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Development of vapor grown carbon fibers (VGCF) reinforced carbon/carbon composites

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C/C composites are developed using vapor grown carbon fibers (VGCF) with two types of pitches as matrix precursor. The composites are carbonized at 1000°C by applying the isostatic pressure throughout the carbonization process and further heat treated at different temperatures up to 2500°C in the inert atmosphere. By applying iso-static pressure one can able to developed VGCF based C/C composites possessing the very high bulk density (1.80 g/cm^3) and apparent density (2.01 g/cm^3) only by heat treatment up to 2500°C without any densification cycle. This high value of density is due to the extremely strong fiber-matrix interactions and self sintering between the VGCF fibers during carbonization process under iso-static pressure. From the SEM study it reveals that, fiber-matrix interactions are strong and fiber boundaries merges with each other, also there is not a evidence of matrix shrinkage cracks in case 1500°C heat treated composites. On the other hand, in 2500°C heat treated composites, there is evidence of uniform fiber-matrix interfacial cracks and porosity in nanometer dimensions. This is due to the change in fiber morphology above HTT 1500°C. But the formation of nano width cracks does not affect on the mechanical properties of composites. The compressive strength increases from 95MPa of 1500°C to 105 MPa of 2500°C heat treated composites. However, hardness decreases due to the increase in the degree of graphitization of composites on 2500°C. The study reveals that by controlling processing condition and the uniform dispersion of VGCF fibers in the matrix phase, it can be possible to developed nano porosity at fiber-matrix interface. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Carbon/Carbon (C/C) composites are a class of advanced materials and it is being used in many structural applications [1, 2] but due to the high processing cost prohibits their application in many areas where the properties are desired but economically not affordable. Basically these composites consist of carbon fibers bonded together with carbon matrix. The matrix carbon is deposited in the fibrous carbon structure by chemical vapour deposition [3] or chemical vapour infiltration or carbonization of thermoset resins [4] or thermoplastic pitches [5] which are infiltrated in fibrous skeleton to get carbon fiber reinforced composites. The carbonization of latter composites is resulted in to the shrinkage and as a consequence formation of cracks, pores and voids in the ultimate C/C composites [6]. Thus, C/C composites possess lower density and hence the poor mechanical properties [7]. To overcome this problem of C/C composites, attempts are made by material scientist by carbonization of these composites under high pressure autoclave [8], development of C/C composites by using the high char yield matrix [9] and densification by conventional liquid infiltration and re-carbonization. The conventional densification process involves multiple cycles of re-infiltration and re-carbonization. This process is not only expensive but also time consuming. Therefore, in the present investigation to reduce the overall cost of C/C composites, the vapour grown carbon fibers (VGCF) are used as reinforcements. These fibers possess excellent thermal and electrical conductivities [10, 11] and good mechanical properties/cost ratio [12]. Because of their low cost of production (100 US$ Kg^{-1}), VGCF are extremely interesting as potential substitute for conventional PAN and pitch based carbon fibers as reinforcement in the development of C/C

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composites. So far vapor grown carbon fibers are being used for reinforcing in polymer matrices to improve the mechanical, thermal and electrical properties [13, 14]. The vapor-grown carbon fibers are produced introducing as aerosol spray of a metal salt (usually Fe^{3+}) into a chamber of hydrocarbon gas heated to 1000–1200°C [15]. The VGCF have a high aspect ratio i.e., length varying between 10–100 μm and diameter in range of 100–300 nm [16, 17], the dimensions of VGCF are quite smaller than that of the continuous PAN or pitch based carbon fibers. Therefore, these fibers possess high active surface area and high surface energy as well surface functional groups.

