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Development, Characterisation and Qualification of Aerospace Ablative Composites

Mohan Kumar .L[1, 2], Anandapadmanabhan EN[1], Usha KM[1], Chakravarthy .P[2]

Scientist, Composites Entity, Vikram Sarabhai Space Centre (VSSC), ISRO Thiruvananthapuram, India [1]

Department of Aerospace Engineering, Indian Institute of Space Science and Technology (IIST), ISRO, Valiamala, Thiruvananthapuram, India [2]

Abstract: Ablative composites are fibre-reinforced matrix composites capable of withstanding high temperatures, pressures and particle impingement. They find wide ranging applications in solid rocket motor nozzles, liquid engine throats, control thrusters, re-entry nose caps, leading edges etc. These components encounter extremely hostile service conditions. The high temperature, pressure, velocity of hot exhaust gases, heat flux, particle impingement of the solid propellant particles etc contribute to harsh environment inside the nozzles. Similarly, during re-retry of space vehicles, the vehicle is to be protected from the frictional aerodynamic heating. High temperature resistant metals or alloys cannot survive these extreme operating conditions. While the metallic structure provides the necessary structural capability, high performance composite materials are required for thermal protection. Ablative composites generally use Carbon or Silica as the reinforcement and phenolic resin as the matrix resin. These are processed using a complex processing cycle starting from impregnating the fibres with phenolic resin followed by moulding or winding prepare tapes over metallic mandrels before polymerization under pressure in Autoclave/Hydro claves. The property of ablation of these high performance composites is utilised to protect the metallic backup structure from thermal degradation during the firing of the solid rocket motors and during re-entry manoeuvres of space capsules. The mechanism of ablation and the desirable properties of ablative composites are explained. This paper describes the synthesis of carbon phenolics and silica phenolics, the most important and widely used ablatives in rocket launch vehicles and re-entry missions. The state-of-the-art technologies in the field of high temperature resistant composite processing are addressed in detail. Various processing techniques like hand layup, tape winding, mounding and curing and their relative importance are clearly enumerated. Special processing techniques, innovative and improvised processes and characterization methods are explained. The common defects and non-conformances encountered during processing too are mentioned. Finally, the qualification and evaluation schemes being followed for ablative composites are addressed.

Keywords: Composites, fiber-reinforced plastics, ablatives, carbon-phenolic, silica-phenolic, hydro lave, curing

I. INTRODUCTION

Ablative composites are aerospace grade composites made of high melting point fibers and polymeric resins with very high char yield. Carbon, graphite, silica, glass, asbestos are the commonly used reinforcements while resins include phenolics and furfural alcohol. An ideal ablative composite should possess high heat of ablation, high enthalpy of phase change, sufficient strength, high specific heat and high thermal shock resistance. At the same time, it should have low thermal conductivity, medium density, low molecular weight for the volatiles evolved during paralysis and as low an erosion rate as possible. [1-3].

Ablation is an orderly heat and mass transfer process in which a large quantity of heat energy is dissipated in a very short period of time by sacrificial loss of material at a rate which can be estimated. It is a very complex process including many physical and chemical transformations including phase changes like melting, vaporisation, sublimation and paralysis. Many endothermic reactions occur during the process. [4,5]

The ablative composites encounter extremely hostile conditions during the motor operation. The high temperature, pressure, velocity of hot exhaust gases, heat flux, particle impingement of the solid propellant particles etc contribute to harsh environment inside the nozzle. High temperature resistant metals or alloys alone cannot survive the operating conditions in a solid rocket motor. While the metallic structure provides the necessary structural capability, high performance composite materials are required for thermal protection. Ablative composites generally use Carbon or Silica as the reinforcement and phenolic resin as the matrix resin.

When the ablative is subjected to a very high heat flux as the hot exhaust gases pass through the nozzle, 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 paralysis temperature of the resin in the

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composite, decomposition of resin takes place. This leads to the formation of char on the surface of the ablative. As time progresses, the extent of char increases or the char front advances into the thickness of the material. Then the surface material starts eroding; erosion of the material can be due to the thermal degradation of the material and/or due to the mechanical erosion caused by metallic particle impingement due to the Aluminium 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 paralysis, the volatile gases evolving at the reaction zone finds its way through the charred zone taking away significant amount of heat. Similarly, melting of the resin as well as the fibers also consume 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 paralysis temperature, the decomposition of the composite starts, evolving gases, leaving the rigid porous carbonaceous substance called passive char. During the further advancement of the heating zone, the paralysis gases developed, absorb the heat from the passive char layer and dissociates itself into solid substrates which fills the porous char and builds pressure in the porous cavities.
As the pressure exceeds a threshold limit, char spoliation takes place. All the above reactions are of endothermic in nature. Ablative systems are basically designed based on thermal considerations but the structural properties also play a vital role during operation.

