CHAPTER-4
DEVELOPMENT OF FIBRE REINFORCED COMPOSITES WITH POLYDIMETHYLSILOXANE RESIN AND THEIR PYROLYSIS

4.1: INTRODUCTION

The most important monolithic ceramics developed as structural materials are aluminium oxide, zirconium oxide, silicon carbide and silicon nitride. These materials, though possess high temperature stability, are brittle in nature. The properties, selected for both mechanical and physical properties of these ceramics can be improved either by alloying (e.g. silicon nitride with alumina to form sialons or zirconia with other oxides such as yttria, ceria or magnesia to give transformed microstructures) or by using the principle of composites.

Ceramic matrix composites are prepared with particulates, whiskers or continuous fibres as reinforcements. Most common techniques to fabricate ceramic matrix composites have been discussed in chapter 1. It was observed in chapter-3 that polydimethylsiloxane (PDMS) is an excellent precursor for making silicon oxy-carbide. Therefore, studies were extended using same resin to make ceramic matrix composites by filament winding technique, prepping, pressure molding techniques. Polymer composites after characterisation were pyrolyzed at 1000, 1200 and 1400 C in presence of nitrogen. The physical changes occurring during first pyrolysis were measured. The composites were characterised by optical microscopy. The first pyrolysed composites were reimpregnated with PDMS and or
polyfurfuryl alcohol resin and repyrolyzed to 1000 °C. The composites were finally characterised for oxidation resistance and mechanical properties.

4.2: PHYSICAL CHARACTERISATION OF THE COMPOSITES AT DIFFERENT STAGES OF FORMATION

Unidirectional composites made with high strength carbon fibres and polydimethylsiloxane were pyrolyzed to 1000 °C. The polymer matrix in the composites showed weight loss and shrinkage generating porosity in the pyrolyzed composites.

The weight loss and cross-sectional shrinkage of the composites with impregnation cycles is shown in figure 4.1. As evident from the figure, composites exhibit a weight loss of 7.5% and shrinkage of 11.5% during first carbonization from polymer stage. Weight loss corresponds to the amount of resin present in the composites. However, shrinkage in the composites is lower than the shrinkage of the matrix alone. It gets restricted by the presence of fibres. On subsequent impregnation cycles, the weight loss decreases with impregnation cycle. The weight loss on subsequent impregnation/carbonization cycles correspond to the matrix pickup during subsequent impregnations. The decrease in weight loss during repeated impregnation/carbonization cycles signifies that the matrix pickup decreases even after first cycle. This is partially due to filling up of the pores and partly due to pore blockage. Table 4.1 shows the fibre volume contents of the composites made with different carbon fibres at different stages of development.

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Fig. 41: Weight loss and cross-sectional shrinkage of the composites with impregnation cycles.

Fig. 41: Weight loss and cross-sectional shrinkage of the composites with impregnation cycles.
### TABLE: 4.1
Fibre volume contents of composites at different stages of development.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fibre type</th>
<th>Vf (%)</th>
<th>Polymer stage</th>
<th>Pyrolyzed stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>HMCF</td>
<td>30.8</td>
<td>34.2</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>HMS(treated)</td>
<td>36.0</td>
<td>40.8</td>
<td>4</td>
</tr>
<tr>
<td>3.</td>
<td>IMCF</td>
<td>27.4</td>
<td>29.8</td>
<td>2</td>
</tr>
<tr>
<td>4.</td>
<td>HTCF</td>
<td>29.5</td>
<td>30.8</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the increase in density and decrease in porosity of the composites with impregnation cycles. On first pyrolysis of the composites, decrease in density is very very small (approximately 1%). However, the open porosity increases appreciably. This is attributed to the shrinkage of the matrix near the fibre within the composites resulting in open-mouth voids and pores. It is because of these open voids and pores that the density of the composites increases appreciably (approximately 25%) during first impregnation and the porosity decreases (approximately 50%). On subsequent impregnations, the available open porosity is very small and therefore the increase in density is small.
Fig. 4.2: Density and porosity of the composites with impregnation cycles.
4.3: EFFECT OF FIBRE TYPE ON PHYSICAL CHARACTERISTICS DURING PYROLYSIS OF THE COMPOSITES