In earlier study, authors are made an attempt to develop the nonaligned VGCF based composites with coal tar pitch matrix (modified coal tar pitch possess Softening point 196°C) [18]. It has been found that, there is significant volume expansion during the carbonization process under continuous flow of nitrogen atmosphere. The significant volume expansion is due to the high internal pressure generated as a cause of the interactions between the fibers (due to the poor fiber dispersion and high aspect ratio). As a result bulk density suddenly reduces from 1.60 g/cm^3 of green composites to 0.85 g/cm^3 of carbonized C/C composites. Further on heat treatment at 2500°C, density increases in small increment from 0.85 to 1.0 g/cm^3 but it is not as expected. Thus, to overcome this problem of VGCF based C/C composites; new cost effective processing technique has been introduced to suppress the internal pressure developed during carbonization process in VGCF based composites. In this process, isostatic pressure is applied during the course of carbonization (heating and cooling cycle) process up to temperature 1000°C in the continuous flow of nitrogen gas. The objective of the present investigation is to develop the C/C composites using vapor grown carbon fibers and characterized them for mechanical properties.

2. Experimental

Vapor grown carbon fiber (Pyrograf III supplied by Applied Science, Inc., USA) was used as reinforcement and their properties [16, 17] given in Table I. The two types of pitches possessing different properties were used as matrix precursor (Table II). VGCFs generally come in a "fluffy mass" where the fibers were intertwined. Therefore, it was very difficult to get dispersed these fibers in the matrix. In this direction in the present investigation, these fibers first dried at 110°C for 3–4 h and dispersion was carried out by ultrasonic stirring in chloroform solution. This mixture dried at room temperature and it was confirmed that most of the vapor grown carbon fibers dispersed. In the present study, VGCF and coal tar pitch matrices were dispersed simultaneously; dispersed mixture was dried and it was used for the development of green composites using a match mold die technique [19] with keeping fiber volume fraction 30 ± 2%. The match mould die consists of female mold and male plunger, made of die steel. On the basis of fiber volume fraction, the required quantity of VGCF mixed with the pitch matrix and mixture was taken in the female mould. After putting the mixture, the male plunger was fitted into the female mold with a stopper of desired thickness. The complete assembly was kept on the hot plate of the hydraulic press; the temperature of hot plate increases and on reaching the desired temperature, the pressure was applied to get the composites of desired thickness. Later on, the hydraulic press plate cool down to room temperature by circulating the water through the plates and at room temperature green composite was taken out from the die mould. The green composites were carbonized at temperature 1000°C under continues flow (0.5 lit/min) of nitrogen gas. The composites specimen packed (in specially design metallic plate assembly) by applying the isostatic pressure (1250 N/m^2) uniformly throughout the carbonization process. This technique not only controls the volume expansion but also matrix micro-cracking occur during the cooling from high temperature. The carbonized composites were further heat-treated to different temperatures i.e. 1500, 2000 and 2500°C. The composites were characterized for physical and mechanical properties. The porosity and apparent density was measured by using Archimedes principle. Kerosene oil was used as a liquid medium for the measurement of density. The compressive strength of the composites was measured on Instron universal testing machine model 4411 as per ASTM standard D695 and scleroscopic hardness tester was used to measure hardness. The morphology of composites was studied by scanning electron microscope (SEM LEO). The interlayer spacing was measured by X-ray diffraction (Bruker D8 advance). The composites made from VGCF (V) with two matrices (M1 & M2) are coded as:

VM1 – VGCF Reinforced Modified Pitch Matrix
VM2 – VGCF Reinforced Mesophase Pitch Matrix

TABLE I Properties of VGCF (PR19) pyrograf III [16, 17]

Properties	Value
Fiber diameter (nm)	100–300
Tensile strength (GPa)	1.7–3.38
Tensile modulus (GPa)	88–166
Density (gm/cm^3)	1.95
Electrical resistivity ($\mu \cdot \Omega \cdot$ cm)	1000
Thermal conductivity (W/m · K)	20

TABLE II Properties of pitches

Properties	Modified pitch (M1)	Mesophase pitch (M2)
Softening point (C)	196	280–290
Carbon yield (%) @1000° C, N2	72	75
Q.I. (%)	20.3	–
T.I (%)	58.1	71
Density (g/cm^3)	1.35	1.25

