till their melting points. Hence, the matrix resin was the focus of attention in this study. The specimens were fabricated from the silica phenolic laminates and liners and were subjected to different temperatures and then were tested for their representative mechanical properties to understand the trend of degradation in properties, if any.

Table 6.32: Effect of temperature on the properties of ablatives (SP)

Parameter	Ambient	200°C	400°C	600°C	800°C	1000°C
Compressive strength - along ply (MPa)	90	75.6	36.2	15.1	15.7	15.6
Compressive strength - across ply (MPa)	255	214	103	26.3	27.1	26.9
Interlaminar shear strength (MPa)	24.1	20.2	9.81	2.42	2.68	2.59

As seen from Table 6.32 and Figure 6.41, there was significant reduction seen in the compressive strength values in both along the ply direction and across the ply directions with increasing temperature. The values are the highest at room temperature conditions. It was observed to be progressively decreasing for specimens treated at higher temperatures.

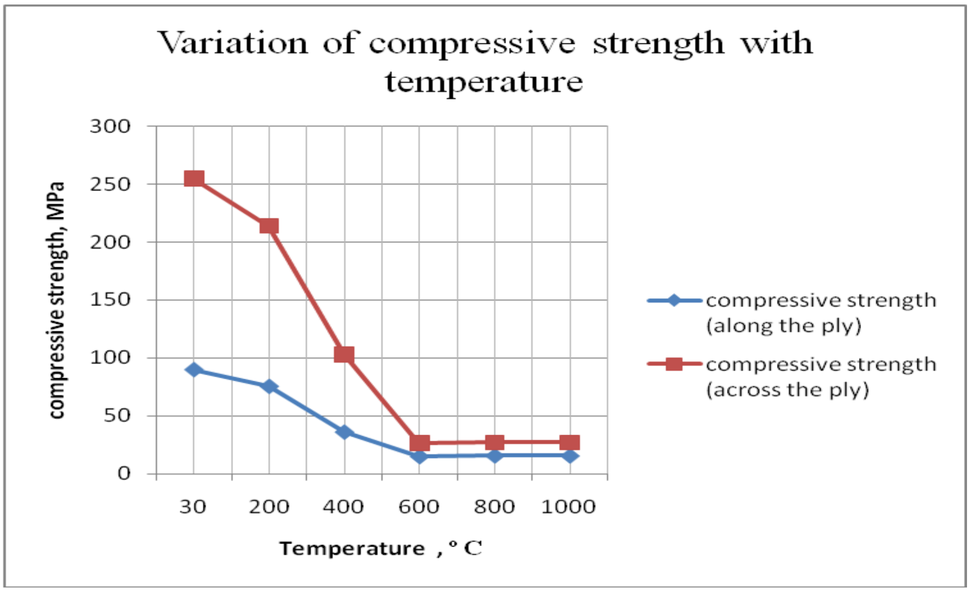


Figure 6.41: Variation of compressive strength values with temperature

As evident from Table 6.32, the compressive strength values of the specimens heat-treated at 200ºC had dropped drastically by around 16%. Further, the values decreased to 60% of the ambient values at 400ºC. At 600ºC, the reduction of compressive strength values were as high as 89%. However, further reduction in strength was not observed for specimens heat treated to 800ºC and 1000º C. The values at 800ºC and 1000ºC were almost similar to the values at 600ºC. In fact, a slight increase of 3 to 4% was noticed for the compressive values at these temperatures.

A very similar trend was observed for the ILSS also as depicted in Figure 6.42. Here also, the highest strength values are at room temperature conditions. The values decreases steadily till a temperature of 600°C and thereafter it stabilizes. Further reduction in properties is not observed beyond a temperature of 600ºC. The ILSS values at 600ºC were only about 10% of the values obtained at room temperature conditions.

The degradation behaviour of the phenolic resin causes the drastic reduction in the mechanical properties. Pyrolysis of the resin started at around 200°C. The matrix underwent thermal degradation at temperatures above 200°C and was the maximum at around 600°C. Mass loss at 600°C was about 15-20% and only about 2-5% was seen in 600-1000°C range.

