

Synthesis of Polycarbosilane, Polymer Impregnation Pyrolysis-based C/SiC Composites and Prototype Development

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ABSTRACT

Due to some extraordinary thermo-mechanical properties, silicon carbide is considered one of the best materials used for high temperature applications in defence and aerospace. Polycarbosilane (PCS) has been widely used as SiC precursor. This paper describes the research and development work undertaken to establish the technologies for synthesis and characterisation of PCS, fabrication process and characterisation of Carbon fibre reinforced SiC matrix (C/SiC) composite laminates and shaped articles. The molecular weight and softening point of the PCS was found to be 1400-1800 Mn and 140-150 °C respectively. Flexural stress of the unidirectional (UD) C/SiC composites and bidirectional (2D) C/SiC composites was found to be 400-450 MPa and 300-350 MPa respectively. Tensile stress of the 2D C/SiC composite was found to be around 200 MPa. Coefficient of thermal expansion and thermal diffusivity of the 2D C/SiC composites at RT- 1000 °C were found to be in range of $0.3-2.2 \times 10^{-6}/\text{°C}$ and $32-6 \text{ mm}^2/\text{s}$ respectively. The fabrication process developed for the UD and 2D C/SiC composites using the indigenous PCS has been also demonstrated to fabricate typical size divergent rocket nozzle and hot structure. Fabrication process of the SiC fibre has also been described in brief.

Keywords: Polycarbosilane; SiC fibre; PIP process; C/SiC composites

1. INTRODUCTION

The environment encountered by the rocket nozzles and other parts of rocket motor like jet-vanes is very severe with typical exhaust gases temperature around 2200 °C at about 3-4 mach^{1,2}. The exhaust gases contain tiny and hard particles of alumina which cause severe erosion in the exposed parts of the nozzle. SiC based materials possess high specific strength, erosion resistance and high temperature capabilities. Therefore, SiC matrix based composites are preferred materials for rocket motors parts of the advanced aero-engines and re-usable hot structures etc. SiC based composites have been at the centre-stage of development for the aforesaid applications³. Though various metallurgical, solid phase and vapour phase technologies are available to manufacture SiC based composites but polymer precursor based processing is being preferred for manufacturing complex shaped ceramics structure. Polycarbosilane (PCS) has been used as SiC precursor for fabricating carbon fibre reinforced silicon carbide (C/SiC) and silicon carbide fibre reinforced silicon carbide (SiC/SiC) composites. These composites are processed using the standard resin transfer method, filament winding and the moulding method³. The technologies to develop PCS, SiC-based composites and SiC fibres are available with few advanced countries only. PCS has been synthesised in a recycling system by heat treatment of tetramethylsilane at 650 °C^{4,5} and the direct

reaction of vinylsilanes or chloromethylsilanes with metallic sodium or potassium⁶.

SiC fibres developed by spinning the molten PCS followed by stabilisation in air and pyrolysis under inert atmosphere^{5,7,8}. Stabilisation process method controls the oxygen content in the SiC fibre which in turn dictates the maximum operating temperature of the fibres. Oxygen content in the air stabilised and electron beam cured SiC fibres is reported to 10-12 % and 1-2 % respectively⁹⁻¹¹. Thermo-structural properties of the SiC fibres can be also enhanced by metal incorporation in PCS^{12,13} e.g., by developing new ceramic precursor consisting of silicon, carbon, boron and nitrogen (Si-C-B-N)¹⁴. However, PCS and its derivatives like SiC fibre are not available to the country. Carbon fibres have been used to fabricate high temperature C/SiC composite products for some select applications^{1,2}.

C/SiC composites have been recommended to use for fabricating nozzles of rockets, jet-vanes and hot structures of hypersonic vehicles^{1,2}. C/SiC composites have been developed using chemical vapour impregnation (CVI) of methyl-tri-chloro-silane vapours into carbon fibres preforms^{15,16}, particularly for propulsion applications. German Aerospace Center developed liquid silicon infiltration (LSI) based C/SiC composites, particularly for advanced braking systems and jet-vanes². Jet-vanes have also been developed at Defence Research and Development Organisation using 3D stitched preforms following the LSI process¹. Polymer impregnation

and pyrolysis (PIP) process has been adopted to fabricate large size C/SiC composite products like thin walled rocket nozzles which reduces the overall weight of the propulsion system compared to the carbon fibre reinforced phenolic composite nozzle systems¹⁶⁻¹⁸. Though, the SiC fibre synthesis process, PIP based process C/SiC composite and their properties are reported but the fabrication details of the large size C/SiC composite products and process criticalities of the SiC fibre technology are guarded and thus not available in the open literature. Therefore, this study is aimed to demonstrate the use of the PCS for fabricating PIP based multi-directional continuous fibre reinforced C/SiC composites, characterisation of the composites and demonstrating the PIP process for fabricating the C/SiC composite shaped articles, like: nozzle divergent cone and reusable hot structure. SiC fibre fabricating process using the indigenous PCS will also be covered in brief.