II. EXPERIMENTAL

a. Processing Of Ablative Composites
Ablative composites were synthesised from phenolic resin as matrix and carbon/silica fibres. Phenolic resin is synthesised from phenol and formaldehyde. The typical properties of the resin matrix are given below:

TABLE I
PHENOLIC RESIN PROPERTIES FOR CARBON PHENOLIC

Sl.No	Important properties	
	Parameters	Typical values
1	Specific gravity at 30°C	1.2
2	Solid content, %	63.5
3	Viscosity at 30°C, cps	250-300
4	Degree of advancement, ml	13.5
5	Free phenol content, %	5
6	Free formalin content, %	2

Carbon fibers were used as the reinforcement for ablatives used for solid rocket motor nozzles. Rayon based Carbon fiber is preferred for Ablative applications as it provides lower thermal conductivity and higher Interlaminar Shear strength because of crenulated cross-section.

Carbon fabric is made by weaving Carbon fibers with carbon content greater than 94%. This is made by successive carbonization of rayon. Poly acryl on it rile (PAN) and Pitch based carbon fabrics can also be used. 8 Harness Satin weave was chosen as the weave pattern considering the drivability for ease of processing.

Typical parameter values of the carbon fabric used is listed below:

TABLE II
IMPORTANT PARAMETERS OF CARBON FIBERS

Sl.No	Important properties	
	Parameters	Typical values
1	Carbon content, %	94-96
2	Sodium content, ppm	600
3	Ash content, %	0.20
4	pH	8
5	Breaking strength, kg/inch width	80-100
6	Areal density, gm/sq.m	250-300
7	Thickness, mm	0.3-0.4
8	Specific gravity	1.75
9	Thread count, ends/inch	45-55

Silica fabric and phenolic resin was used for the synthesis of the silica phenolic composite for liquid engine throats. The typical properties of the resin matrix used here are given below:

TABLE IIIII
PHENOLIC RESIN PROPERTIES FOR SILICA PHENOLIC

Sl.No	Important properties	
	Parameters	Typical values
1	Specific gravity at 30°C	1.2
2	Solid content, % at 170 ° C	74
3	Viscosity at 30°C, cps	400-600
4	CI-Degree of advancement, ml	14.5
5	Free phenol content, %	20
6	Free formalin content, %	0.5
7	Refractive index at 30° C	1.575
8	Water content, %	12
9	pH	7.6
10	Ash content, %	0.4
11	Sodium content, %	0.4

The time and temperature dependent properties of viscosity and degree of advancement of the resin are monitored regularly till the impregnation phase. In addition to these properties, the thermal properties are evaluated through TGA and DSC studies. The weight loss at ambient to 250°C range, in 250 to 700°C range and the residue at 700° C is evaluated.

Molecular characterization is done through Gel Permeation Chromatography (GPC). High molecular weight %, medium molecular weight % and % of free phenol are estimated. Through NMR analysis, average number of protons/ring, average number of rings/molecule, average number of ethylene bridges/ring and the average molecular weight is estimated. High Silica

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fabric is manufactured by the acid leaching of glass fabric. Typical parameter values of the silica fabric used is listed below:

TABLE IV
IMPORTANT PARAMETERS OF SILICA FIBERS

Sl.No	Important properties	
	Parameters	Typical values
1	Silica content, %	99
2	Weave pattern	8 HS Satin
3	Areal shrinkage, %	5 (max.)
4	pH	4
5	Breaking strength, kg/inch width	25-40
6	Areal density, gm/sq.m	575-675
7	Thickness, mm	0.75-0.90
8	Specific gravity	1.90-2.10
9	Thread count, ends/inch	45-55

b. Impregnation

The carbon/silica fabric was impregnated with phenolic resin. Initially, the fabric is dehydrated above 100°C to drive out the moisture. Then it is passed through a resin tank to absorb the resin. It is them passed through heating zones to advance the resin. The resultant material is called prepreg.