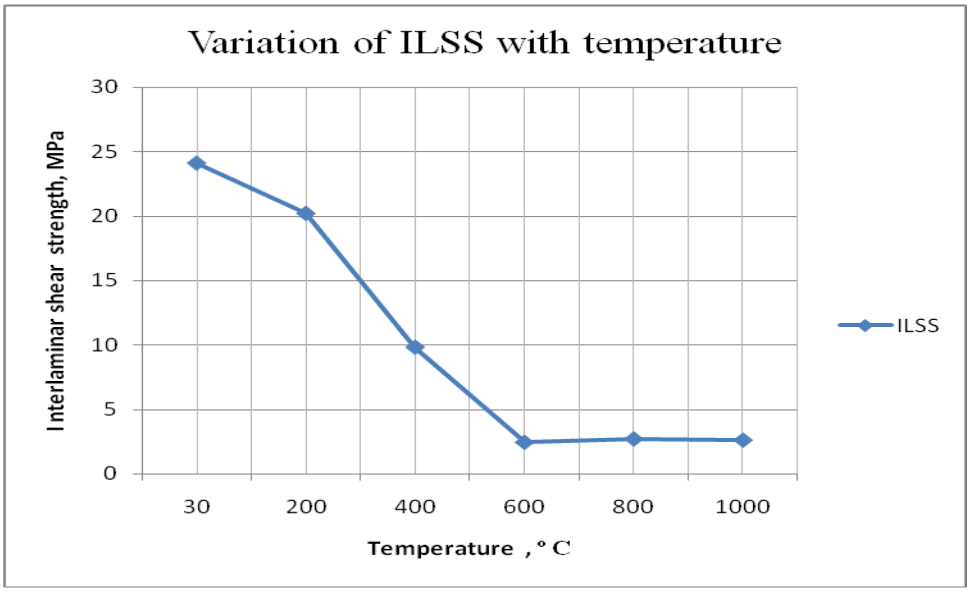


Figure 6.42: Variation of ILSS with temperature

Accordingly, the reduction in strength from ambient to 600°C was about 90-95%. Beyond 600°C, much volatile evolution or mass loss was not observed.

Due to pyrolysis, resin degraded, volatiles evolved and pores were generated. Strength reduced drastically as the structural integrity was lost. During testing also, entrapped volatiles due to rapid heating created severe internal pressure build up leading to delaminations. Matrix shrinkage led to volumetric shrinkage of the specimens. After the composite was charred at 600°C, the char which remained solidified had some char strength which resisted the mechanical load. This prevented further reduction in the strength values. In fact, the specimens charred above 600°C, exhibited reasonably good char strength.

6.9 Effect of ageing on properties

On many occasions, the ablative composites may not be used in the functional environment immediately after processing. The ablative liners used in the solid rocket motor nozzles or the liquid engine throats assembled in the engines may not be put into the operating environment within a short time after the completion of processing. Hence, it was necessary to understand whether any degradation in properties or performance happens on storage with time. Since the mechanical and thermal properties or the structural health of the ablative composite cannot be rechecked once the composite element is integrated to the subsystem in the rocket, it is all the more important to understand the ageing behavior of the ablative composites.

With this objective in mind, while the specimens were made for evaluation of mechanical and thermal properties, additional specimens were fabricated and stored in a hermetically sealed container. From these sets of specimens a few representative samples were tested at six month intervals to understand the behaviour.

Table 6.33: Effect of storage on the properties of ablatives (SP)

Time line, months	T	T+6	T+ 12	T+18	T+24	T+30	T+36	T+42
Density (g/cc)	1.78	1.77	1.78	1.76	1.80	1.77	1.78	1.78
Erosion rate- along ply (mm/s)	0.028	0.027	0.029	0.031	0.030	0.028	0.028	0.027
Erosion rate- across ply (mm/s)	0.021	0.019	0.021	0.021	0.023	0.023	0.021	0.021
Heat of ablation (cal/g)	7920	7880	8120	8015	7988	8100	7852	8003
Thermal conductivity - along ply (W/mK)	0.60	0.60	0.60	0.60	0.60	0.59	0.60	0.62
Thermal conductivity - across ply (W/mK)	0.47	0.45	0.47	0.49	0.47	0.50	0.49	0.47
Specific heat (J/kg.K)	893	989	757	888	944	799	803	888
Mechanical properties								
Compressive strength - along ply (MPa)	78.5	77.3	78.0	80.1	74.3	78.6	81.4	76.5
Compressive strength - across ply (MPa)	280	293	274	301	268	294	288	270
Compressive modulus - along ply (GPa)	10.1	9.9	10.0	10.6	9.4	10.0	10.5	11.0
Compressive modulus - across ply (GPa)	10.2	9.5	9.9	10.8	11.3	11.0	9.4	10.0
Interlaminar shear strength (MPa)	35.1	39.2	43.1	34.8	36.5	38.8	33.2	37.7

As seen from Figures 6.43 to 6.45 and Tables 6.33 and 6.44, no significant degradation was seen in the mechanical or thermal properties after evaluation of seven sets of specimens.