2. MATERIALS SYNTHESIS: SCIENCE AND TECHNOLOGIES

2.1 Synthesis of Polydimethylsilane

Polydimethylsilane (PDMS) was synthesised by reacting sodium with dichlorodimethylsilane at 100-120 °C under inert atmosphere. The reaction was carried out in a three necked flask fitted with a mechanical stirrer, dropping funnel, condenser and inert gas inlet tube to purge inert gas. The reaction mixture with toluene solvent was allowed to reflux for 5 h. After completion of the reaction, toluene was removed by distillation followed by cooling the reaction mixture to room temperature. Distilled water was added to the reaction product to precipitate the PDMS. The precipitated PDMS was washed repeatedly with distilled water for complete removal of the unreacted reactants. PDMS was dried at 250 °C under N₂ to remove the trapped solvent and water to obtain free flowing PDMS granules.

2.2 Synthesis of Polycarbosilane

PDMS granules along with PBDPSO catalyst were heated slowly up to 250 °C under inert atmosphere to obtain uniform temperature. Temperature was further raised to 380 °C and maintained for 4-10 h in order to initiate the thermal backbone re-arrangement reaction. The PDMS granules got converted into viscous liquid polycarbosilane. The viscous polycarbosilane was distilled at 300-350 °C to separate liquid PCS and solid PCS. Liquid PCS was found to be about 40 % (w/w) of the PDMS granules. Temperature of the remaining 60 % mass was raised up to 420 °C and the temperature was maintained for 2 h. The remaining mass was allowed to cool under high purity N₂ atmosphere to obtain solid honey coloured material, which is termed as solid PCS.

2.3 Characterisation of PCS

PCS was characterised inhouse using, Fourier Transform Infrared spectroscopy (FTIR). The prominent and characteristic peaks were found at 2956 cm⁻¹, 2092 cm⁻¹, 1416 cm⁻¹, 1248 cm⁻¹ and 1043 cm⁻¹. These peaks are attributed to C-H bond, Si-H bond, C-H vibration (Si-CH₃), Si-CH₃ bond and Si-CH₂-Si bond respectively. Elemental

composition analysis of the solid PCS was carried out using CHNOS analyser. Weight fraction of C, H, N, O and S was found to be 41.24 %; 10.24 %; 0.386 %; 0.0 % and 0.001 % respectively. Silicon percentage is determined by subtracting the % weights of C, H, N, O and S from 100; it is found to be 48.13%. The molecular weight distribution of the solid PCS is determined with gel permeation chromatography and its value was found to be in the range 1400-1800 Mn for the PCS having softening point of 140-150 °C.

2.4 SiC Fibre Feasibility

“Green PCS fibres of diameter ranging 30-60 microns” were obtained using melt spinning of the solid PCS. The PCS having softening point in the range 140-150 °C was allowed to melt in a spinneret. The molten PCS was pushed through the specific designed spinning die with the help of adequate pressure (typical range of 10-15 atm) and fibres were wound on a cylindrical fixture. The PCS fibres were stabilised in air at 140-220 °C in an oven to carry out the surface cross-linking (oxidative curing). The stabilised PCS fibres were pyrolysed up to 1000-1400 °C by heating them at the rate of 20-50 °C/h. A typical scheme of SiC fibre process is shown in Fig. 1. Similar process has been adopted by others^{14,15}. During pyrolysis, there is a net reduction of about 30 % mass of the stabilised fibres and density of the fibres increases from about 1.0 g/cc to 2.5 g/cc which causes a significant shrinkage in the fibres. In this study, the fibres could be pyrolysed without much distortion in their shape. Diameter of the SiC fibres was found to be in the range 18-40 microns depending on the starting PCS type and green fibre diameter. Typical image of the as spun fibre and pyrolysed fibre are as shown in Fig. 2. A typical X-Ray Diffraction (XRD) spectra of the SiC fibres pyrolysed up to 1200 °C is as shown in Fig. 3. The characteristic peaks of SiC are visible in the XRD spectra.