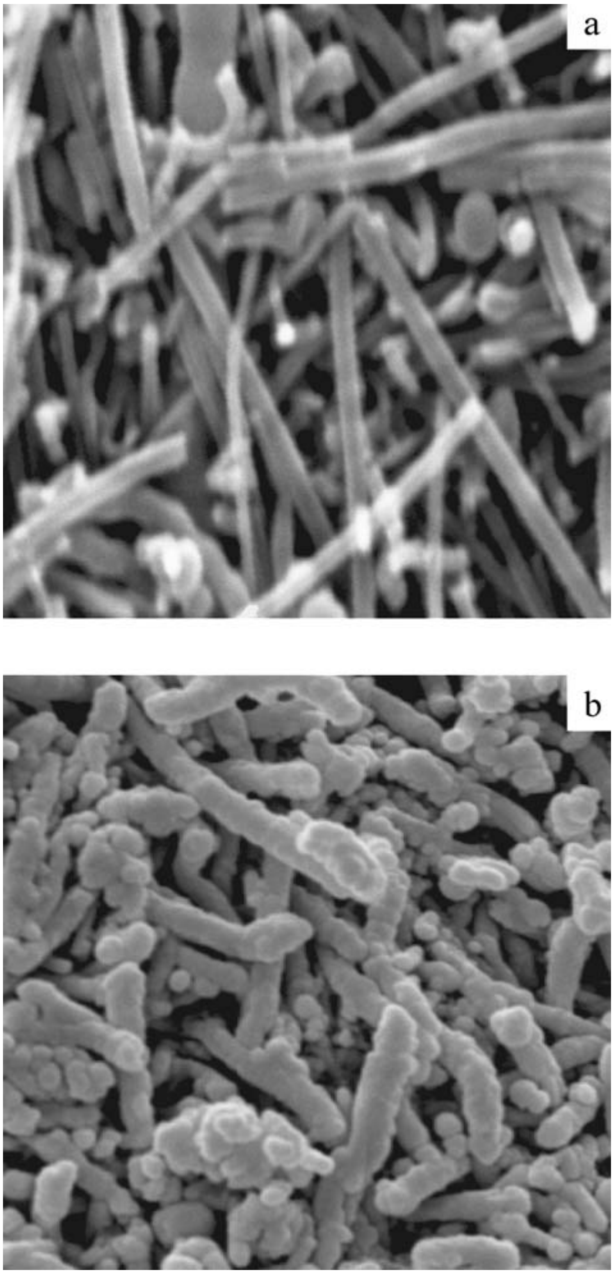

Figure 1 SEM micrographs (a) as received VGCF and (b) VGCF heat treated at 2500°C.

3. Results and discussion

3.1. Morphology of VGCF fibers and C/C composites

Fig. 1 shows the SEM micrographs of VGCF as received and VGCF heat treated at 2500°C. The as received fibers are nearly in cylindrical shape (Fig. 1a) with rough surface i.e. on smooth surface of cylindrical fibers possessing some irregularities or some beads. After heat treatment at 2500°C (Fig. 1b), the fibers morphology changes due to shrinkage in the fiber diameter because during the processing of these fibers, they are only heat treated at around 1200°C by CVD process [15]. Some of the fibers are in lathe shaped and some of them in crenulated shaped. This is due to the change in outer surface morphology of the fibers as a consequence graphitization of non-graphitic outer core. Fig. 2 shows the XRD pattern of as received VGCF and VGCF heat treated at 2500°C. The asymmetric d_{002} diffraction pattern (Fig. 2a) of as received VGCF is due to the tree-ring like morphology of VGCF [20, 21]. Basically these fibers consist of regularly order graphitized core covered with concentric layers of pyrolytic carbon of lower crystallinity than the inner core [21, 22]. As received VGCF possess the average interlayer spacing value 0.34292 nm and after heat treatment at 2500°C, it is 0.3371 nm. The XRD pattern of VGCF heat treated at 2500°C is some what symmetric due to the graphitization of concentric outer layer of pyrolytic carbon of VGCF fibers (Fig. 2b). It is interesting to note that, as received vapor grown carbon fibers possess the degree of graphitization 12.5% and after heat treatment at 2500°C, degree of graphitization increases and it is 80%.