Table 6.34: Effect of storage on the properties of ablatives (CP)

Time line	T	T+ 6 months	T+ 12 months	T+18 months	T+24 months	T+30 months	T+36 months	T+42 months
Density (g/cc)	1.421	1.421	1.419	1.422	1.421	1.421	1.420	1.418
Erosion rate- along ply (mm/s)	0.034	0.034	0.033	0.033	0.032	0.034	0.032	0.034
Erosion rate- across ply (mm/s)	0.033	0.034	0.034	0.033	0.031	0.032	0.034	0.034
Heat of ablation (cal/g)	8510	8898	7981	8325	7898	7598	8001	8456
Thermal conductivity - along ply (W/mK)	1.07	1.07	1.06	1.07	1.05	1.09	1.07	1.09
Thermal conductivity - across ply (W/mK)	0.77	0.81	0.77	0.82	0.81	0.79	0.77	0.77
Specific heat (J/kg.K)	1245	1301	1244	1299	1350	1298	1325	1354
Mechanical properties								
Compressive strength - along ply (MPa)	247	266	233	250	265	233	280	239
Compressive strength - across ply (MPa)	457	488	501	445	495	507	460	462
Compressive modulus - along ply (GPa)	13.2	12.9	11.9	13.0	12.5	11.5	12.5	12.9
Compressive modulus - across ply (GPa)	13.7	13.3	11.9	12.4	13.0	11.9	12.8	13.1
Interlaminar shear strength (MPa)	35.4	40.7	33.2	38.6	40.1	34.0	36.6	39.9

These tests spanned over a period of 7 semesters (i.e. 42 months). From the results, it was inferred that properties are not likely to degrade within this time span if the specimens are stored properly, adequately protected from environmental effects. It indicated that as the resin in the composite is completely cured and has been in a stable condition, there is no degradation in the resin or the fibre due to storage. No further physical or chemical degradation is happening in the composite with storage.

