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CARBON-CARBON COMPOSITES BY PREFORMED YARN METHOD

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ABSTRACT

The conventional techniques of manufacturing carbon-carbon(C/C) composites have reportedly encountered problems because the resulting C/C composites exhibit non-uniform properties such as bending strength and density. A novel method of manufacturing C/C composites by preformed yarns (PY) is used. The matrix powder consists of coke powders and the binder. The preformed yarn contains the matrix powders inside the carbon fiber bundle and coated on circumference with nylon-6 polymer. This preformed yarn is then chopped and hot pressed at about 600°C to get bars and pellets. These are again heat treated at 1500°C and further impregnated by one more pitch cycle, again heat treated at 2200°C. The tests for hardness, compression strength, Creep strength, resistance to oxidation, and fracture toughness are conducted on these pellets and bars. The micostructural analysis in SEM is done. These tests reveal that the properties obtained from PY method are superior to the properties obtained from any other conventional method.

Key words: Tow, Precursor, Preformed yarn, Carbon fiber, Carbon-Carbon composites.

1. INTRODUCTION

One of the most important reinforcement fibers in all kinds of composites is carbon fiber. Carbon /Carbon (C/C) is a lightweight, high-strength composite material capable of withstanding temperatures over 3000°C in many environments. Composite structures can be tailored to meet varied physical and thermal requirements through weaving architecture design (Fatz et al., 1992). C/C offers a high performance, cost effective alternative to refractory metals. Aerospace components commonly fabricated from C/C includes rocket motor nozzle throats and exit cones. Aerospace structural C/C composites are often manufactured using woven 2D or 3D C-fiber fabrics, and are sometimes densified using hot isostatic pressing (Pudhi, 1992). Conventional production methods of manufacturing C/C composites include CVD in which a thermosetting resin binder is carbonized. A preform of carbon fibers having a specified shape is heated in a furnace to a high temperature, while a hydro-carbon gas is fed to the furnace. The gas is thermally cracked to form carbon, which then deposits uniformly on the fiber surfaces. The resulting preforms are then charred to carbon, and densified by adding carbon by chemical vapor deposition (CVD). In other processes, the yarns or woven/nonwoven fabrics of carbon fibers are shaped into various structural shapes, with the use of a thermosetting binder such as phenolic or epoxy resin (Corum et al., 2001).The structure is subsequently heated in an inert gas atmosphere to carbonize the resin. These conventional techniques have reportedly encountered problems because the resulting C/C composites lack uniformity in properties such as bending strength and density (Davis and Meier, 2004). The processes are also complicated and time consuming. Across Co. Ltd has developed a unique manufacturing process of C/C composite, utilizing preformed yarn which is superior to conventional method of CVD or impregnation method (Alman et al., 1998).This unique method has enabled drastically reduced processing time. This improvement allows various kinds of customers needs for reasonable time periods. The new method has also resulted in dramatic cost reductions for the manufacturing of C/C composites (Economy et al., 1992). PAN fibers are white with a density of 1.17 g/cm^3 and molecular structure comprised of oriented, long-chain molecules (Bary, 2005).

A multiaxis three-dimensional (3D) flat woven preform and a weaving method have been developed. The structure has five yarn sets, which are bias(+) and bias(-), warp, filling and Z-yarns.(Bilisik and Mohamed, 2010). Petroleum pitch is processed in a complicated way. In Pitch-based fibers, pitch is a complex mixture of aromatic hydrocarbons and can be made not only from petroleum but also from coal tar, asphalt or PVC (Chang et al., 1988). When PAN is thermally treated in an inert atmosphere at 400 to 600 °C; the heat causes the cyano repeat units to form rings (Khan et al., 2008). Activated carbon fibers contain a large amount of open pores and are mainly used for gas absorption applications (Huang, 2009). Single-walled carbon nanotubes (SWNT) presents outstanding mechanical properties and therefore are considered very promising reinforcing materials associated to polymeric matrices for high performance applications (Wardle et al., 2008; Salvetat et al., 1999).

