Introduction

1.1 General Background

During the recent decades, an accelerated increase has been noticed in the demand for lightweight composite components to be used in a variety of aerospace applications (Gay, 2003). Carbon (C) fibre based composites are considered as attractive materials for use in engineering components in general and aerospace applications in particular at both room and elevated temperatures. It is well-known that carbon is available in many allotropic forms, such as diamond, graphite, amorphous carbon, glassy carbon and carbon monofoam. Among these materials, graphite is known to be the most stable allotrope from thermodynamic considerations. Graphite has a layered hexagonal crystal structure with atoms linked by a mixture of both sp² σ and π bonds. In this structure, the C-atoms are located at the corners of two dimensional hexagonal, which in turn are stacked as layers. These layers are held together by weak Van der Waal's forces. Graphite is considered as an attractive material for a large number of engineering applications, because of its low density (1.5-2.0 g/cc), chemical inertness, high electrical and thermal conductivity, as well as its ability to absorb neutrons. Another interesting property, which makes it promising for several engineering applications at elevated temperatures, is its increase in strength with increasing temperatures (Manocha, 2003). In spite of the abovementioned interesting properties, monolithic graphite is not suitable for widespread use as a structural material, because of its brittle mechanical behaviour, flaw sensitivity, and high anisotropy (Kelly, 1986). These limitations justify the worldwide emphasis on rapid development of graphitized C-fibre based composites for various types of high performance structural applications. The commonly used C-fibres are produced from either pitch or poly-acryl nitrile (PAN) based precursors (Chawla, 1993). These precursors are subjected sequentially to carbonization and graphitization processes, such that the metastable amorphous carbon is transformed into graphite. The physical and mechanical properties of the C-fibres fabricated from either pitch or PAN based precursors are shown in Table 1.1.

The C-fibre based composites may be classified into two groups on the basis of the type of matrix: (i) carbon and (ii) non-carbon (e.g. polymer, metallic or ceramic). Low density as well as high specific strength and elastic modulus of the C-fibres make them useful as reinforcement for polymers, metals, carbon, and ceramic matrices. Addition of C-fibres as reinforcement in a composite serves not only to increase its strength, but also its electrical and thermal conductivity. Moreover, the use of C-fibre as reinforcement lowers the net thermal expansion or contraction of the composite, which in turn leads to significant improvement in the dimensional stability of these materials. Both high thermal conductivity and low thermal expansion of the C-fibres makes the composites having these as reinforcement useful as heat sinks in the electronic packaging components, and for components in the space structures that require dimensional stability. Moreover, the above mentioned thermal properties are also responsible for excellent thermal shock resistance of these composites. As the thermal conductivity of the C-fibres increases with the degree of graphitization, applications requiring high thermal shock resistance should use graphitic fibres, such as the high-modulus (HM) pitch-based or vapour grown C-fibres.

| Sl. No. | Density (g/cc) | Coefficient of thermal expansion (x10 ⁻⁶ /°C) | Thermal Conductivity (W/m.k) | Tensile strength (GPa) | Young Modulus (GPa) |
|------------------------|-------------------|---|------------------------------------|------------------------------|----------------------------|
| Pitch based C-fibre | 1.9-2.2 | -0.9 to -1.6 | 400 to 1100 | 1.38 to 2.75 | 170 to 965 |
| PAN based C-fibre | 1.8-1.9 | -0.4 to -0.75 | 20-80 | 3.4 to 6.2 | 220 to 450 |

Table 1.1: Properties of C-fibres processed from pitch-based and PAN-based precursors.

It is intuitive that the C-fibres are more compatible with carbon than other matrices, because harmful chemical reactions and residual strains due to thermal expansion mismatch at the fibre-matrix interfaces are not expected. The C-fibre reinforced carbon matrix (C/C) composites are designed to combine the high specific strength and stiffness of the C-fibre with the refractory properties of structural ceramics, and to have much greater reliability as structural components due to their improved fracture resistance (Savage, 1988; Hüttener, 1990; Savage, 1993; Fitzer, 1998). The C/C

composites are of interest, primarily because of their ability to retain both strength and structural integrity till 3000 °C either in vacuum or in inert environment (Fitzer, 1980; Fitzer, 1998; Schmidt, 1999,a,b,c; Lacoste, 2000). Not only the mechanical properties are retained, but also the tensile strength of the C/C composites is found to increase with rise in temperature (Goto, 2003).