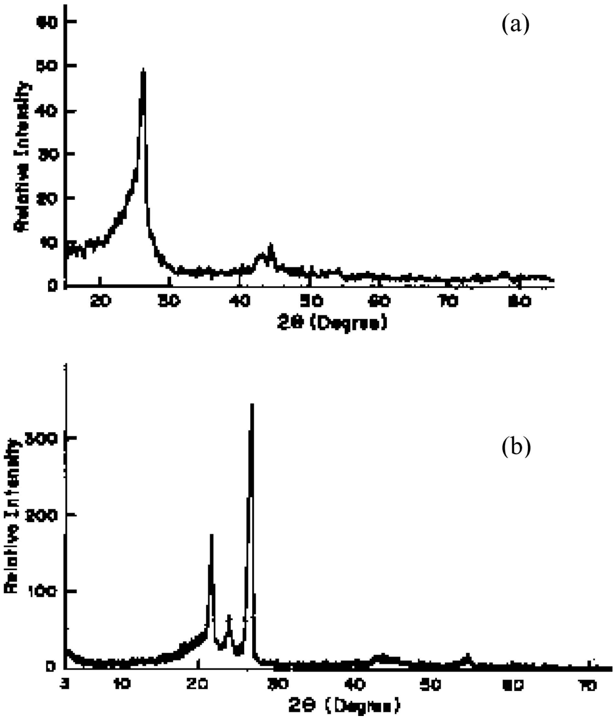

Figure 2 XRD pattern of (a) as received VGCF and (b) VGCF heat treated at 2500°C.

Fig. 3 shows SEM micrographs of C/C composite after carbonization at 1500°C. Fig. 3a shows cross section view of C/C composites (VM2) parallel to molding direction. The fibers are oriented in *x* and *y* direction and the fibers are strongly bonded together with the carbon matrix (VM2). Fig. 3b shows the cross section view of perpendicular to molding direction. In this case all the fibers oriented in almost in one direction and fibers are strongly bonded together. The fibers boundaries are merges together or the interphase between the fibers and the matrix in the range of few nm. To confirm these observations the composites sample examined under SEM at 100 nm scale (magnification × 70 K) and it is observed that there is layer of carbon matrix between VGCF fibers in the range of 20–30 nm (Fig. 3c) and no gap between fiber and matrix visible. The fibers are well bonded with carbon matrix and in some cases there is bonding between the fibers. Possibly one can expect this is due to the self sintering between fibers under isostatic pressure because of vapor grown carbon fibers possess large surface area. Therefore, these fibers are form active surface complexes at room temperature and even in absence of any binder; these fibers compacted like composite i.e. these fibers are agglomerated in fluffy mass or intertwined, is shown in Fig. 3d. Fig. 4 show the SEM micrographs after heat treatment at 2500°C of C/C composites. Generally it is observed that in C/C composites matrix, micro-cracks developed due to the thermal contraction between the fibers and matrix as well as due to the matrix shrinkage during carbonization process [23] at a time of cooling from high temperature. But in case of VGCF composites this phenomena is not observed during carbonization even at 1500°C (Fig. 3a and b). On the other hand, after heat treatment at 2500°C of same composites, there is development of uniform cracks throughout composites cross sections. This is due to the shrinkage of fibers cross section and decreases in diameter at temperature beyond 1500°C because VGCF used are not experienced the temperature more than 1200°C during their synthesis by CVD process.