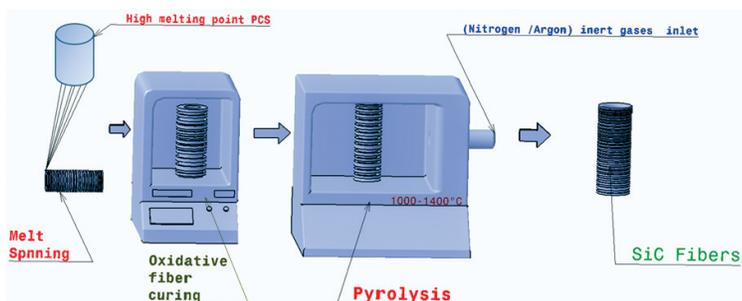


Figure 1. SiC fibre fabrication scheme.

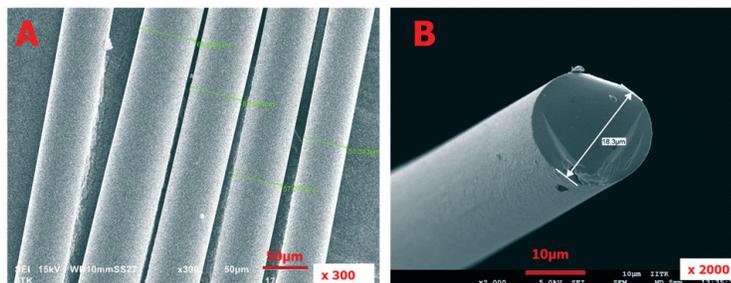


Figure 2. (a) High magnification images of the as fabricated PCS fibre and (b) SiC fibre.

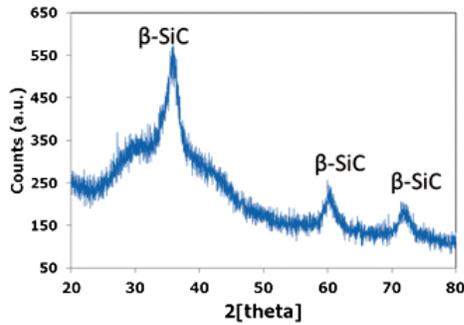


Figure 3. XRD spectra of SiC fibres.

Since, the peaks are not very sharp, it indicates that, the SiC fibres are not fully crystalline. There are numerous challenges in SiC fibre technology like: continuous spinning of low molecular weight PCS polymer, uniform oxidative stabilisation, defect free pyrolysis, protection coating, interface coating and weaving of the SiC fibres to fabricate preform etc. All these identified challenges need to be addressed appropriately and proper process methods have to evolve to overcome the challenges and to fabricate the SiC/SiC composites.

In absence of the SiC fibres, the composite fabrication process has been developed using the carbon fibres. Composite fabrication process is similar for the carbon fibre and SiC fibre, therefore the process of the C/SiC composite can be easily converted to SiC/SiC composite once the indigenous SiC fibre technology get mature. C/SiC composite process using the indigenous PCS is explained in the subsequent section.

2.5 Fabrication of C/SiC Composites Using PIP Process

T300 carbon fibre tows and carbon fabric were used for fabricating unidirectional (UD) and bi-directional (2D) fibre reinforced composite laminates respectively. The stack of the fibre tows is termed as UD fibrous preforms whereas the stack of the fabric layers is termed as 2D preform. A schematic of the fabrication process of PIP based C/SiC composites is as shown in Fig. 4. The following steps were used to fabricate the UD/2D C/SiC composites:

- (i) PCS and Divinylbenzene (DVB) were mixed in the ratio of 5:1 and diluted in petroleum ether to obtain a diluted ceramic precursor solution
- (ii) The fibre tows were wound on a slotted fixture to obtain UD preforms. The fabric was cut into pieces of 200 mm x 200 mm and the pieces were stacked keeping warp and weft fibres at 0/90° order to obtain 2D preform
- (iii) The UD/2D preforms were impregnated with the PCS+DVB solution using the vacuum impregnating system
- (iv) The impregnated preforms were kept in open to remove the solvent of the solution up to 95 per cent by weight, the impregnated preforms are termed as prepregs
- (v) The composite laminates were fabricated using the thermal moulding, where UD/2D prepregs stack were heated in a moulding die at the rate of 1 °C/min up to 150-350 °C, 2 h - 4 h under the required load to obtain 40-60 per cent fibre volume fraction (V_f) in the composites
- (vi) The moulded composites (UD or 2D) were removed from