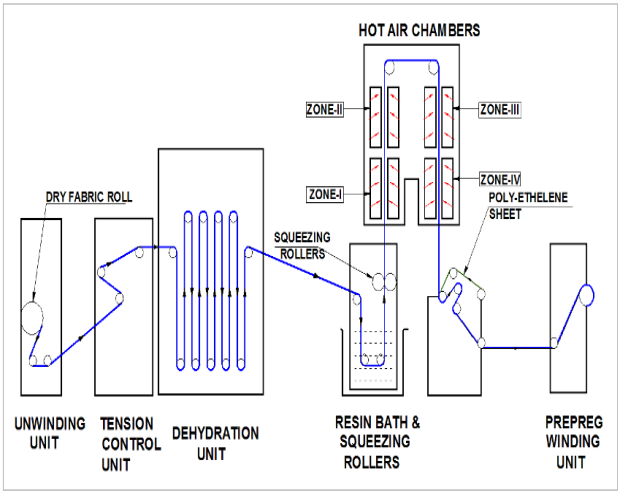

Fig. 1: Block diagram of an impregnation plant

The important parameters of the prepreg are,

TABLE V
IMPORTANT PARAMETERS OF PREPREGS

Sl.No	Important properties		
	Parameters	Carbon phenolic	Silica phenolic
1	Volatile content, (%)	5.6	4
2	Dry Resin content, (%)	41.1	34.6
3	Wet Resin content, (%)	46.7	38.5
4	Degree of advancement, (ml of water) Chang's index,	25.6	32

c. Processing of the liners

The prepreg is cut into the form of plies using a template and are either stacked together or wound on a metallic mandrel. The prepreg layup is compacted either giving vacuum or in a hydraulic press to get good as-wrapped density.

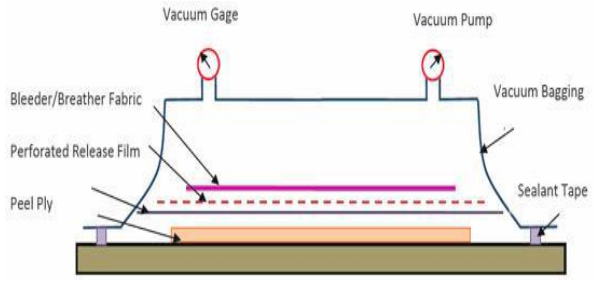

Fig. 2: Schematic of layup of prepreg

Fig.2 shows a schematic of the layup with bleeder/breather film, perforated release film and the vacuum bag in position. Perforated release film serves dual purpose; perforations allow the excess resin and volatiles to freely flow out of the liner and the release film prevents the unwanted adhesion of the liner to the mould. The bleeder material shall absorb the excess resin squeezed out of the liner. The vacuum bag is made from special grade polymer films capable of withstanding the curing temperature and pressure. For curing in Hydroclaves, impermeable high temperature resistant rubber bags with about 600% elongation are used. Fig. 3 shows the schematic of a liner being wound on a metallic mandrel.

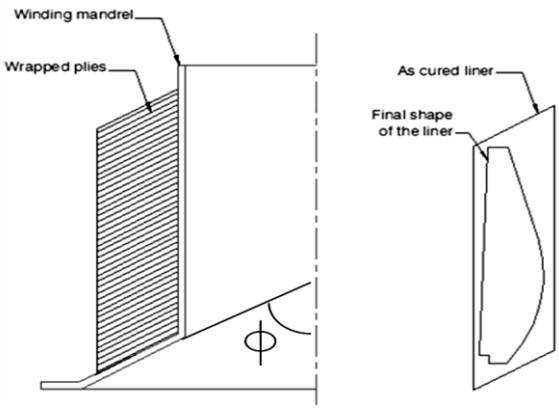

Fig. 3: Angular winding on a metallic mandrel

d. Curing or Polymerisation

After layup is put in vacuum bag it was cured at 150 ° C under pressure. Cross-linking of molecules of the polymer or polymerisation is achieved by curing under high temperature and pressure. Curing is done either in an oven, autoclave or hydroclave. In an oven, only heating is possible, whereas in an Autoclave/Hydroclave pressurisation is also done. The pressurising medium is air in an Autoclave which can go upto 10 bar pressure, while in a Hydroclave, pressure upto 65 bar can be applied since water is the pressurisation medium.

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e. Post Curing operations

After curing, the ablative composite is machined to the required configuration using special tools. Polycrystalline diamond (PCD) or Tungsten Carbide tools were used due to the abrasive nature of the material. Machining of ablatives is totally different from conventional materials like metals; here the material removal is in the form of carbon or silica powder and not in the form of chips. This necessitates dust collection suction systems at the cutting location which has to move along with the tool post. Coolant is not used during the machining of ablatives as it would cause deterioration in the properties of the composite.