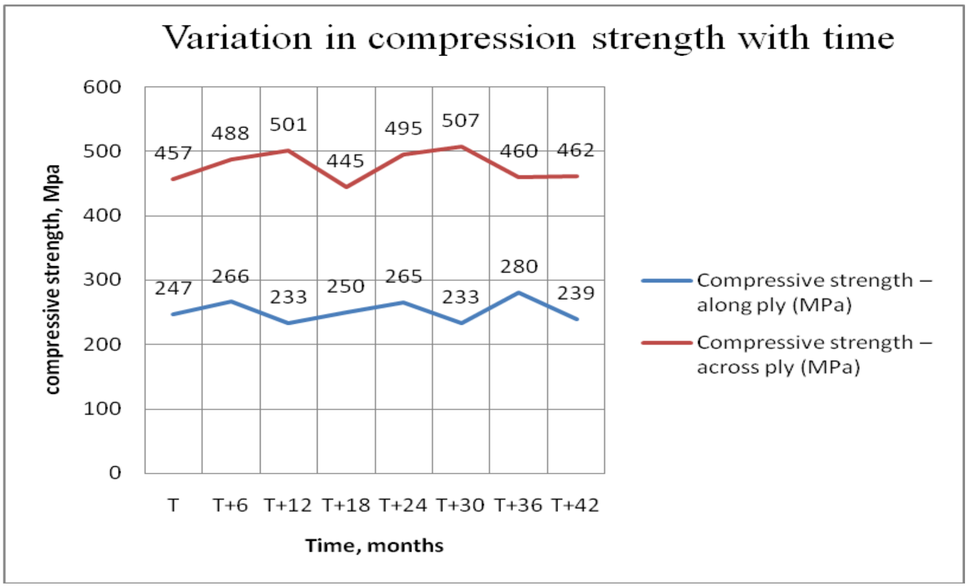


Figure 6.43: Variation of Compressive strength with time

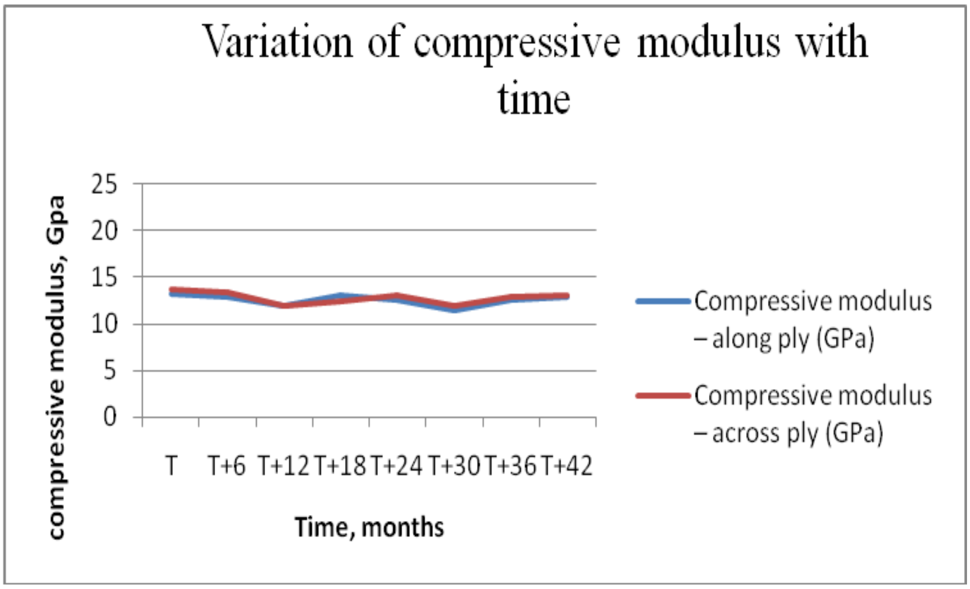


Figure 6.44: Variation of Compressive Modulus values with time

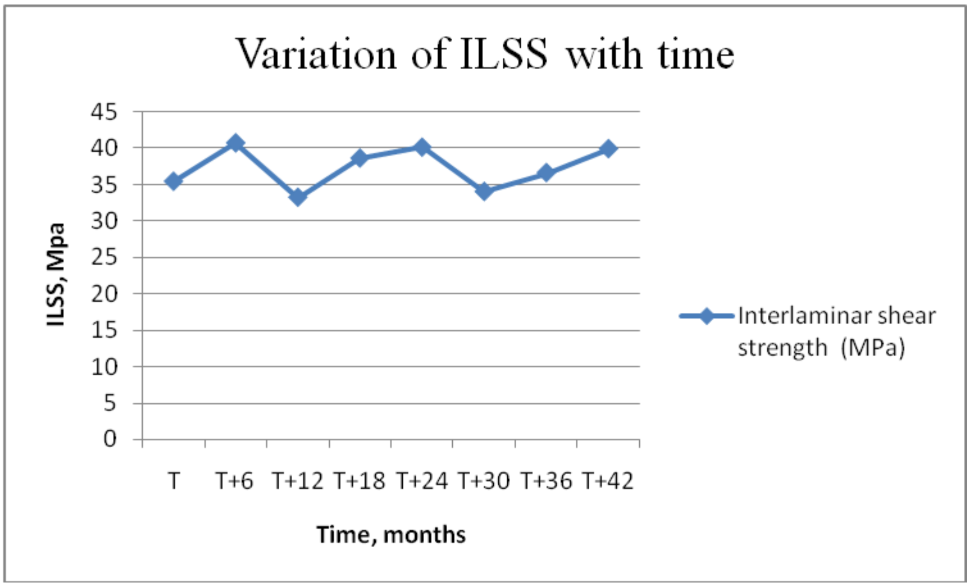


Figure 6.45: Variation of ILSS values with time

Similarly, as seen from Figures 6.46 to 6.48, the density and thermal properties like heat of ablation, thermal conductivity and specific heat also did not change significantly with respect to time during the period of the study.