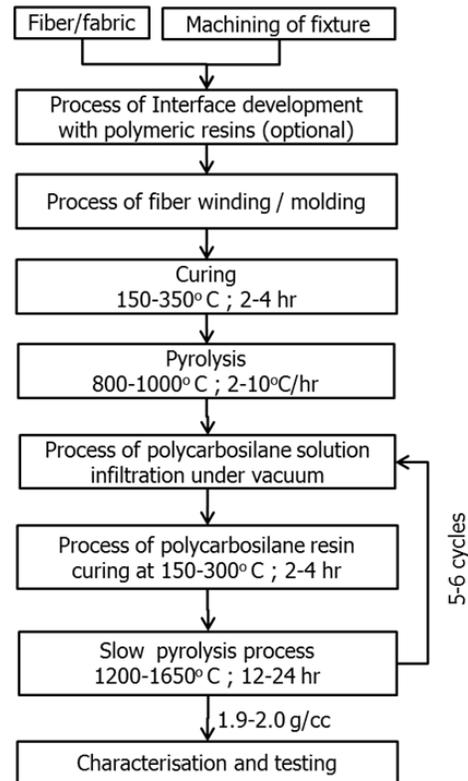


Figure 4. Schematic of the processing of PIP based C/SiC composites.

the moulding die and were kept in an inert atmosphere furnace to pyrolyse them up to 1400-1600 °C at the rate of 2 °C/min

- (vii) The process of PCS solution infiltration, curing and pyrolysis was repeated several times (typically 5-6 times) to densify the composites
- (viii) Density and open porosity of the composites were measured by Archimedes principle.

3. CHARACTERISATION

3.1 Structure and Phase Analysis of Pyrolysed PCS

Polymer derived SiC can become α -SiC, β -SiC or their mixture depending on the pyrolysis temperature. At lower temperature, it is found to be dominated by β -SiC while at higher temperature α -SiC is the main phase. A typical XRD spectra of the PIP based C/SiC composites is as shown in Fig. 5.

3.2 Physical Properties

Density of the C/SiC composite laminates after 6-7 infiltration/ pyrolysis cycle was found to be in the range of 1.7-1.9 g/cc. Effect of the composite laminate size was significant on the density of the composite for similar numbers of infiltration cycles. UD C/SiC composite strips of size 200x10x2 mm could be densified up to 1.9 g/cc while the 2D C/SiC composite laminates of size 200 mm x 200 mm x 50 mm could be densified only up to 1.7 g/cc. High pressure impregnation or large numbers of process cycles are recommended to densify the thicker composites.

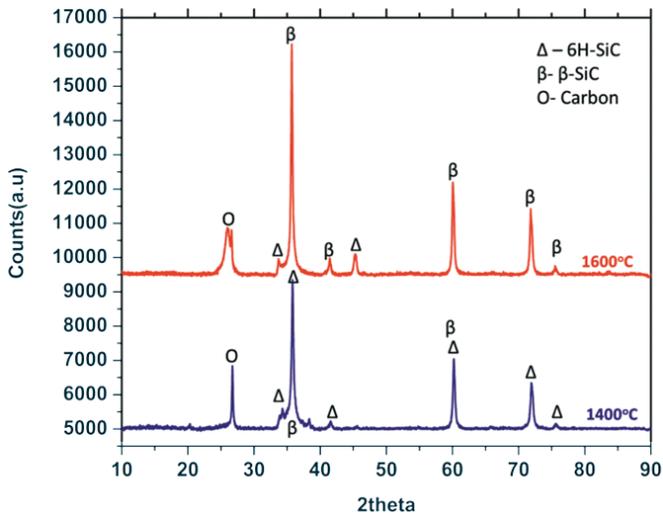


Figure 5. Effect of pyrolysis temperature on phase composition of PIP based C/SiC composites.

3.3 Mechanical Properties

Flexural stress of the UD and 2D C/SiC composite specimens was determined as per ASTM C-1341 using 3-point bending fixture. A minimum of six specimens (of different density levels) were tested on Universal Testing Machine (Instron 5967) with a crosshead speed of 0.5 mm/min. Tensile stress of the UD and 2D composite specimens was determined as per ASTM C-1273-15. Rectangular strips of the UD composites and dog bone shape specimens of the 2D composites were used. A minimum of three specimens from each batch/process conditions were tested under tension with a crosshead speed of 1.0 mm/min.