The dynamic viscoelastic behavior of composite materail reveals an increase in the storage modulus (G′), indicating higher stiffness in case of fiber-filled composites as compared with the virgin matrix. (Janardhan et al., 2000). According to the invention, a

raw material comprising more than two kinds of carbon fibers with different length and meso-phase carbon as a binder is mixed, and molded and subjected to heat treatment. In this case, random orientation of short carbon fibers is effective for obtaining a highly densified and highly strengthened C/C composite (Toshoku Cho and Akimitsu Okura, 2004). The mechanical properties of composites will be influenced by the existence of interfacial reaction (Abdullah et al., 2009)

1.1 Preformed Yarn Method

Conventionally, C-C composite used to be Expensive and time consuming to manufacture due to its complicated processing method such as chemical vapor deposition (CVD) (Salvetat et al., 1999). A simplified manufacturing process using a new method called PY (preformed carbon fiber yarn), results in great reduction in time and cost.

2. MATERIALS & PROCESS

2.1 Materials

The components used in the manufacture of carbon-carbon composites are;
1. Carbon fiber (PAN based) as reinforcement
2. Pitch, coke and nylon-6 as matrix materials

2.2 Properties of Carbon fiber used

The reinforcing material used in the manufacture of C-C composite is carbon fiber (C_f). The properties of carbon fiber are given in the Table 1.

Table 1 Properties of carbon fiber at Room Temperature.

Diameter	7 µm
Fiber length	5-6 m
Density	1.8g/cc
Tensile strength	124 MPa
Young's modulus	230 GPa
% elongation	1.5%

2.3 Material Composition

The material composition of three different materials used for the preparation of specimen is given in the Table 2.

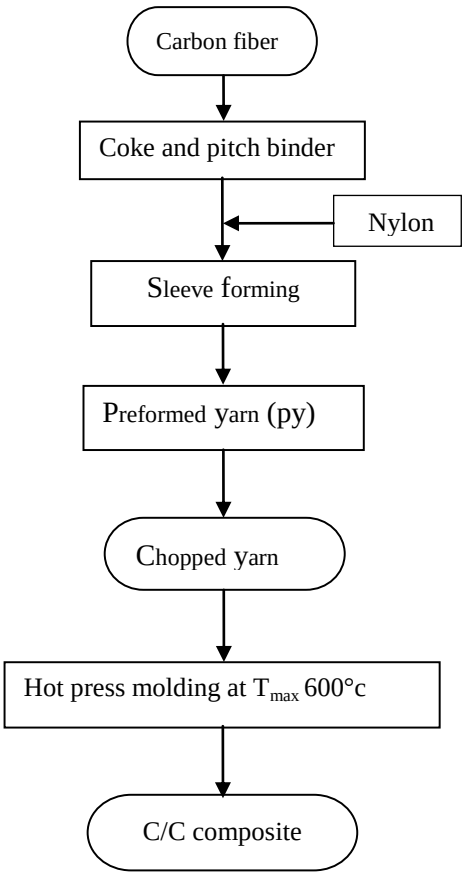
2.4 Die Preparation

For fabrication of composite material a die is prepared which is of size 15×2×2 cm and material alloy steel. A 10 ton capacity press is used for the hot pressing during the process. The C-C composites of 30%, 40% and 50 % carbon fibre volume fraction are prepared according to the flowchart shown below.

Table 2 Compositions of preformed yarn

	Type	Matrix		C_f wt%	Sleeve wt %
		Wt %	Binder ratio		
1	PYB 50	35	50	50	15
2	PYB 60	35	60	45	20
3	PYB 75	35	75	40	25

Flow Chart for C-C C synthesis



3. EXPERIMENTATION

The Brinnel hardness test, Compression test, creep test, fracture toughness test and oxidation tests were conducted on C-C composites produced by preformed yarn method.