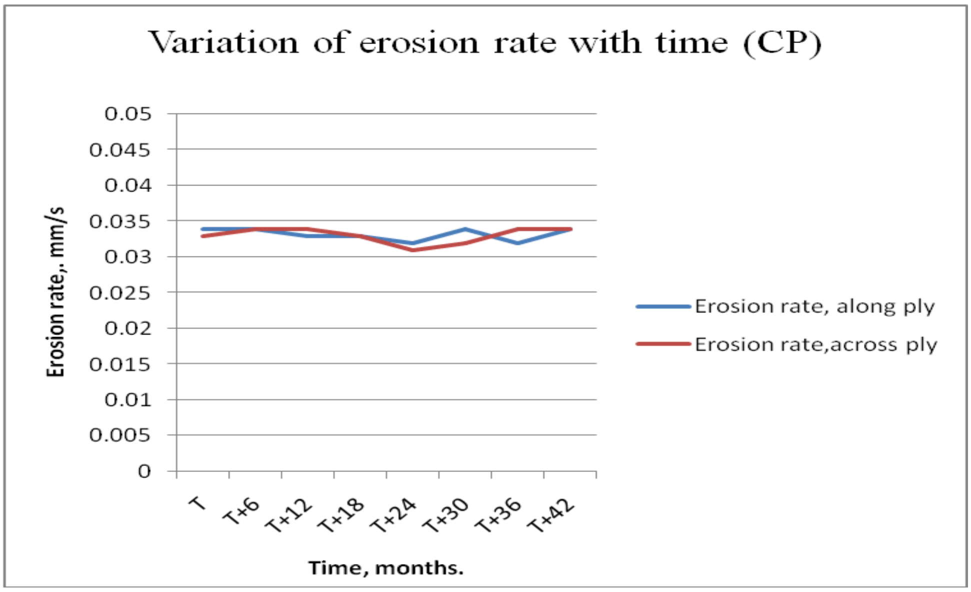


Figure 6.46: Variation of erosion rate with time

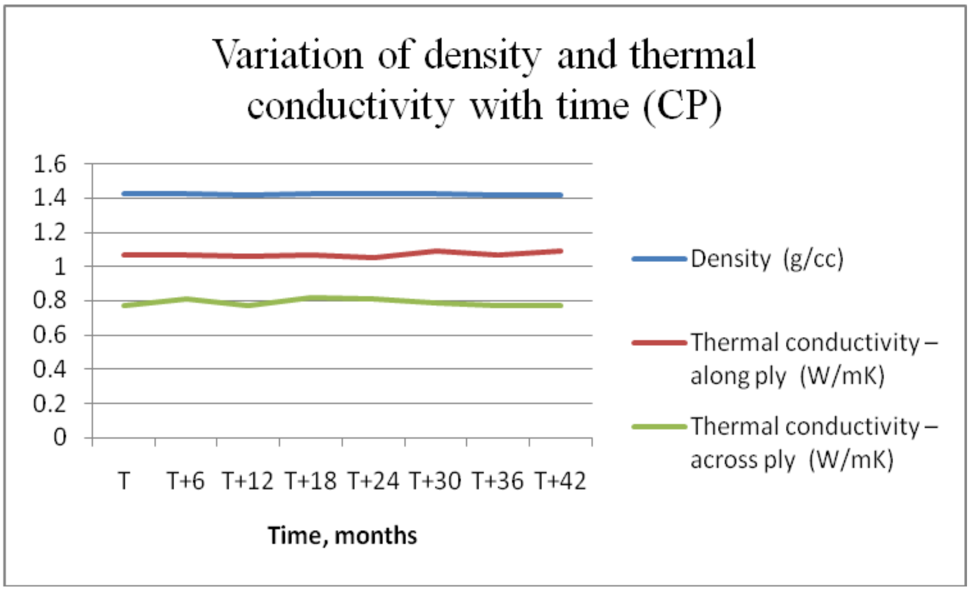


Figure 6.47: Variation of density and thermal conductivity with time

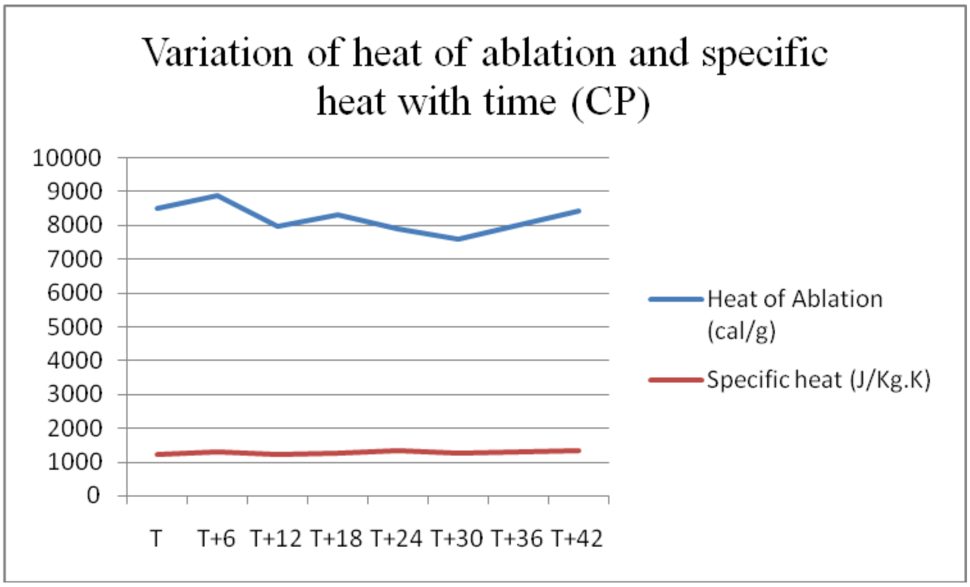


Figure 6.48: Variation of heat of ablation and specific heat with time

The minor variations seen in the values are not following any definite pattern of increasing or decreasing trend and are attributed to random variations due to difference in the test conditons only.

CHAPTER 7

CONCLUSIONS

Ablatives, a class of elite polymer thermosetting composites systems were studied in detail with respect to the critical raw material properties and process parameters. After enumerating all the raw material and process parameters, these were further filtered to identify the most sensitive parameters for detailed in depth investigations. The important thermostructural properties required for an ablative were finalized along with the test methods for evaluating them.

The complete characterization of the reinforcement fibres (carbon and silica) and matrix resin (phenolic) was done and the critical properties influencing the composite properties were identified. Impregnation of the carbon and silica fabric with phenolic resin was done and the resultant carbon phenolic and silica phenolic prepreg were characterized to identify the critical properties influencing the composite properties. Subsequently, ablative laminates and liners were processed using a standard process sequence and the critical process variables in each stage were identified. Laminates were subjected to nondestructive evaluation of visual inspection, alcohol wipe test and ultrasonic (pulse-echo and through transmission) testing to study the integrity and uniformity. After ensuring that the