3.3.1 Flexural Strength

Effect of pyrolysis temperature, V_f and density of the composite on flexural stress/strength (sth) of the UD C/SiC composite is as shown in Fig. 6. Y-axis shows the pyrolysis temperature (°C) - V_f (%) - density (g/cc). It is evident from the Fig. 6 that the strength was highest for the composites pyrolysed at 1400 °C and it is found to be increased with increasing V_f and density. Higher strength at 1400 °C is interpreted due to the phase composition (Fig. 5) and extensive fibre pull out and

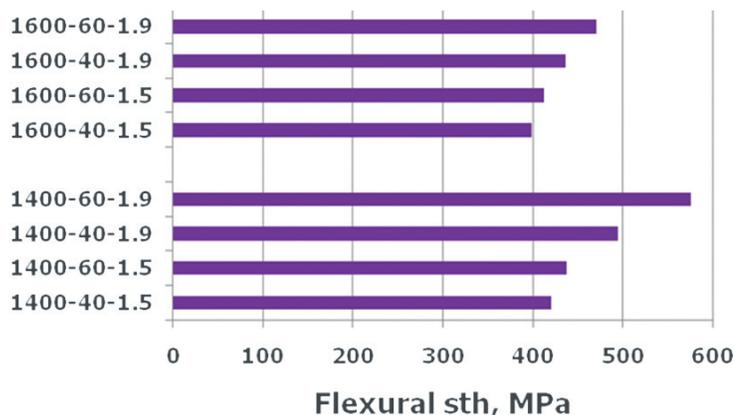


Figure 6. Flexural stress of UD C/SiC composites made under different conditions of temperature and fibre volume content.

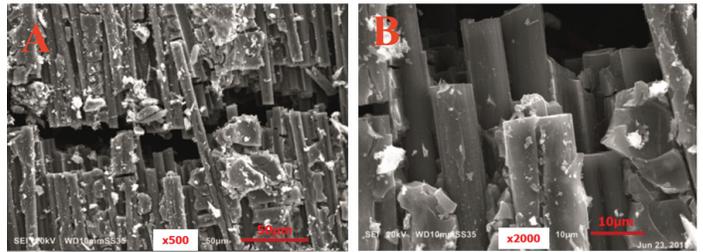


Figure 7. Microstructure and fibre pull out in the flexural stress tested UD C/SiC composite.

weak interface (Fig. 7). Fibre matrix reaction might happen due to oxygen impurities present in the PCS. But, the surface of the fibres (in the broken specimens) appears to be free from any chemical reaction (Fig. 7). It indicates that, there is no surface reaction between the carbon fibre and SiC matrix. Perhaps this is the main reason for extensive fibre pull out. The fibre pull out is considered beneficial for improving the toughness of the composites.

Similar to the UD C/SiC composites, 2D C/SiC composites were densified and tested for the mechanical and thermal properties. A typical flexural stress vs extension curve of the 2D C/SiC composite pyrolysed at 1400 °C ($V_f = 50\%$ and density = 1.7 g/cc) is as shown in Fig. 8. The zig-zag nature of the curve

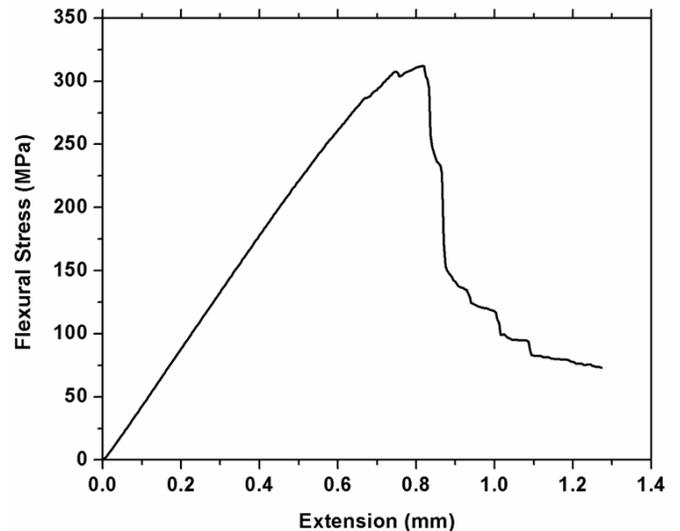


Figure 8. Flexural strength of 2D C/SiC composites pyrolysed at 1400 °C.

(beyond the ultimate stress value) and extended area under the curve indicate that the composite has reasonably good toughness. Despite majority of the reinforcing fibres fail at the ultimate stress value but the stress level falls gradually beyond the ultimate stress value. The gradual failure is due to the result of extensive fibre pull out in PIP based C/SiC composites (Fig. 7).