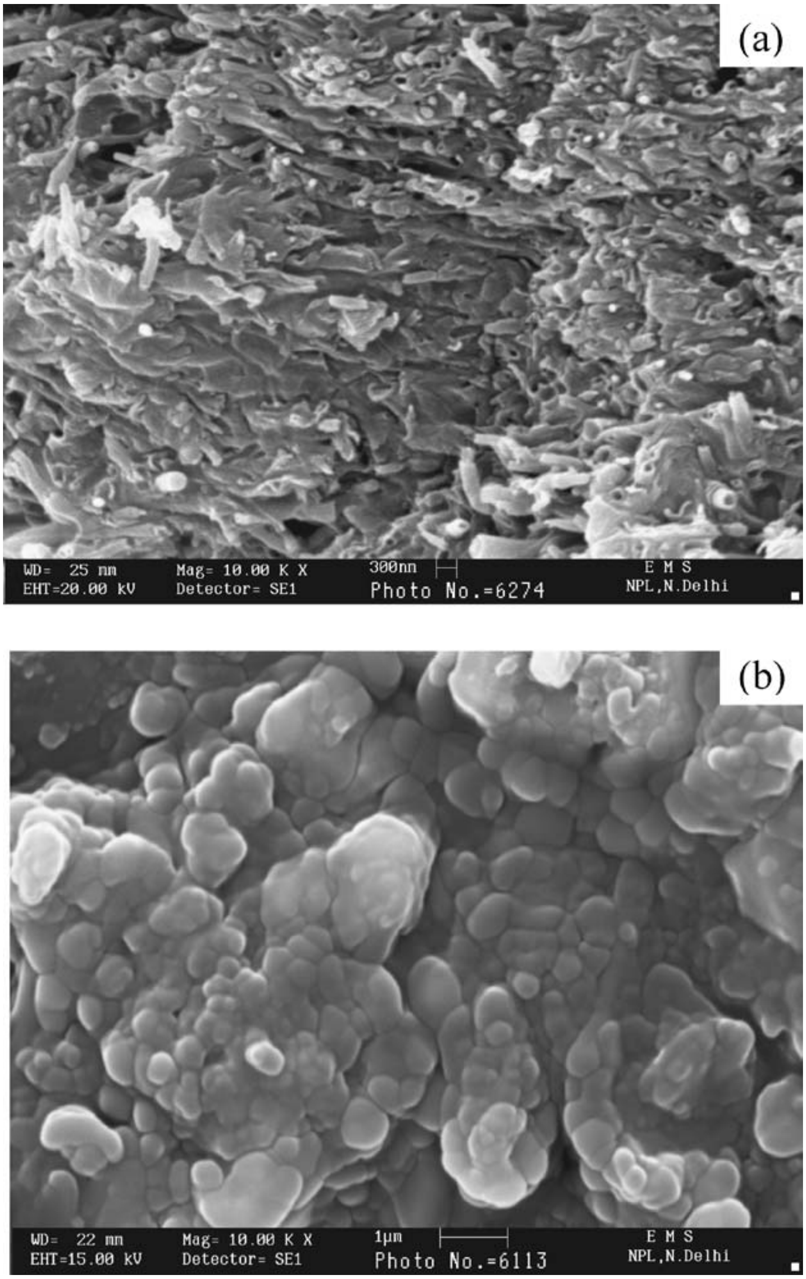

Figure 3 SEM micrographs of C/C composites heat treated at 1500°C (a) Parallel to moulding direction, (b) Perpendicular to moulding direction, (c) at higher magnification and (d) agglomerated VGCF.