4. RESULTS AND DISCUSSION

4.1 Hardness Test

Test results shown in Table 3. Indicates that the increase in composition of carbon fiber (C_f) increases the hardness of the material as indicated in Figure 1.

4.2 Compression Test

The results of compression test are as shown in the following Table 4 and plotted in Figure 2.

Table 3 Variation of Hardness vs. % C_f

Composition	1	2	3
% C_f	30%	40%	50%
BHN	37.89	43.81	49.56

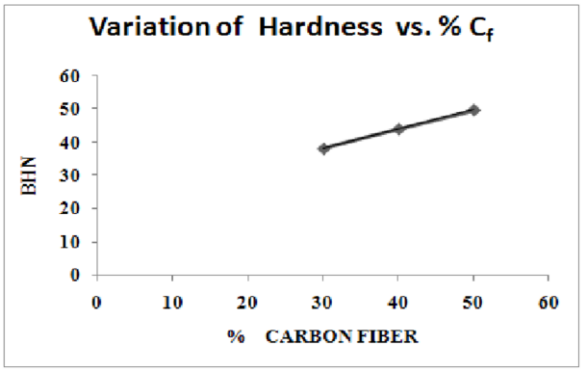


Figure 1 Brinell hardness vs. volume fraction of Carbon

Table 4 Compression strength (MP) vs. % C_f

S.No	1	2	3
% C_f	30%	40%	50%
Compression strength(MPa)	60	62	63

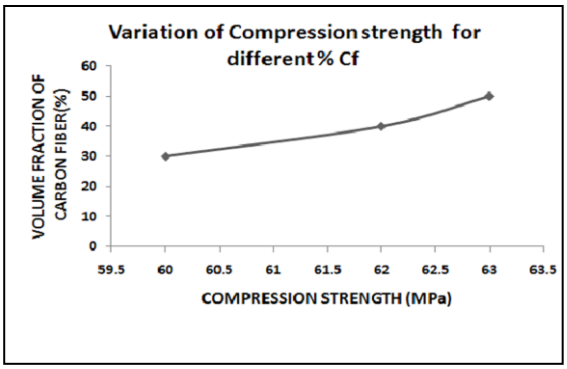


Figure 2 Compression strength vs. Volume fraction of Carbon

4.3 Creep Test

The creep test was conducted on the composites of different compositions in creep testing machine. Table 5 shows the results of creep test conducted on the material having 30% of carbon fiber. The plot of Strain vs. time for 30% C_f composition is shown in Figure 3. Table 6 shows the results of creep test conducted on the material having 40% of carbon fiber. The plot of Strain v/s Time for creep test 40% C_f composition is shown in Figure 4. Table 7 shows the results of creep test conducted on the material having 50% of carbon fiber. The plot of Strain v/s Time for creep test 50% C_f composition is shown in Figure 5.

4.4 Fracture Toughness Test

The Izod impact test result a fracture energy 4 J for all three types of carbon carbon composites tested.

Standard test method ASTM E 399 is used to measure the fracture toughness. The specimens for fracture toughness test are shown in Fig. 6 and the test set up is as shown in Fig.7.

Table 5 Results of Creep test on Composition 1

Strain	Time taken in sec For 8 Kg at 200^0C	Time taken in sec For 6 Kg at 200^0C	Time taken in sec For 8 Kg at Room Temp.	Time taken in sec For 6 Kg at Room Temp
0.01	11	15	22	26
0.02	23	35	58	72
0.03	48	65	92	122
0.04	72	93	165	265
0.05	133	169	322	510
0.06	245	326	573	785
0.07	386	512	826	1135
0.08	586	695	1138	1521
0.09	767	876	1525	2012

Table 6 Results of Creep test on composition 2

Strain	Time taken in sec For 8 Kg at 200^0C	Time taken in sec For 6 Kg at 200^0 C	Time taken in sec For 8 Kg at Room Temp.	Time taken in sec For 6 Kg at Room Temp
0.01	12	15	22	31
0.02	22	29	48	73
0.03	48	57	97	165
0.04	78	111	168	329
0.05	131	217	318	563
0.06	213	376	631	887
0.07	348	561	971	1308
0.08	545	783	1381	1703
0.09	748	1018	1705	2109