The types of C/C composites in use or under development can be related closely to the history of their evolution through several decades of research. The development of C/C composites began in 1958, and was nurtured under the United States. Air Force space plane program, Dyna-Soar, and Apollo projects of the National Aeronautics and Space Administration (NASA), U.S.A. Although the initial development of the C/C composite materials was very slow, yet it attracted wide-scale attention for research by the late 1960s (Frye, 1969; Schmidt, 1972). In particular, the research on the C/C composites systems has been intensively driven by the demands for high temperature light-weight materials to be used in the NASA's space shuttle programme. One of the major applications is in the thermal protection system (TPS) for nose cones and leading edges of hypersonic and re-entry type vehicles, which are exposed to elevated temperatures (>2000 °C) (Fitzer, 1980; Lacoste, 2000). The criteria that led to the selection of C/C composites for use in TPS of the space flight vehicles were based on the following requirements: (a) maintenance of reproducible strength levels at temperatures up to 1650 °C, (b) sufficient stiffness to resist both flight loads and large thermal gradients, (c) low coefficient of thermal expansion to minimize induced thermal stresses, (d) tolerance to impact damage, and (e) suitable manufacturing processes for near net shaping within the state of the art. Furthermore, the development of C/C composites has been strongly motivated by prospective military applications during the 1970s, particularly for development of ballistic missile technology (Fitzer, 1971; McAllister, 1976; Lamieq, 1977; Fitzer, 1978; Girard, 1978; Thomas, 1978). Moreover, the C/C composites have been also found to be suitable for applications such as jet engine components and rocket nozzles, because of their ability to retain strength, erosion resistance, and other favorable properties at elevated temperatures (> 1500 $^{\circ}$ C), which explains why the aerospace industry has invested highly towards the development of these composites over the past decades (Fitzer, 1987).

The actual as well as potential areas of applications of the C-fibre composites are quite diverse and can be broadly classified as aerospace, automobiles, marine, medical, civil, electrical and electronics, musical instruments, games and mining. Some of the recent engineering applications of these composites including those considered as potential or futuristic are shown in Table 1.2.

The method of fabrication of the C-fibre reinforced composites is quite elaborate. The first step in processing of these composites is preparation of the performs, which are infiltrated with liquid polymers, polymer precursor, epoxy or phenolic resin, depending on the type of matrix, followed by further thermal processing. The C-fibre preforms contain either unidirectional fibres or woven fabric. The fabrics can have C-fibres arranged in two (2D), or three (3D) or four (4D) dimensional layouts based on the type of physical and mechanical properties desired for the expected applications. Therefore, the accepted nomenclature for the C/C composites is nD, where n represents the number of directions of the fibre within the fabricated preform. It should be noted that use of multiple directions of fibre reinforcement leads to reduction in the fibre volume fraction, which in turn is responsible for reduction in strength (Sarkar, 2010). But the properties of the composites appear to become more uniform in all directions with increasing values of 'n'. It is however logical that with increase in the value of n, the process of fabrication of the preforms becomes more complex. Multidirectional fibre preforms are usually prepared by a number of different processes including weaving, knitting, braiding and filament winding. A schematic illustration of different varieties of fibre architecture used in the continuous fibre reinforced composites is shown in Fig. 1.1, whereas certain terminologies related to the preparation of fibre preform are described in Table 1.3 (Frank, 1989). The mechanical properties of the C-fibre based composites are known to be a strong function of the type of fibre architecture (Rao, 2008).

The purpose of using the matrix in the composites is to hold the fibres in place, such that the applied load is transferred effectively to the fibres. The carbon matrix can be formed by two basic approaches: (a) through the carbonization of an organic solid or liquid precursor, such as resin or pitch; or (b) through the chemical vapour infiltration (CVI) of a hydrocarbon followed by its decomposition to carbon. The properties of the matrix indirectly depend upon the type of matrix precursor and the processing conditions. Possible precursors include pitches, thermosetting resins and hydrocarbon gases (Burns, 1992). For preparation of the C/C composites, the polymer precursor is subjected to heat treatments for the purpose of carbonization, which is followed by graphitization (Murdie, 1992). It is well-known that fractionated and modified pitches have carbon yields of up to 90%, because these precursors are easily graphitized (White, 1989). Typically, there is an optimum graphitization temperature, at which the highest strength can be obtained for a given composite composition (Stoller, 1974; Edie, 1986). By careful control of the precursor-type and the nature of high temperature treatment during processing, the degree of graphitization of the matrix may be varied considerably, thus imparting the desirable range of thermal and mechanical properties to the finished composite product.