laminates were defect free, specimens were fabricated from them as per the accepted standards. Evaluation of mechanical and thermal properties was done and the results were tabulated. From the results of the tests, the effect of each variable on the composite properties was quantified and studied and inferences were made accordingly. The possible effects of certain other related factors like effect of temperature and effect of ageing on the properties of the ablative composites were also studied and reported.

It was observed that tensile breaking strength of the fibres played a major role in the mechanical properties of the composite. The carbon content and the sodium content in the carbon fibres too had a significant influence on the thermal characteristics. The influencing effect of the resin content in the carbon phenolic and silica phenolic prepreg on the fundamental properties of the ablative composite was studied and it was found that the optimum range for silica phenolic prepreg is 35 to 40% and that for carbon phenolic is 40 to 45%. For resin contents below this range, delaminations and resin lean lines were seen rendering the composite unusable. For higher resin contents, the properties showed a decreasing trend since the fibre content is proportionally reducing with increasing resin content. The most influential process variables during polymerisation were found to be the cure temperature and cure pressure and these were investigated in detail for both carbon phenolic and silica phenolic ablative composites. The cure temperature of 150°C and a cure pressure of 40 bar were concluded as the optimum for carbon phenolics while the corresponding values for silica phenolics were 150°C and 65 bar. The best mechanical and thermal properties were obtained for these curing parameters.

