SUMMARY

The rapidly increasing technological advances that we see around us have been possible because of the development of newer materials with requisite properties. Engineers and Technologists have always been in search for stronger and stiffer materials. In the beginning and middle of the twentieth century, highly sophisticated steel and new metal alloys were developed. An ideal engineering material should be strong, tough and light. Conventional engineering materials namely metals and alloys, come also to satisfying these requirements. These are strong and tough but not light. Lightness of a material is an important property in certain applications where it controls the performance and fuel consumption such as in aircraft etc. For such applications, there is real need for materials having greater specific strength and specific stiffness than are attainable with existing metals.

Non metallic materials are low density materials. In the last few decades, much efforts have been made to develop strong and stiff non metallic materials. This led to the development of whiskers, fibers and plastics. However, most of these materials did not satisfy all the requirement of the engineers. Whiskers and fibers though have high specific strength and high stiffness, but these as such cannot be used as construction materials. Plastics on the other hand though light, lack in strength, stiffness and service temperatures. Therefore, an obvious approach to obtain an ideal engineering material would be to combine two materials with complementary properties in the form of composites.
Composite is made by combination of two or more dissimilar materials in order to achieve properties that the constituent materials cannot provide by themselves individually. The dimensions of one of the constituents of a composite material are smaller than those of the second, first being known as reinforcement and the other as matrix. The reinforcing materials play predominant role, since it is the reinforcement which takes upmost of the load when composites are subjected to loading. The various reinforcements are Carbon fibers, Boron fibers, Glass fibers, Silicon carbide fibers, Alumina finers etc. The other constituent of the composite is matrix, which plays equally important role in influencing the properties of the composites. Matrix systems are chosen depending on the end application environments especially temperature. Different matrix systems available include polymers, metals ceramic etc.

Accordingly, the fibre reinforced composites can be classified as:

1. Polymer matrix composites
2. Metal matrix composites
3. Carbon / carbon composites

Over past two decades, ceramics are being looked at as potential constructional materials for applications, under hyperthermal environments such as engines, turbines etc. However, Ceramics have the major drawback of brittle fractures. A potential solution to the reliability problem caused by low fracture toughness in ceramics is also fiber reinforced ceramic matrix composites. Therefore this subject has been in the
frontiers of materials R and D activities. Several routes such as melt infiltration, reaction bonding, chemical vapour infiltration, polymer pyrolysis etc. have been employed to synthesize silicon based ceramic-matrix composites. Latter technique of polymer pyrolysis to get ceramic has unique advantages of getting ceramic matrix of desired chemical compositions and physical properties at relatively low processing temperatures. Also the well established techniques of polymer composites processing can be used. Therefore over past decades, extensive research has been carried out on synthesis and applications of various organometallic polymers such as polycarbosilanes, polysilazanes, polysiloxanes etc., which on pyrolysis convert to ceramics with high yield. Though all these preceramic polymers yield good ceramics but all are not beneficial as matrix precursor for fibre reinforced composites. Therefore, the present work was undertaken to study the suitability of commercially available polydimethylsiloxane as matrix precursor for making fiber reinforced ceramic matrix (silicon oxy-carbide) composites. It was also planned to develop in-house preceramic silicon based polymer through sol-gel technique and to develop fiber reinforced ceramic matrix composites.

The work incorporated in the thesis has been divided into five chapters. First chapter gives an introduction about various high technology constructional materials specially fiber reinforced composites. It also contains literature survey and elucidates the necessity to undertake the work.
Various experimental techniques used in the present studies for preparation of the preceramic polymers and composites and their characterization techniques etc. have been illustrated in chapter II. The pyrolysis behavior of polydimethylsiloxane (PDMS) thermally cured at 90°C, as well as chemically cured with p-aminopropyl triethoxysilane has been studied by controlled heating of the cured samples to 1000°C. The physical transformations taking place were monitored. Fiber reinforced composites were made using this resin and different carbon fibers by filament winding, prepregging, pressure molding technique. Polymer composites after characterization were pyrolyzed to 1000°C and 1400°C in presence of nitrogen. The physical changes occurring during first pyrolysis were measured. The composites were characterized by optical microscopy. The first pyrolysed composites were reimpregnated with PDMS and or polyfurfuryl alcohol resin and repyrolysed to 1000°C. The composites were finally characterized for oxidation resistance, mechanical properties etc.