3.3.2 Tensile Stress/strength

Representative tensile stress vs. strain curves of the 2D C/SiC composites are as shown in Fig. 9. The trend of the stress value with respect to the pyrolysis temperature was found to be similar to that of the UD C/SiC composites

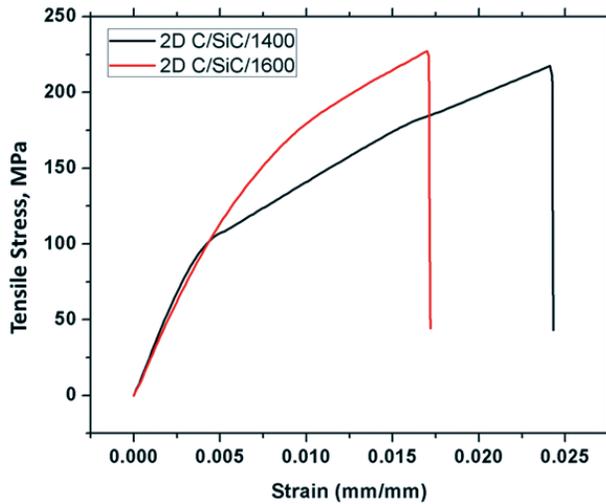


Figure 9. Effect of pyrolysis temperature on tensile stress of 2D C/SiC composite.

i.e. strength of the composites pyrolysed at 1400 °C is higher than those pyrolysed at 1600 °C. Lower strength at 1600 °C is interpreted due to the brittle interface and fibre surface reaction with the inherent oxygen present in the matrix. Tensile strength of the UD C/SiC composites was found to be about 1.7 time of the average value of the tensile strength of the 2D C/SiC composite.

3.4 Thermal Properties

Coefficient of thermal expansion (CTE) of the 2D C/SiC composite in in-plane direction was determined using the Dilatometer (NETZSCH DIL 402C) at ARCI, Hyderabad. Specimen of size 6x6x25 mm were cut from the composite in the way, that the axis of the warp fibres was kept in parallel to the length of the specimen i.e equals to 25 mm (Lo). The specimens were heated at the rate of 5 °C/min in flowing argon atmosphere. The change in length of the specimen (dLo) was measured with respect to the per unit rise of temperature (ΔT). Thermal diffusivity of the 2D C/SiC composite was determined as per ASTM E-1461-13 in through thickness direction. The measurement was carried out in inert atmosphere from room temperature to 1200 °C.

3.4.1 Coefficient of Thermal Expansion (CTE)

The CTE was determined by using the relation

$$CTE = \frac{dL_o}{\Delta T * L_o}$$

and it is as shown in Fig. 10. It varies from

3.0×10^{-7} to 2.2×10^{-6} m/m °C in temperature range of 200 °C to 1000 °C. In-plane CTE of the PIP based 2D C/SiC composites is found to lower than the CTE of the C/SiC composites processed via CVI and LSI processes¹⁷⁻¹⁸.

From the Fig. 10, it is evident that the CTE decreases up to 250 °C, followed by an increasing trend up to 1000 °C. It is well known fact that the matrix of the PIP based C/SiC composites contains multiple cracks perpendicular to the fibre axis. CTE tends to decrease in the initial phase (up to 250 °C) due to absorption of the thermal expansion of the constituents within the matrix microcracks present in the composite. CTE of the carbon fibres is lower than that of SiC, therefore, CTE of the C/SiC composite in any direction is controlled by constituent

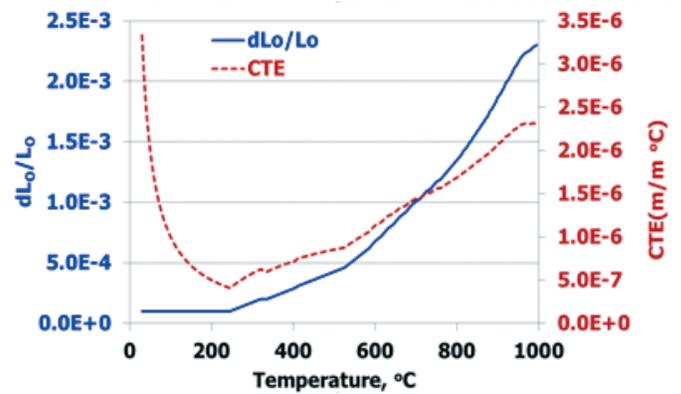


Figure 10. Thermal expansion of 2D C/SiC composite.

which has the least CTE. In case of the C/SiC composites, the axial CTE of the carbon fibre is the least. Therefore, the in-plane CTE of the 2D C/SiC composite is close to that of the CTE of the carbon fibres in their axial direction¹⁷⁻¹⁸.