Fig. 1.1: Schematic illustration of C-fibre architecture (Frank, 1989).

A major disadvantage of the C/C composites is their poor oxidation resistance, which can be overcome either by application of a suitable protective coating or by infiltration of liquid silicon in order to form SiC on the surfaces by in-situ chemical reaction. It may be noted that SiC has very strong oxidation resistance due to the formation of the protective film of SiO₂. First attempts to infiltrate the carbon/carbon composites by liquid silicon were carried out more than twenty years ago (Evans, 1974; Hillig, 1975; Gadow, 1986), and subsequent years of research were devoted to optimize this process. One of the hurdles in this process is the degradation of the C-fibres during infiltration of molten silicon. The best results are obtained by coating the C-fibres (Carotenuto, 1994) prior to infiltration of silicon, so that the degree of fibre degradation is considerably reduced. Also, highly graphitized C-fibres like the HM fibres are recommended for use in the fibre preform, which is more stable in contact with silicon than the ordinary carbonized fibres.

The polymer-matrix composites are much easier to fabricate than metal-matrix, carbon-matrix, or ceramic-matrix composites, because of the relatively low processing temperatures required. For the thermosets, such as epoxy, phenolic, and furfuryl resin, the processing temperature typically ranges between room temperature (RT) and 200 °C; while for the thermoplasts, it ranges from 300 to 400 °C. The C-fibre based composites with polymeric matrices like epoxy (C/E composite) and phenolic resins (C/P composite) are produced by either hand or machine operated lay-up of the prepreg laminates, followed by treatment in an autoclave at elevated temperature and pressure using a programmed cure cycle (Davies, 2007).

The thermosets (especially epoxy) have been used for a long period as the polymer matrices for C-fibre based composites. Epoxy or polyepoxide is a thermosetting polymer formed from the reaction of an epoxide "resin" with polymine "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end. The hardener consists of polyamine monomers, for example triethylenetetramine (TETA). The epoxy-hardener mixtures are subjected to curing usually in the presence of heat and pressure, when the thermoset resin hardens gradually due to the completion of the polymerization process, followed by cross-linking of the constituent molecules. The thermoset materials once cured, cannot be remelted and loses the flexibility, to be moulded into a given shape because of the formation of molecular chains spread in three dimensions through cross-linking. The higher the number of cross-linked chains, the more rigid and thermally stable the material is expected to be. The process of curing is

controlled through choice of temperature, resin and hardener compounds. Some formulations benefit from heating during the period of curing, whereas others simply require sufficient time of holding at the ambient temperature. The epoxy resin is one of the most widely used matrices for the C-fibre reinforced composite materials, because of its excellent impregnation and adhesion to these fibres as well as low shrinkage (Morgan, 1985; Ullett, 1994). The low molecular weight of the uncured epoxide resins in the liquid state results in exceptionally high molecular mobility during processing. Epoxy has an excellent combination of mechanical properties and corrosion resistance, is dimensionally stable, exhibits good adhesion to the C-fibre, and is relatively inexpensive compare with phenolic resin.

Phenolic resin is usually a product of the reaction of phenol (carbolic acid) and an aldehyde (such as formaldehyde), which is catalyzed by an acid or base. Thus, phenolic resin is a general term used to describe a group of thermosetting resins created by reacting a phenol with an aldehyde, followed by curing and cross linking. During the last decade, PAN based C-fibre reinforced phenolic composites have gained significant attention for use in the TPS of re-entry vehicles or rocket engine components due to their excellent ablation resistance and mechanical properties.