The angle at which the prepreg plies are oriented to the direction of the hot gas flow was observed to be a very critical factor affecting the properties and performance of ablatives. A series of experiments were done to study the effect of the direction of fibres in the reinforcements to the direction of the flow in the nozzle. Fibres were oriented at different angles from 90° to 0° to the nozzle flow and characterisation for mechanical and thermal properties were completed. Simulation tests and evaluation of erosion and char advancement rate were also done. Thermal and ablative properties were found to vary significantly with respect to the angle of the ply with respect to the flow. Erosion rate is highest for parallel wound (0°) liners and the least for 90° liners. This is because for parallel wound liners, layer separation is occurring under shear flow while total ply retention in 90° ply is superior. Char advancement rate is lowest for parallel wound (0°) liners and the highest for 90° ply liners as conductivity of fibres increase heat conduction rate. For both carbon phenolic and silica phenolic, it is observed that ply orientation of 90° gives the best compressive properties since the entire fibres are available to resist the load. While for parallel wound liners, failure due to shear happens much earlier. Hence, it was concluded that the optimum ply orientation has to be decided based on the operating conditions. For convergent and throat regions of the nozzle where the temperature and pressure is comparatively higher, an intermediate value of 45° to 60° gave the best results while for comparatively benign regions like divergents, 0° orientation would be sufficient.

The effect of fibre orientation in the prepreg, which is one of the most critical factor influencing the properties and functional performance of ablatives was also investigated by processing laminates of two different fibre architectures. Two different types of patterns, one with normal random fibre architecture and the second with a tape formed using 45° bias-cut plies were used in the experimental studies. Though the mechanical properties were not superior, the better functional performance of the 45° bias-cut orientation was evident from the uniform and repeatable performance in a simulation test motor.

Other contributing factors like effect of temperature and effect of ageing of the composite on the properties were also investigated. It was observed that there was a drastic reduction in the mechanical properties with temperature upto 600°C.However, if the composites are properly stored there was little deterioration in properties due to ageing upto 48 months.

With this, a comprehensive compilation of the most influential factors affecting the properties and functional performance of carbon phenolic and silica phenolic ablative composites has been completed. This information is expected to be useful in process optimization of ablatives leading to considerable advantages like reduction in cost, process time and improvement in quality and reliability. The outcome of this research work is expected to contribute significantly to the proper and better understanding of the critical process parameters which significantly influence the final product characteristics. This shall enable the designers to optimize the dimensions of the ablatives used in solid rocket motor nozzles and thermal protection systems for reentry vehicles so that the inert weight is minimised. The results are also expected to significantly reduce the cost and/or the duration of processing of ablative components. This shall lead to a more scientific and technical process design philosophy eventually leading to better ablatives with superior thermal and mechanical properties. Significant gains in terms of cost, process cycle time and inert mass are expected. Since most of the specific process parameters and raw material properties are still kept as closely guarded proprietary information in the international scenario, this information shall prove to be valuable to process Engineers working in the field of ablative thermal protection systems.

Scope for further research

The subject of ablative composites is very vast with a number of raw materials and processing techniques. This study was limited to a selected set of raw materials and the most common process sequences. Carbon fibres made from the rayon precursor were studied. Further investigations can be attempted on PAN based fibres and pitch-based fibres also which can be used as reinforcements. Similarly, silica fibres made through the acid leaching route were used for this study; silica fibres processed through the marble melt spinning route may also be studied for their properties and compared. Similarly, one standard phenolic matrix resin was used for the studies. Many resin systems are being experimented for achieving better ablative properties. Instead of the condensation polymerization in the present resin, addition cure phenolic resin can be studied so that the volatile evolution can be avoided. A number of studies are being currently pursued by mixing different types of organic and inorganic additives and nanoparticles in the resin systems to improve the properties. Studies can be attempted with such promising new resin systems to see if these can be scaled up to the ablative composite level. Though at the resin level, many new additives give encouraging results, processing difficulties prevented the successful scaling up to the ablative product level. Research in this direction to overcome the processing and scaling up issues can be attempted.

Several process parameters like preheating of prepreg before tape layup, use of liquid nitrogen or carbon dioxide for cooling the prepreg to prevent unwanted advancement of the resin, roller pressure for compaction etc are being attempted in an attempt to improve the quality. The effect of these may also be studied to improve the understanding of their contributions. A comparative study of the products cured using different equipments like ovens, autoclaves and hydroclaves could also be attempted. The effect of application of vacuum during curing and the stage of curing till which vacuum is to be maintained can also be an interesting focus of further studies. The possibility of semi-curing at a lower temperature, cooling to ambient conditions and then completing the curing can be seen and the comparative study of the properties with a composite cured in the regular cycle can be done. The effect of post-curing the composite can be done to study whether there is any deterioration or improvement in the thermal and mechanical properties.