3.4.2 Thermal Diffusivity

The thermal diffusivity is found to be decreased with test temperature from 32 mm²/s to 7 mm²/s in the temperature range of RT–1200 °C as shown in Fig. 11. Thermal diffusivity of the basic constituents of the C/SiC composites decreases with temperature. Due to this reason, thermal diffusivity of the C/SiC composites found to be decreased with the testing temperature.

Thermal properties of the indigenous PCS based C/SiC composites are found to be better than LSI and CVI based C/SiC composites reported in the literature¹⁶⁻¹⁸.

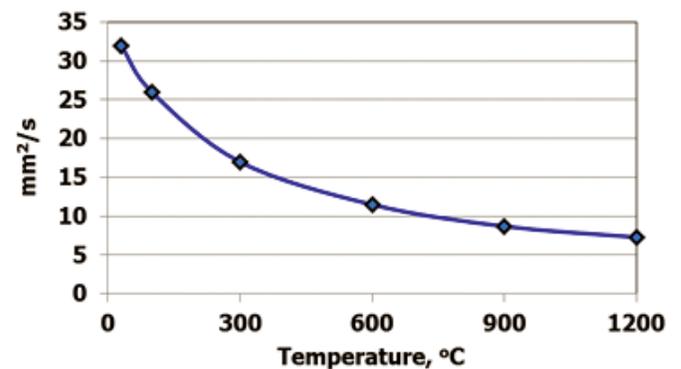


Figure 11. Thermal diffusivity of 2D C/SiC composite.

3.4.3 Comparison of UD, 2D C/SiC Properties with Literature

Mechanical and thermal properties of the UD and 2D C/SiC composites fabricated using the indigenous PCS are compared with the properties of the C/SiC fabricated elsewhere using PIP, LSI and CVI processes (Table 1). It is evident that the properties obtained in the present study are found to be equivalent to the properties reported for the PIP and CVI based C/SiC composites and better than the properties reported for the LSI based C/SiC composites.

Mechanical properties of the PIP based C/SiC composite depend on the type of SiC precursor used as source material;

Table 1. Comparison of mechanical and thermal properties of PIP based UD and 2D C/SiC composites with C/SiC properties reported elsewhere

Property	Units	Present study		CVI ¹⁶⁻¹⁸	LSI ¹⁶⁻¹⁸
		UD	2D	2D	2D
Fibre Volume fraction (V_f)	Vol.%	40-60	50-55	42-44	45-50
Density	g/cm ³	1.82-1.90	1.7-1.75	1.7-1.8	2.4
Flexural stress	MPa	454-720	300-350	250-330	180-200
Tensile strength	MPa	350-550	185-230	200-250	80-190
Young's modulus	GPa	175-200	55-70	60-80	60
Strain to failure	%	0.2-0.4	0.2-0.35	0.3-1.1	0.15-0.35
Thermal diffusivity in through thickness direction	mm ² /s	-	35-7	-	30-35
CTE ($\times 10^{-6}$) in parallel to fiber axis	m/m°C	-	-0.5-2.5	2-3	1.0-1.5

fabrication temperature; density/residual porosity; type of carbon fibre; V_f and interface type. Pyro-carbon or boron nitride interface are being used for developing an optimum bonding between the reinforcing fibre and the matrix^{17,18} for the CVI based C/SiC composites. Deposition of SiC matrix through gaseous route provides uniformity and the best grain size which result better mechanical properties. Therefore, CVI based C/SiC composites possess better properties. In absence of the interface, the reinforcing fibres tend to react with the matrix and thus leading brittle fracture. Therefore, interface is very important for the CVI based C/SiC composites. In case of LSI based C/SiC composites, the reinforcing fibres tend to react with the residual silicon and their strength comes down drastically. Therefore, the overall mechanical strength of the LSI based C/SiC is inferior compared to the PIP and CVI based composites for the similar fibre types and comparable fibre volume fractions.

The matrix obtained through PCS is considered to be free from any traces of residual silicon. Due to presence of additional carbon than the theoretical requirement, the matrix material obtained from the PCS and DVB does not react with the reinforcing carbon fibres. Non-reactive nature of the PCS generated SiC matrix ensures a weaker interface which is required for better toughness and fibre pull out. Therefore, the properties of the UD C/SiC and 2D C/SiC composites fabricated in this study are found to be on par with the CVI based C/SiC composites and better than the LSI based C/SiC composites.