It is well known that during fabrication of carbon-carbon composites, the type of carbon fibres has significant effect on the pyrolysis shrinkage and properties of the composites[54,139-141]. Composites made with furan resin and carbon fibres having surface groups such as high strength and surface treated carbon fibres, when pyrolyzed exhibit higher shrinkage than those made with non surface treated carbon fibres.

In order to study this effect in composites made with polydimethylsiloxane, unidirectional composites were made with high strength carbon fibres, intermediate carbon fibres, high modulus carbon fibres and high modulus surface treated carbon fibres. These composites were pyrolyzed to 1000 °C and the physical changes taking place during pyrolysis were studied.

Figure 4.3 shows the shrinkage during pyrolysis of the composites made with different carbon fibres. As seen from the figure, composites made with different carbon fibres exhibit pyrolysis shrinkage of 8% to 12%. In this case also composites made with high surface energetics carbon fibres (treated HM, high strength) exhibit higher shrinkage than those having lower surface groups (HM and IM). However, the effect is not so pronounced as in the case of carbon-carbon composites where the shrinkage difference is 15 to 24% [142,143]. It means that the bonding between polydimethylsiloxane and carbon fibres is not much affected by the presence of surface groups on commercial carbon fibres.
Fig. 4.3: Shrinkage during pyrolysis and impregnation cycles of the composites made with different carbon fibres and silicon oxy-carbide matrix.
Figures 4.4 and 4.5 show the variation of porosity and density respectively for different composites. These composites follow the same pattern as in figure 4.2. The open porosity increases on first pyrolysis and decreases on subsequent impregnation. The density of the composites does not change much during first pyrolysis but increases appreciably during first impregnation. All the composites exhibited good integrity after first pyrolysis. On comparing the data of pyrolyzed composites made with different carbon fibres (level 0 in figures 4.3, 4.4 and 4.5) it is found that composites made with High strength carbon fibres and lab treated high modulus carbon fibres exhibit more cross sectional shrinkage, lower porosity and higher densities than other composites. This suggests that different extent of bonding takes place between the fibres and matrix in these composites depending on the surface groups present on carbon fibres. On subsequent impregnations, the density of all the composites is found to increase. However, the increase in density during first impregnation is maximum for the composites made with high strength carbon fibres and surface treated high modulus carbon fibres. Though the porosity of the pyrolyzed composites made with IM fibres & HM fibres was maximum, but the increase in density during first impregnation was minimum. This is due to the reason that most of the pores in these composites were big enough with smaller enterants that the impregnants could not enter the complete pores. This was also found on visual and optical examination of the composites. This suggest that the pore structure in the matrix during first pyrolysis is also
Fig. 4.4: Porosity during pyrolysis and impregnation cycles of the composites made with different carbon fibres and silicon oxy-carbide matrix.
Fig. 45: Density of the composites made with different carbon fibres and silicon oxy-carbide matrix during pyrolysis.
controlled the fibre type and governs the increase in density of the composites during subsequent densification cycles. After three densification cycles the porosity of all the composites made with high strength and high modulus carbon fibres was found to lie in the range 1.6 - 1.68 g/cc.