It is well-established that the fibre-matrix interfacial bonding has a strong influence on the mechanical behaviour of all kinds of C-fibre based composites (Chawla, 1993). The mechanisms of fibre-matrix bonding include chemical bonding, van der Waals bonding, and mechanical interlocking (Chung, 1994). Chemical bonding provides the greatest bond strength, provided the density of atomic-scale contact as well as strength of their interactions across the fibre-matrix interfaces is sufficiently high. For intimate contact to take place on atomic scale, the matrix or matrix precursor must be able to wet the surfaces of the C-fibres during its infiltration into their preforms. Chemical treatments and coatings can be applied to the fibres to enhance the wetting characteristics. Another way of enhancing the amount of wetting is the application of high pressure during infiltration. A third method is to add a wetting agent to the matrix or matrix precursor before infiltration. As the wettability is known to increase with temperature, a suitable temperature should be chosen for infiltration in order to enhance the amount of wetting, without causing any degradation of the C-fibres. The occurrence

of a chemical reaction between the fibres and the matrix also helps in wetting and bonding between the fibres and the matrix. However, excessive interfacial reactions are known to degrade the fibres (Manocha, 1988), and the reaction products are undesirable for mechanical, thermal, or moisture resistance properties of the composite.

| Table 1. | 2: En | gineerir | ng a | applicat | tions | of | C-fibre | reinforced | carbon | and | polymer | matrix |
|----------|--------|----------|------|----------|-------|------|---------|------------|--------|-----|---------|--------|
| composit | es (Sa | wage, 1 | 993 | 3; Chun | g, 19 | 994; | Gay, 20 | 003). | | | | |

| Areas | Composites | Application | | |
|----------------------|------------|---|--|--|
| | C/C, C/P | Nose Tip for ballistic missiles. | | |
| | C/E | Re-entry vehicle shell, Rocket motor casing. | | |
| | C/P | Re-entry vehicle shell for ballistic missiles. | | |
| | C/P | Nozzle liner, throat back up. | | |
| Aerospace Industry | C/E | MIRAGE 2000 elevons, radio bay doors, fins, | | |
| | C/E | rudders, Fuseleg for Boeing 787, Pressure vessel. | | |
| | | Aircraft brake system, Fins for ballistic missiles, | | |
| | C/C | space shuttle orbiter, turbine rotor of LTV | | |
| | | missiles, turbine engine flap. | | |
| | C/C | Racing car brake, high speed train, automotive | | |
| | C/C | engine. | | |
| Automobiles | C/F | Car body, the hood, doors and rear end of | | |
| Automobiles | C/L | Peugeot car. | | |
| | C/P | Heat shields for Rolls Royce, Jaguar, Ford. | | |
| | C/E | Bi-cycles. | | |
| | C/E | Floats, buoys, fairings. | | |
| Marine Industry | C/P | Fishing boat, shoulder bearing, torpedo nose, tail | | |
| | 0/1 | cones, cradles. | | |
| Medical Industry | C/C | Bio-medical devices. | | |
| | | Retrofitting, seismic retrofitting, and repair of | | |
| | | damaged structures. The advantages of CFRP | | |
| Civil engineering | С/Е, С/Р, | over steel as a prestressing material, namely its | | |
| Industry | mainly | light weight and corrosion resistance. In the | | |
| madstry | CFRP | United States, prestressed concrete cylinder | | |
| | | pipes account for a vast majority of water | | |
| | | transmission mains. | | |
| Electrical and | C/C C/P | Solar panel substrates, parabolic RF Antenna | | |
| Electronics Industry | C/E, C/I, | reflectors, Covers of think pads from | | |
| Electromes medistry | C/L | Lenovo/IBM and Sony, turntables. | | |
| Musical instruments | C/E C/P | Violin bows, guitars, pick guards, Blackbird | | |
| Widstear mistraments | C/L, C/I | guitar. | | |
| | | Paint ball, racquet. | | |
| Games | C/E, C/P | pool/billiards, snooker cues. | | |
| | | Shank plate in the basketball sneakers. | | |
| Mining Industry | C/P | Ducts. | | |

Mechanical interlocking of the fibres with the matrix provides a very important contribution to the overall strength of the interfacial bond, particularly if the fibres form a multi-dimensional network (Chung, 1994). Otherwise, in case of a unidirectional layout, the fibres are modified so as to have a rough surface in order to ensure sufficient degree of mechanical interlocking to take place. Crenulated or ribbed C-fibres have superior ability for mechanical bonding or 'keying' to the matrix, which often result in the improved out-of-plane properties such as interlaminar shear strength (Kowbel, 1990).