III.RESULTS AND DISCUSSIONS

Dimensions of the required part were measured and Non-destructive testing was done to confirm that no defects were present in the liner. Common defects likely in ablative composites include delaminations, cracks, voids, porosity, resin lean lines, resin rich lines, resin starvation, resin patches, non-uniform resin distribution, waviness, wrinkles etc. Visual inspection, tap test and alcohol wipe test was done initially. This was followed by Ultrasonic inspection by Pulse echo and through transmission methods. Wherever the signal strength was less or suspected delaminations were reported, tangential radiography was done to rule out the presence of delaminations. Co-cured specimens were tested for mechanical and thermal properties. Specimens were fabricated from the end rings of the liners as per ASTM standards and tested. The test results are summarized in Table 6 and Table 7. Most critical thermal properties affecting the functional performance of the ablative composite are Heat of ablation and erosion rate at the service conditions. Heat of ablation and erosion rate were measured after subjecting the specimen to a heat flux of 750 Watts per unit area for 15 seconds. Specific heat and thermal conductivity were also evaluated. The achieved values are given below:

TABLE IVI
THERMAL PROPERTIES OF THE ABLATIVE COMPOSITE

	Parameter	Carbon	Silica
1	Heat of ablation @ 750 W/sq.cm (cal/g)	7250 - 8750	7600
2	Thermal conductivity (W/mK)- along ply	1.07	0.45-0.51
3	Thermal conductivity (W/mK)-across ply	1.11	0.54-0.71
4	Specific heat (J/kgK)	849.5	1186
5	Erosion rate –along ply(mm/s)	0.037	0.09
6	Erosion rate –across ply(mm/s)	0.033	0.87

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, Interlaminar shear strength and Compressive modulus were evaluated. Since tensile loads are not experienced by the nozzle liners, tensile properties were not evaluated. The achieved values are given below:

TABLE VII
MECHANICAL PROPERTIES OF THE ABLATIVE COMPOSITE

	Parameter	Carbon	Silica
1	Density (g/cc)	1.440-1.456	1.75-1.80
2	Compressive strength –along ply (MPa)	246.94	77.2
3	Compressive strength –across ply (MPa)	390.02	275
4	Compressive modulus –along ply (GPa)	16.08	10.7
5	Compressive modulus –across ply (GPa)	11.87	12.1
6	Interlaminar shear strength (MPa)	27.07	22.4

After completion of the synthesis and characterization, the ablative composite is put into the actual operating environment. For this a subscale motor is designed and tested. New concepts are first qualified by conducting sub-scale hot tests. Test Simulation Motors (TSM) provide ideal platform for sub-scale tests. Pressure, temperature, strains, vibration and acoustic levels are measured in the hot test. Design margins on the nozzle are validated by post-test evaluation. Dimensions and mass of the ablative liners are measured before and after the test to assess the mass loss, erosion rate etc. Elaborate instrumentation was carried out to collect data regarding the backwall temperature, pressure and strain during the operation. During the test, the ablative performed satisfactorily and all the backwall temperature measurements had read ambient values indicating that the ablative is capable of withstanding the operating conditions satisfactorily and thus can protect the metallic structure. Detailed post-test evaluation was completed. Figure 4 is a picture of the tested ablative surface. The eroded surface is clearly seen in this photograph.

Fig. 4: Photograph of the ablative composite after the test

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IV. CONCLUSION

The development of high performance thermal protection ablative composites has been discussed in detail. The experimental details of synthesis and processing of carbon/silica phenolic ablative composites are explained. The processed ablatives were characterized and all the critical properties have been evaluated. All the properties are meeting the required specifications. Inspection and Non-destructive testing of the components have been carried out to ensure the quality and reliability. Thus the material has been qualified for aerospace use in solid rocket motors.

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REFERENCES

[1] Dr. M. Balasubramaniam, Composite Materials and Processing, CRC Press, USA, 2013.
[2] N. Winya, S. Chankapoe, C. Kiriratnikom., Ablation, mechanical and thermal properties of fiber/phenolic matrix composites, World Academy of Science, Engineering and Technology 69 2012
[3] M. Vandenboom, S.D. Heister, "Application of Advanced Materials in a Composite Rocket Nozzle" July 10, 1998.
[4] Önder Güney, Erdem Demirkesen., "Influence of Curing Conditions on the Mechanical Properties of Silica-Phenolic Composites: A Comprehensive Study", International Advanced Research Journal in Science, Engineering and Technology Vol. 2, Issue 11, November 2015.
[5] Sutton, K., An Experimental study of a Carbon-phenolic ablation material, NASA Technical Note NASA-TN-D 5930. T.L.Elegange and R.R. Bowman, Nozzle fabrication for space shuttle solid rocket motor, AIAA/SAE 14th Joint Propulsion Conference, July 1978.
[6] H.R. Clements and G.T. Ward, Development of fabrication techniques for large solid booster nozzles, AIAA 6th Solid Propellant Rocket Conference, Washington DC.,.
[7] Mohan Kumar. L, Nikhil K Mawari, et al, Development of Bias wrapping technology for Ablative liners in S139 Solid rocket motor, INCCOM13 Proceedings, November 2014.
[8] Gutowski Timothy G, Advanced Composite Manufacturing, Wiley, 1997.Tomoko sano (editor), t. S. Srivatsan (editor), michael w. Peretti (editor), advanced composites for aerospace, marine, and land applications, wiley, 2014.