4.4: OPTICAL MICROSCOPY OF THE COMPOSITES

Composites made with polydimethylsiloxane, pyrolyzed to different temperatures were embedded and polished. The polished samples were examined under optical microscope. Figure 4.6 shows the optical micrographs of these composites at different stages. As seen from the figure, there is good bonding between reinforcing fibres and polymer matrix almost in all the composites. The fibres are also well distributed. On pyrolysis differential behaviour is observed in the composites. In composites made with HM fibres & IM fibres (fig. 4.6 e & f) there relatively larger gaps between fibre and matrix. The matrix seem to have shrunk away from the fibres, whereas, in case of composites made with HT and surface treated HM fibres, the gap between fibres and matrix is either not there or comparatively very very smaller. At many places, the matrix is well adhered to the fibres. However, in all composites, voids and pores can be seen in the bulk matrix. When viewed under polarised light, the matrix does not exhibit any anisotrophic structure. This means that the matrix is isotrophic and glassy in character.
Polymer Composite:

(a) HM Fibres X 1000
(b) IM Fibres X 1000
(c) HMS Fibres X 500
(d) HT Fibres X 500

Fig. 4.6.A Optical micrographs of the composites made with different carbon fibres.
Fig. 4.6.B Optical micrographs of the composites made with different carbon fibres.
Densified composites were tested for flexural strength and flexural modulus. Figure 4.7 and 4.8 show the flexural strength and flexural moduli of the composites made with different types of carbon fibres. As seen from these figures, composites made with high strength carbon fibres exhibit higher flexural strength and modulus than all other composites. One might have expected higher modulus for the composites made with high modulus carbon fibres. However, it is not the case. Composites made with high strength carbon fibres are more compact and have the highest density. It may be because of this reason that these composites exhibit higher strength and modulus than all other composites. Figure 4.9 shows the Scanning Electron Micrographs (SEM) of the fractured composites made with different carbon fibres. As seen from these figures, all the composites exhibit mixed mode failure with different extent of fibre pullout. Composites made with high strength (fig. 4.9a) and treated high modulus fibres (fig. 4.9b) exhibit short length fibre pullout with matrix sticking to the fibres whereas composites made with HM fibres (fig. 4.9c) exhibit long fibres protruding out of the matrix.

In carbon-carbon composites, usually the composites made with high strength carbon fibres exhibit catastrophic failure with low strength. But this is not the case for composites made with silicon oxy-carbide. This confirms that polydimethylsiloxane resin does not make very strong chemical bonding with carbon fibres and therefore on pyrolysis, the
Fig. 4.7: Flexural strength of the composites made with different carbon fibres and silicon oxy-carbide matrix.
Fig. 4.8: Flexural moduli of the composites made with different carbon fibres and silicon oxy-carbide matrix.
Fig. 4.9. SEM micrographs of the fractured pyrolysed composites made with different carbon fibres.
fibre/matrix bonding is of intermediate type, neither too strong, which may lead to catastrophic brittle failure of the composites, nor too weak that the composites fail in pure shear or delaminate.

4.6: HEAT TREATMENT OF THE COMPOSITES TO HIGH TEMPERATURE

The densified composites were further heated to 1200°C and 1400°C. Figure 4.10 shows the increase in density of the composites with heat treatment temperature. As seen from the figure, the density of all the composites increase on higher heat treatments' temperature. The trend in increase in density suggests that the increase in density is due to compaction of the matrix during high heat treatment temperature which is accompanied by a crosssectional shrinkage of about 5%. The size of the composites heated to 1200 & 1400°C were small. Therefore, these composites could not be tested for mechanical properties.

4.7: COMPOSITES WITH HYBRID MATRIX

In order to study the effect of type of impregnants and hybrid matrix, composites were made with hybrid matrix system, in which some of the composites made with different types of carbon fibres after two impregnations with PDMS resin and pyrolysis were impregnated with polyfurfuryl alcohol resin followed by pyrolysis. Figures 4.11 & 4.12 show the change in porosity and density of such composites. On comparing these values of the final composites with those of the composites made with hybrid matrix, it is found that latter composites have higher densities and lower porosities than former composites.
Fig. 4.10: Density of the composites with heat treatment temperatures.
Fig. 4-11: Porosity of the composites made with different carbon fibres and hybrid matrix during pyrolysis and impregnation cycles.
Fig. 4.12: Density of the composites made with different carbon fibres and hybrid matrix during pyrolysis and impregnation cycles.
Though the difference in densities of the former and latter composites is not much, there is marked difference in their mechanical properties. Figure 4.13 and figure 4.14 show the flexural strength and flexural moduli of the hybrid composites. As seen from these Figures, composite made with hybrid matrix exhibit strength more than twice that of those made with PDMS alone. Not only this, the latter composites exhibit less amount of fibre pullout as seen from SEM micrograph of the fractured composites (figure 4.15). This means that the impregnated polyfurfuryl alcohol resin which enters into the pores and voids in the bulk matrix and at the fibre/matrix interphase makes chemical bonding with the host matrix and fibres. This chemical bonded resin, on pyrolysis result in carbon bridges between PDMS derived silicon oxy-carbide matrix and carbon fibres. It is because of these carbon bridges that the flexural strength of the composites with hybrid matrix gets improved.