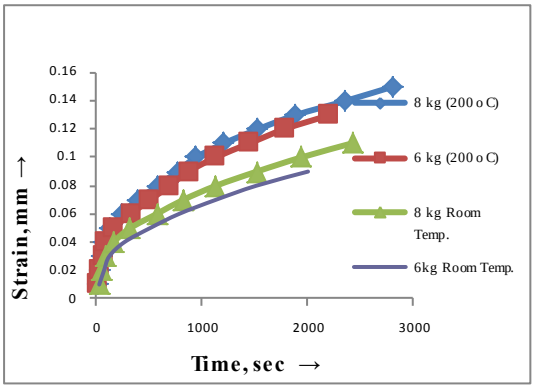


Figure 3 Strain v/s time for composition 1

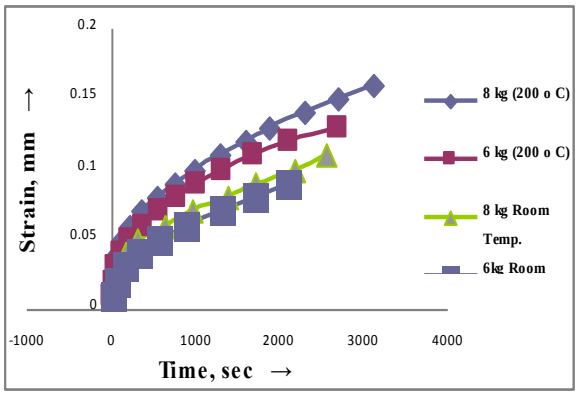


Figure 4 Strain v/s time for composition 2

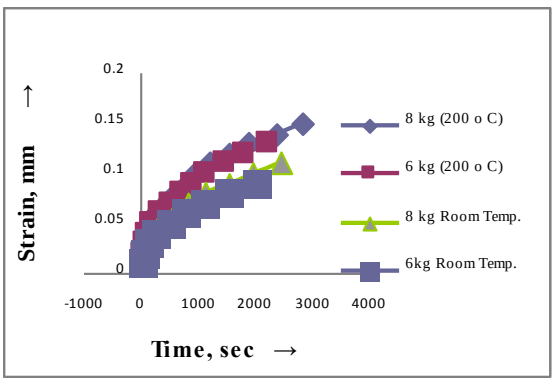


Figure 5 Strain v/s Time for composition 3

The Load at fracture P_Q value is used to determine the corresponding conditional K_Q value using SENB specimen. This is calculated from the following equation.

$$K_Q = P_Q S / B W^{3/2}). f(a/W) \quad (1)$$

$$K_Q = \{ P_Q S/BW^{3/2} \}[2.9(a/W)^{1/2} - 4.6 (a/W)^{3/2} + 21.8(a/W)^{5/2} - 37.6(a/W)^{7/2} + 38.7(a/W)^{9/2}] \quad (2)$$

where, B -Specimen thickness (m), W - Specimen width (m); A- Original crack length (m), a- Ligament (m), σ_{ys} - Yield strength (MPa), K_Q - Conditional Fracture toughness MPa $m^{1/2}$

Non-catastrophic fracture is observed in specimens with 30%C_f and 40% C_f material composition. But specimen with 50% C_f has exhibited brittle failure during fracture test. The fracture test calculations using above equations gave fracture toughness value of 10.67MPam$^{1/2}$ for specimens with 50 %C_f. Another observation is that even though all specimens were of same dimension, the load at fracture was higher for specimens with higher percentage of carbon fiber compared to that with low volume percentage of C_f.