4. PRODUCT DEVELOPMENT

C/SiC composites are used or proposed for hot structures for aerospace systems which experience severe service conditions^{2,8}. These applications demand erosive resistance structure for long service durations. However, for the missile systems, service time is short but the aero-thermal conditions impart higher erosive loads¹. NASA and European Union have developed state-of-the-art facilities for the fibre reinforcements, preforming, processing and characterisation of the C/SiC composite products for defence and aerospace applications^{2,3,16-18}. To demonstrate fabrication process of large size C/SiC composite products, two typical prototypes are chosen and

fabricated. The fabrication process is briefly described in the subsequent sub-sections.

4.1 Nozzle Divergent Cone

The PIP based C/SiC composites with ceramic coating would result a dense radiation cooled nozzle. Considering the gas tightness requirement of the nozzle, match die moulding technique was adopted which reduces through thickness pore channels. To realize a testable nozzle, a moulding tool has been designed and developed with inbuilt PID controlled heating system. The process developed for the PIP based 2D C/SiC composites was adopted for fabricating the nozzle divergent cone. The required size and shape prepregs were cut and stacked on the male mould. After obtaining the required thickness of the stack, the female mould was placed over the male mould. The male and female moulds were tightened followed by heating them at predefined heating rates, similar to the 2D C/SiC composite laminate moulding cycle. After curing, the component was taken out and processed as per the procedure described in section 2.5. The selected nozzle divergent cone is has length of 450 mm with base diameter of 280 mm and throat diameter of 120 mm as shown in Fig. 12. Four nozzle components are realised to study the effect of density, resin composition and V_f on the permeability and densification efficiency. Greater details of the fabrication and the results of functional features of the nozzle divergent cone would be disclosed in the subsequent research papers at an appropriate time.

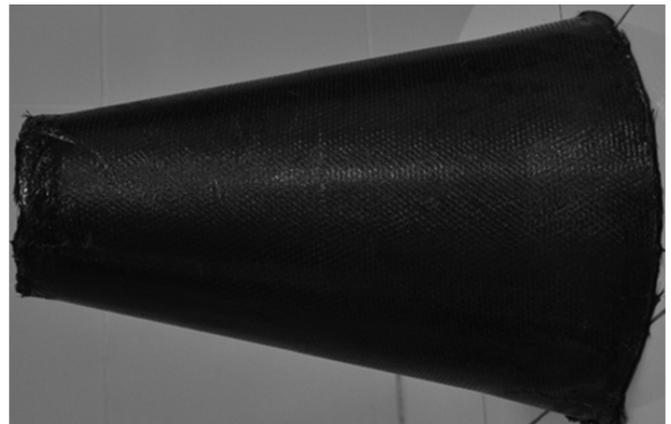


Figure 12. PIP based C/SiC nozzle prototype.

4.2 Hot Structures

Hot structure of the reusable hypersonic cruise vehicle are required to be fabricated using ceramic composite. As stated earlier, large size and non-symmetrical shaped C/SiC composite products are difficult to fabricate using LSI and CVI/CVD. Considering the futuristic requirement of the defence systems, a typical shape hot structure having height = 300 mm and one of the dimensions of the base equals to 250 mm was chosen as shown in Fig. 13. Fabrication process for the structure was similar to the nozzle divergent cone (section 4.1).



Figure 13. Prototype for a typical hot structure prototype.

Two components were fabricated and densified successfully. The components were found to be defect free and uniform w.r.t. to density at different locations. The components would be tested for their functional properties later. Greater details of the fabrication and functional features of the hot structure would be disclosed in the subsequent research papers at an appropriate time.

5. CONCLUSIONS

Indigenous technologies have been demonstrated for synthesis of PDMS, PCS, PIP process for fabricating C/SiC composites and also to develop test prototypes have been demonstrated. The mechanical and thermal properties of the indigenous material are found to be on par with the materials developed elsewhere. The indigenous technology initiative efforts have also resulted in demonstration of the SiC fibre technology. The scale down rocket nozzle divergent cone is expected to have much better performance compared to the C/Phenolic nozzles being used in the present rocket motors. The PIP technology has also opened a path to develop C/SiC composites based hot structures to replace the ablative material-based systems. The C/SiC composite process would become basis to fabricate SiC/SiC composites once SiC fibre process get matured.

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