4.8: STUDIES ON OXIDATION RESISTANCE OF COMPOSITES

Carbon/Carbon composites are considered as promising high temperature composite materials capable of maintaining mechanical properties upto 3000 °C under inert atmosphere. However, in presence of air, these composites get readily oxidised. In fact, this was this particular drawback of carbon/carbon composites which led to the search for alternative ceramic matrices. During the present studies, it was found that silicon oxy-carbide does not react with oxygen even at temperatures upto 1000 °C. Therefore, the composites made with
Fig. 4.13: Flexural strength of the composites made with different carbon fibres and hybrid matrix.
Fig. 4.14: Flexural moduli of the composites made with different carbon fibres and hybrid matrix.
Fig. 4.15: SEM micrographs of the fractured hybrid matrix composite.
silicon oxy-carbide were also tested for oxidation resistance at 1000°C. Additional more samples of carbon/carbon composites were coated with PDMS and pyrolyzed at 1000°C. All the three composites i.e. (A) Uncoated carbon/carbon composites, (B) Carbon/carbon composites coated with silicon oxy-carbide and (C) Composites made with silicon oxy-carbide were tested for oxidation resistance by heating the samples to 1000°C in presence of flowing air. The ends of the composites (C) were beforehand sealed with silicon oxy-carbide to prevent the initiation of oxidation from the fibres ends. Figure 4.16 shows the weight loss of these composites with temperature. As seen from the figure, carbon/carbon composites start losing weight at 550°C and suffer complete weight loss by 820°C. Carbon/carbon composites coated with silicon oxy-carbide exhibit good oxidation resistance with a weight loss of only 1-2% at 1000°C. Composites made with silicon oxy-carbide do not exhibit weight loss at all up to 1000°C. This shows that silicon oxy-carbide is a good oxidation resistant matrix. In order to pursue the studies further, all the composites made with different types of carbon fibres and silicon oxy-carbide as matrix precursor were tested for oxidation resistance. Figure 4.17 shows the weight retention of the composites at 1000°C. As seen from the figure all the composites, irrespective of the types of fibre used exhibit 100% weight retention at 1000°C in presence of air. It confirms that composites made with silicon oxy-carbide as matrix can be safely used up to 1000°C in presence of air.
Fig. 4-16: TGA curves in air of (A) C/C Composites, (B) C/C Coated with Si-o-c and (C) Composites made with Si-o-c.
Fig. 4.17: The weight loss retention of the composites at 1000°C.
4.9: XRD OF THE COMPOSITES

Figure 4.18 shows the X-ray diffractogram of the composite containing high modulus carbon fibres. This diffractogram shows a sharp peak at $2\theta = 25.4^\circ$ & $44^\circ$ and broad bands with maxima at $2\theta = 22^\circ$, $34^\circ$ and $72^\circ$. This diffractogram exhibit both types of sharp peaks and broad bands. The sharp peaks such as $2\theta = 25.4^\circ$ and $44^\circ$ are due to the high modulus carbon fibres whereas broad bands at $2\theta = 22^\circ$ and $72^\circ$ are due to glassy(amorphous) structure of silicon oxy-carbide.
Fig. 4.18: X-ray diffraction of the composite containing high modulus carbon fibres.