Table 7 Results of Creep test on composition 3

Strain	Time Taken in sec For 8 Kg at 200^0 C	Time Taken in sec For 6 Kg at 200^0 C	Time Taken in sec For 8 Kg at Room Temp.	Time Taken in sec For 6 Kg at Room Temp
0.01	12	18	20	23
0.02	25	33	45	56
0.03	48	71	89	108
0.04	73	112	173	215
0.05	98	187	312	387
0.06	151	291	534	683
0.07	213	420	789	1012
0.08	346	546	1015	1365
0.09	479	733	1362	1768
0.10	651	917	1651	2271

Figure 6 SENB specimens of C/C composites

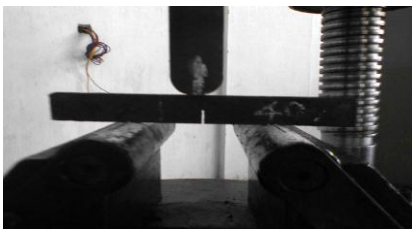


Figure 7 Fracture toughness test setup

4.5 Optical Micrographs

The Microstructures of material 1, 2, and 3 under 500 X magnification is shown in the Fig.8. It shows the distribution of short carbon fibers. It can be seen that as the gap between each fiber reduces as % volume fraction of carbon fiber increases. SEM views for compositions 1, 2 and 3 are shown in Fig.9, Fig.10 and Fig.11

respectively. The SEM analysis reveals that the interfacial bond between the carbon fibers and carbon matrix is not good hence the properties of the materials are much less than the theoretical values. This is because of low sintering temperature (1500^0C) applied at the time of fabrication process. If high sintering temperature is applied (above 2300^0C), the interfacial bond becomes perfect. Bridging of crack with carbon fibers is also observed in microstructural studies.