| Sl. No. | Terms | Definition |
|---------|--------------|--|
| 1 | Yarn | Yams are finer fibre bundles with some twist. |
| 2 | Rovings | Large twistless fibre bundles |
| 3 | Warp | In weaving, the warp is a set of lengthwise yarns |
| | ·····r | through which the weft is woven |
| 4 | Weft or Fill | In weaving, weft or fill is the yarn which is drawn through the warp yarns to create a fabric. |
| 5 | Weaving | A fabric formation process using interlacing of yarns. |
| 6 | Fabric | Any non-woven, woven, knitted, braided fibrous structure. |
| 7 | Woven | A woven cloth is formed by weaving. It only stretches in the bias directions (between the warp and weft directions). |
| 8 | Knitting | Knitted fabrics are interloped structures, wherein the knitting loops are either produced by the introduction of the knitting yarn in the cross- machine direction (weft knit) or along the machine direction (warp knit). |
| 9 | Braiding | A fabric formation process, which intertwines three or more yarn in bias direction. |
| 10 | Plain Weave | Woven fabric characterized by the repeating interlacing of two warp (0°) and two weft of filling (90°) yarns. |
| 11 | Satin weave | The satin weave is characterized by four or more cool fill or weft yarns floating over a warp yarn or vice versa. Four or more warp yarns floating over a single weft yarn can be designated as 4H, 5H, 6H and so on. |
| 12 | Preform | The fibrous structure for a composite before introduction of matrix. |

Table 1.3: Terminologies used to describe the different types of fibre architectures used in the C-fibre based composites (Frank, 1989).

Chapter 1

One of the major advantages of the C-fibre based brittle matrix composites is their damage tolerant behaviour, which is responsible for non-catastrophic failure. The fracture mechanism is complex and involves matrix microcracking, crack bridging by fibre, interfacial debonding of fibre and crack deflection, which leads to increase in the crack path torturousity along with rise in the energy of fracture (Chawla, 1993; Kostopoulos, 2000). The failure modes of the C/C composites are unique, because of the presence of relatively weak planes, when matrix dominated properties control the failure modes (Savage, 1988). The planes of weakness need to be identified, so that the design stress for these materials can be determined by carrying out appropriate mechanical tests and through calculations using suitable theoretical models. The effect of C-fibre architecture on fracture behaviour of these composites is not well-understood so far, and requires further in-depth study. It should be noted that the state of stress in case of the multidimensional C/C composites is complex, in spite of uniaxial load application. Further development of the C/C composites requires detailed understanding of the structure-property relationships of these materials, particularly those with multidirectional fibre orientation.

Carbon-carbon composites are designed for engineering components subjected to severe environments involving wear, abrasion and erosion. Wear takes place due to repeated or periodically occurring sliding of two surfaces. Damage by abrasion and erosion is known to be caused by the sliding and impact, respectively of the irregularly shaped particles against the surfaces of the tested specimens. Abrasive wear involves the loss of material by the passage of hard particles in contact with a given surface, while erosive wear is caused by the impact of particles against a solid surface. Both abrasion and erosion are rapid and severe forms of wear and can result in significant losses, if not adequately controlled (Moore, 1981). Only limited information is available about the tribological behaviour (erosion, continuous impact abrasion and reciprocating wear) of the multi-dimensionally reinforced C-fibre based composites. As major applications of the C/C composites are in the leading edge and nose cones of the space shuttle orbiter (Curry, 1983; Curry, 1988) as well as in the nozzle-liner, their solid particle erosion behaviour is of interest. Moreover, the applications of these materials in brake discs of

aircrafts and racing cars as well as in other components subjected to friction, require a thorough evaluation of the wear properties.

In a number of engineering applications, the components are subjected to static or dynamic loads simultaneously with friction, an example of which is the brake disc in aircraft or racing car, as mentioned above. Thus, on the basis of the nature of applications of the C-fibre based composites, it is intuitive that the relationships of their strength, fracture and tribological behaviour with their fibre architecture and volume fraction on one hand, and with the nature of matrix on the other, need to be well understood for further development of these materials. Hence, the present work is focused on a comparative study of the mechanical behaviour and tribological properties of 2D, 3D and 4D C/C composites as well as of 3D C/C-SiC, 2D C/P and 2D C/E composites at different selected temperatures, with emphasis on the effects of fibre orientations, type of matrix material, and siliconization on the above-mentioned properties.