Machining parameters like speed, feed and depth of cut can be studied for different ablative materials with respect to their effect on properties. The effect of using coolants during machining vis-à-vis using a suction based dry dust collection system can also be studied. The undesirable effects of using liquid coolants may be studied both from the angle of the difficulties during machining as well as from the possible reduction in the properties of the ablative due to the interaction with the coolants. The ageing studies can be further extended for more duration to understand the shelf life of these composites and the initiation of the reduction in property values, if any. The effect of storage conditions like humidity and temperature can also be studied. The compatibility of carbon and silica phenolic composites with different propellants like solid, liquid and cryogenic may also be studied to compare their relative performance.

The values of several process variables investigated were specific to the raw materials used, process equipments, fixtures and toolings used in the studies. The universal applicability of these results may not exist. However, the broad trends of behavior definitely exist. The wide dispersion seen in some properties were due to the difficulties encountered during specimen preparation. The dimensional tolerances, geometric tolerances like parallelism, flatness and perpendicularity and correct orientation of the fibres influenced the test results. A sensitivity study on the various specimen tolerances and orientation related parameters can be studied. The testing conditions also play a vital role in the test results. Almost all tests were done at ambient conditions. However, in the actual operating conditions, the ablative is subjected to very high heating rates and the entire operation is completed in a matter of seconds. Hence, the actual performance may be evaluated by devising a simulated heating setup capable of achieving very high heating rates similar to the rocket operating conditions and the loads be applied at this condition. This may give a more realistic appraisal of the performance of the composite.

Many tests were limited to specimen level alone due to the prohibitive cost and time involved. To understand the scale effects, if any, full scale tests may be attempted with the selected parameters.

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Publications

I. In Journals

1) L.Mohan Kumar, K.M. Usha, E.N.Anandapadmanabhan & P.Chakravarthy, “Effect of fibre orientation on the properties and functional performance of ablative materials for solid rocket motors”, Trans Indian Inst Met (2017) 70(9):2407-2413 DOI 10.1007/s12666-017-1102-1.

2) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, “Investigative studies on the critical prepreg variables influencing the functional performance of ablative composites for extreme environments in launch vehicles and reentry missions”, Mater. Res. Express 6 (2019) 085613 https://doi.org/10.1088/2053-1591/ab1ac7.

3) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, “Advanced Ablative composites for Aerospace Applications”, IOP Series: Materials Science and Engineering 360 (2018) 012036. doi:10.1088/1757-899X/360/1/012036.

4) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, “Development of a novel tape wrapping technique for ablative composites”, Material Science Forum, Vol. 830-831, pp 417-420 (2015).

Paper communicated to journals

1) L.Mohan Kumar, R.P. Tushar, K. M. Usha, E. N. Anandapadmanabhan & P.Chakravarthy (2019) Synthesis, characterisation, testing and qualification of High performance phenolic/carbon random fibre oriented Ablative thermal protection composite for reentry applications- communicated to Int. J. Materials and Product Technology. (communicated, peer-reviewed and revisions suggested; revised manuscript submitted and is under consideration)

II. In National and International conferences

1) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "High performance thermal protection ablative composites for solid rocket motors", International Conference on Aerospace and Mechanical Engineering - ICAME '15 December 2015. Procedings published by Mc Grawhill; ISBN (13): 978-93-85965-16-6.

2) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "Fibre- orientation of ablative composites in solid rocket motors"- won the best oral presentation award at the International Conference on Emerging Trends in Materials and Manufacturing - iMME'17 - March 2017 at NIT, Trichy.

3) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "Advanced Manufacturing Processes for Aerospace Ablative Composites" - National Aerospace Manufacturing Seminar (NAMS-2016) by Society for Aerospace Manufacturing Engineers (SAME) - (won the best paper award.)

4) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "Process variables influencing the functional performance of ablative composites in rocket launch vehicles and re-entry vehicles"

National Conference on Material Science and Technology (NCMST-2015) at IIST.

5) L.Mohan Kumar, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "Synthesis, characterisation and qualification of carbon phenolic ablative composites for solid rocket motors of launch vehicles" National Conference on Material Science and Technology (NCMST-2016) at IIST .

6) L.Mohan Kumar, Tushar RP, Jayakumar G, K.M.Usha, E.N.Anandapadmanabhan & P.Chakravarthy, "Design, processing, characterisation and qualification of silica fibre reinforced phenolic resin ablative composites for liquid propellant rocket engines"- ISAMPE National Conference on Composites - INCCOM-14 at Hyderabad, January 2016.