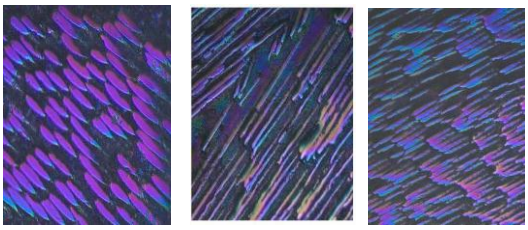


Figure 8 Microstructures of material1,2&3 at500X

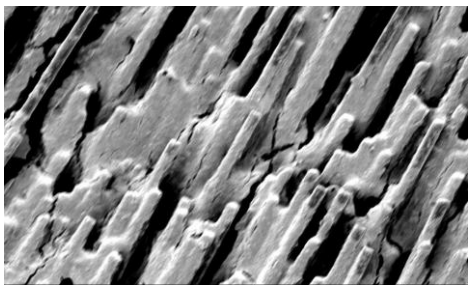


Figure 9a SEM of material-1 at X1000

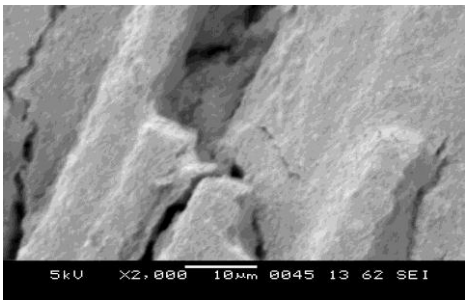


Figure 9b SEM of material-1 at X2000

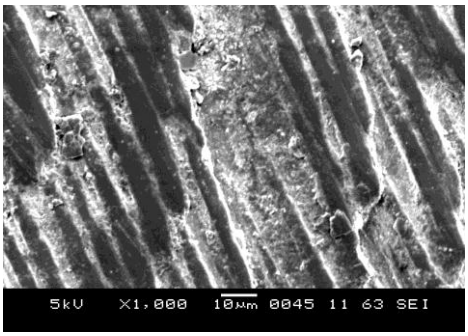


Figure 10a SEM of material-2 at X1000

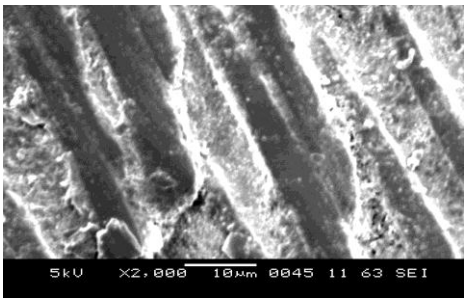


Figure 10b SEM of material-2 at X2000

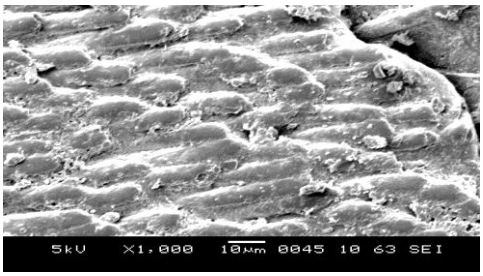


Figure 11a SEM of material-3 at X1000

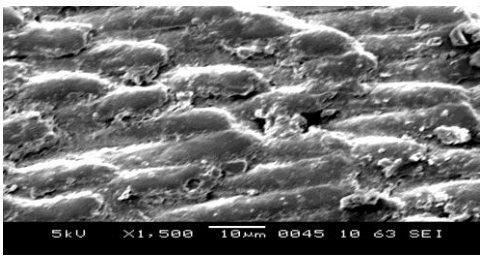


Figure 11b SEM of material-3 at X1500

4.5 Oxidation test

Oxidation test is carried out by placing the composite sample in the form of powder in theromgravimetry experimental setup and direct graph is obtained. Plot of DTG (ug/min) vs. Temperature ^{0}C, Plot of DTA uV vs. Temperature(^{0}C) and Plot of TG mg vs. Temperature(^{0}C) for 30%, 40% and 50%C_f composites are shown in Fig 12, Fig 13 and Fig 14 respectively.

By increasing the percentage of carbon fibers in C/C composites, the oxidation resistance can be increased in carbon-carbon composites.

4.6 Analysis of physical properties

Various physical properties are tested for composites prepared by perform yarn method with 30%, 40% and 50 % of carbon fiber by volume. These properties are compared with the C-C composite (50% Carbon fiber ratio by volume) manufactured by conventional method and listed in the following Table 8.