Preceramic polymer was also synthesized in the laboratory by sol-gel technique from tetraethyloxysilicate (TEOS). TEOS is hydrolyzed with water to which was added furfuryl alcohol under constant stirring. The effect of various constituent contents and reaction parameters on the properties of preceramic polymers have been studied. Then preceramic polymer were cured and pyrolyzed as such as well as were transformed into carbon fibre reinforced composites and pyrolysed to 1000°C. Various physical transformations taking place during pyrolysis of these composites were characterized for mechanical properties,
porosity, oxidation resistance, macrostructure etc.

Studies made on the pyrolysis behavior of unreinforced polydimethylsiloxane, cured under different conditions have been complied in chapter III. Concentration of curing agents has great influence on the curing of PDMS. In the present studies concentration of curing agent (r-amo propyltriethoxy silane) has been varied from 0.5% to 4%. It has been found that though 1.5 to 2% curing agent results in a solid polymer, but the crosslinking is not complete. As a result the ceramic yield at 1000 °C is 84% with lot of cracks. However, addition of 4% curing agent increases the ceramic yield to 88%. Thermally cured PDMS exhibit higher weight loss (23%) during pyrolysis as compared to chemically cured PDMS (wt. loss 12%). This is again attributed to high degree of crosslinking in thermally cured PDMS samples. Studies were also performed to mix polyfururyl alcohol resin and to study the pyrolysis behavior of the mixture. Aim was to get silicon carbide. It was observed that though PFA and PDMS on mixing seem to be homogeneous mixture, of curing pyrolysis they result in two distinct layers of silicon oxy carbide & carbon.

Unidirectional composites were made with carbon fibers and PDMS. These composites were pyrolyzed to 1000 °C and 1400 °C in presence of nitrogen. Various observations made during pyrolysis of the composites and results obtained on the pyrolysed composites are compiled in chapter IV. It was observed that the integrity of the composites is maintained during pyrolysis. In polymer composites, the matrix is well adhered to the fibers and
it remains so even on heating to 1000°C and 1400°C. The type of carbon fibers has been found to have effect on the shrinkage during pyrolysis of the polymer composites. Composites made with Intermediate modulus carbon fibers exhibit maximum shrinkage followed by those made with high strength and high modulus carbon fibers. Like in carbon-carbon composites, this behavior may be attributed to the extent of fiber matrix bonding in polymer composites. The pyrolysed composites were porous having porosity of 30-35%. These composites were impregnated with either PDMS or with PFA and further carbonized to 1000°C. The density and mechanical properties of the composites were found to increased with impregnation. Though densities were same with two impregnates, the flexural strength of the composites impregnated with PFA increased by three times whereas those with PDMS increased by about 100%. This is attributed to the microstructure of the secondary matrix. Composites heated to different temperatures were studied by XRD. It was found that composites heated to 1000°C are amorphous in nature whereas those heated to 1400°C develop crystalline silicon oxy carbide structure. Latter composites were found to be better oxidation resistant than former composites.

Effect of constituents concentration and processing conditions on the formation of silicon containing polymers through sol-gel was studied. Chapter V contains these studies along with the results obtained during pyrolysis of the composites made with these resins. It was found that lower water:TEOS ratio (0.5 molar ratio) with addition of furfuryl alcohol result in a resinous liquid. This resin was thermally
cured at 150°C. It resulted into a crosslinked solid mass which on pyrolysis to 1000°C resulted in silicon oxy-carbide. Unidirectional composites made with these resins on pyrolysis resulted in dense composites with about 15-20% porosity and higher flexural strength. However, these composites were found to have lower oxidation resistance than those made with PDMS.

Various conclusions drawn from the present studies are compiled in chapter VI. It has been concluded that the polydimethylsiloxane resin is good for producing ceramic coatings. As precursor for making ceramic matrix composites, reimpregnation with other carbon yielding resins such as PFA is repaired. Silicon containing preceramic polymers can be synthesized using sol-gel technique. These resins contain more oxygen. The composites made with these resins are better than those made with siloxanes resins. However presence of excess oxygen lowers the oxidation resistance of the composites.