1.2 Objectives and scope of the present work

The C-fibre based composites used for this study can be divided into two categories based on their matrices, which are: (a) carbon (2D C/C, 3D C/C, 4D C/C and 3D C/C-SiC) and (b) polymer (2D C/P and 2D C/E). The major objectives of the investigation carried out on the above-mentioned composites are as follows:

a) Comparative study of the structure-mechanical property relations at room temperature (RT) for the C/C composites with three different fibre orientations (2D, 3D and 4D) and 2D C-fibre based composites with different matrices (carbon, phenolic and epoxy);

b) Evaluation of relevant tribological properties and mechanisms of degradation under different test conditions with focus on the effects of matrices, as well as C-fibre orientations and volume fractions;

c) Examination of the effect of silicon infiltration on mechanical and tribological behaviour of the 3D C/C composites.

The scope of experiments has been formulated so as to examine the response of the investigated composites to static loading under uniaxial or flexural conditions, as well as severe environments involving erosion, abrasion with application of cyclic load, and reciprocating wear under static load. The mechanical behaviour of the investigated composites has been studied with emphasis on determination of tensile and flexural strengths, evaluation of resistance to fracture using linear-elastic and elastic–plastic fracture mechanics approaches as well as examination of failure mechanisms and damage tolerance. Furthermore, the tribological studies carried out on the selected C-fibre based composites comprise: (i) evaluation of solid particle erosion resistance and efficiency; (ii) assessment of continuous impact abrasion resistance at both RT and elevated temperatures (250 °C and 500 °C); as well as (iii) measurement of wear rates and coefficients of friction for low amplitude reciprocating wear tests carried out at different temperatures (RT, 250 °C and 500 °C).

1.3 Lay out of the thesis

The thesis is divided into eight chapters, the contents of which are discussed in brief as follows:

Chapter 1 presents a general background dealing with structure and properties of the C-fibre reinforced composites with carbon or polymer matrices. An overview of the objectives and scope of the present work is also presented in this chapter.

Chapter 2 provides a critical review of the existing literature related to structureproperty relations of C-fibre reinforced carbon, phenolic or epoxy matrix composites with emphasis on the studies related to their strength and tribological behaviour. The purpose of this review is to compare and analyze the results of previous studies, so as to arrive at guidelines for further research in the present work.

Chapter 3 contains information on the structure and methods of fabrication of different types of C-fibre based composites used for this research work. Processes used for fabrication of 2D, 3D and 4D C/C composites, 3D C/C-SiC composite as well as polymer matrix composites including 2D C/P and 2D C/E composites have been discussed in this chapter. Experimental procedures for various mechanical and tribological tests have been also discussed here.

Chapter 4 comprises a detailed description of the experimental results for tensile, flexural and fracture toughness tests. The effect of different fibre orientations, matrices and volume fractions on strength and resistance to fracture has been discussed. Moreover,

the failure mechanisms of different composites have been illustrated, with due emphasis on the role of operating toughening mechanisms.

Chapter 5 presents a comparative study of the results of solid particle erosion tests for different C-fibre reinforced composites. Erosion resistance, erosion efficiency and morphologies of the eroded surfaces of the tested composites have been discussed.

Chapter 6 presents a comparative study of the results of continuous impact abrasion tests carried out on different C-fibre composites at RT and at higher temperatures (250 °C and 500 °C). Continuous impact abrasion rate as well as surface topography and morphology of the damaged surfaces of the tested composites have been discussed in this chapter.

Chapter 7 presents a comparative study of the results of low amplitude wear tests for different C-fibre reinforced composites at RT and at higher temperatures (250 $^{\circ}$ C and 500 $^{\circ}$ C). Wear rate, coefficient of friction as well as topography and morphology of the worn surfaces of the tested composites have been discussed in this chapter.

Chapter 8 presents the summary and the major conclusions drawn from the present work. A critical analysis of the results provides ideas and directions for further investigation, which have been also discussed in this chapter.