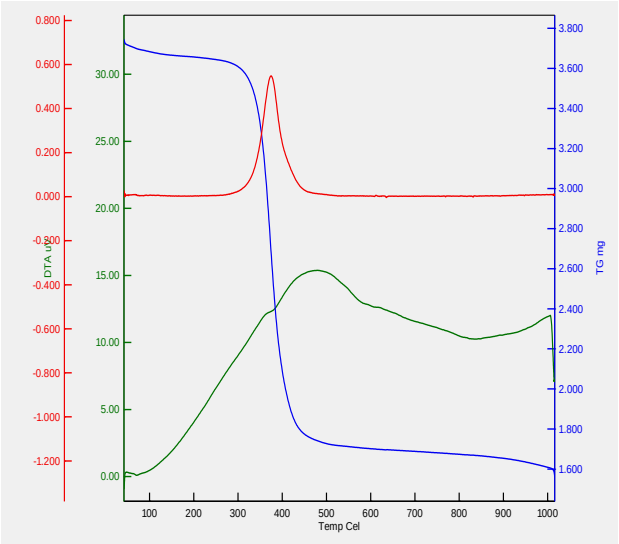


Figure 12 Plot of DTG vs. T for composition 1

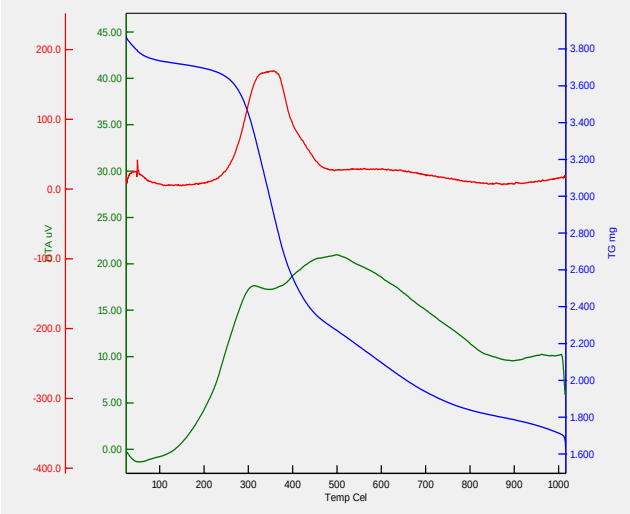


Figure 13 Plot of DTG vs. T for composition 2

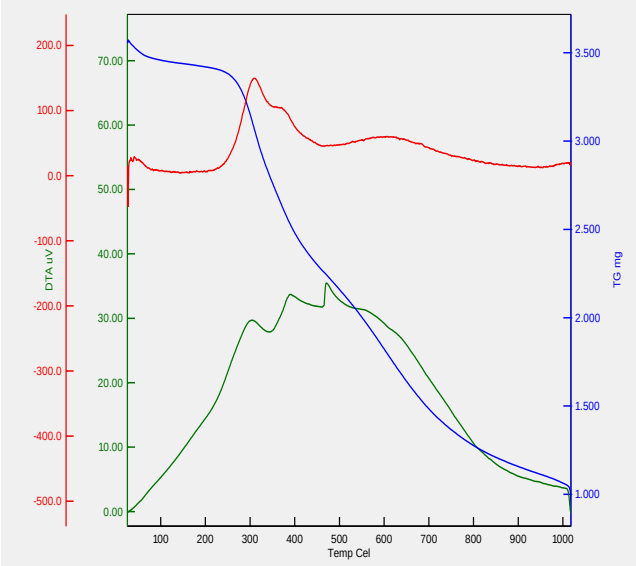


Figure 14 Plot of DTG vs. T for composition 3

Table 8 Various physical properties at different conditions for C-C composites with varying volume % of Carbon fiber

TYPE	AC 100	AC 200	AC 250	C/C
Carbon fiber ratio by volume (%)	30	40	50	50
Processed temperature (°C)	2000	2000	2000	2000
Density (g/cm^3)	1.7	1.7	1.7	1.7
Flexural rigidity (kgf/mm^2)	8	15	55	4
Compression strength (kgf/mm^2)	8	10	24	8
Charpy impact value ($kgf\text{-}cm/cm^2$)	10	13	53	2
Rate thermal expansion (10^{-6}/°C)				
Against length	2	1.1	0.6	4.0
Against thickness	---	8.4	8.2	4.0
Heat conductivity (Kcal/m. hr .°C)				
Against length	15	30	59	100
Against thickness	---	11	9	100
Specific heat (cal/g.)				
at 20°C	0.18	0.18	0.18	0.17

5. CONCLUSION

The Carbon-Carbon composites possess relatively very high rigidity and elastic modulus, high compressive strength even up to 2000^0C. Because of its superior strength, weight, and stiffness properties they offer 25-30% savings in structural weight which is of a strategic importance in a military aircraft. They enable the designer to tailor-make the strength and stiffness in the desired direction as well as cut down drastically the number of parts to be assembled. From the hardness test, compression test, impact test, MOR test and fracture toughness test it is observed that as carbon fiber % increases the material properties also increases. But, these properties are much less than the theoretical values because of low sintering temperature. The creep rate increases with addition of more carbon fiber, because of imperfect bond between the carbon fibers with carbon matrix, as observed in SEM photographs. Bridging of crack with carbon fibers is observed in microstructural studies. Non-catastrophic fracture is observed in 30%C_f and 40%C_f material composition. By increasing the volume fraction of carbon fibers in C-C composites, the oxidation resistance increases. Superior physical properties were also confirmed for C-C composites produced by perform yarn method.

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