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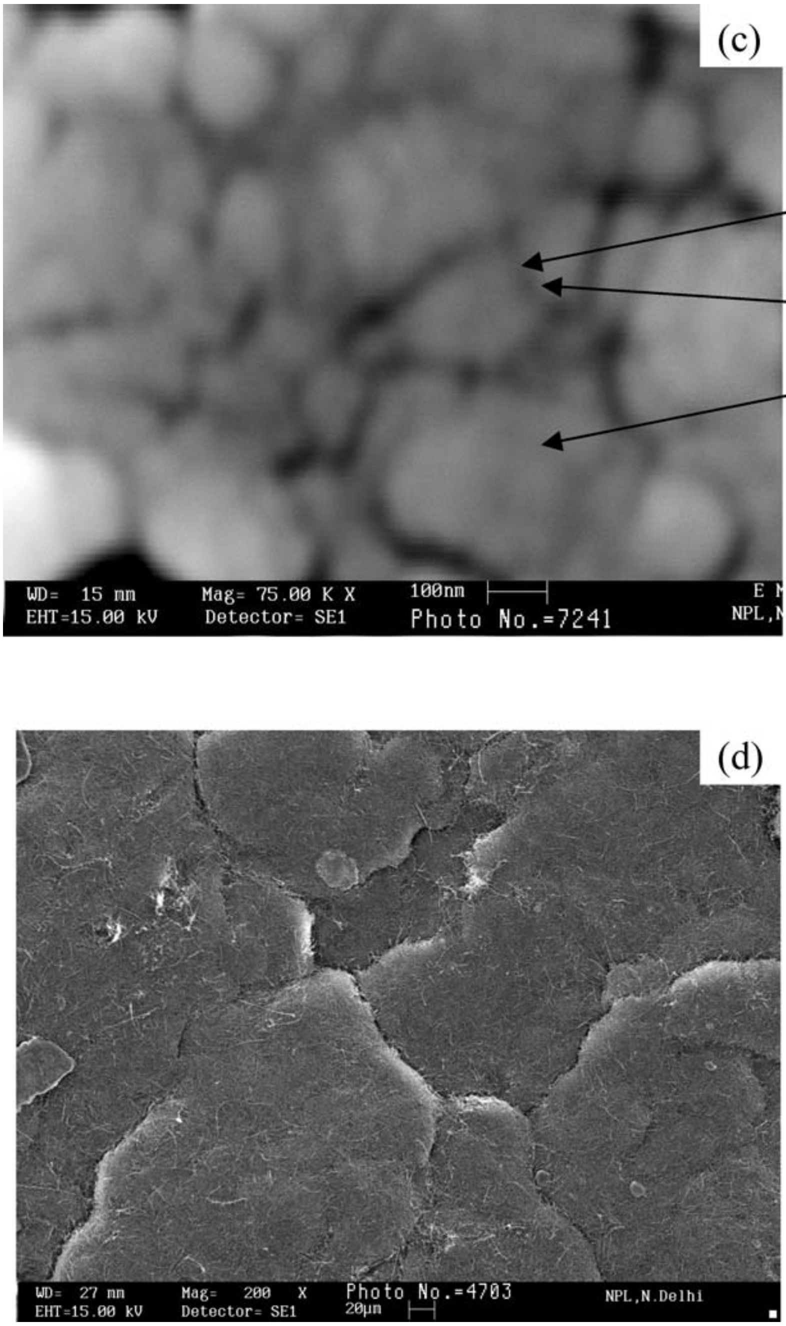


Figure 3 Continued.

This resulted in to the change in fiber diameters and due to the strong bonding between VGCF fibers and matrix, the fibers shrinks away from interface by breaking the interfacial bond and creates the interfacial crack possessing width of few nanometer (nanocracks). With increasing the temperature the cracks length increases through the nano-interface. However, in case of self sintered fibers in the same composites, still bonding between fiber to fiber persists. This can be due to the fact that, the interface developed between self sintered fibers may be so strong, even the thermal stresses exerting at temperature 2500°C are not enough to break bond. Therefore, the cracks developed at the fiber-matrix interface are not propagating through this type of interface; this is shown in Fig. 4a. The crack density is higher in case of perpendicular to molding direction surface (Fig. 4b). Fig. 5 shows the XRD pattern of VGCF based C/C composites heat treated at 1500 and 2500°C. Fig. 5a shows the XRD pattern of VGCF fiber reinforced mesophase pitch (VM2) matrix composites heat treated at 1500°C. The asymmetric peak of d_{002} at 2θ between 25–27° is due to the VGCF and graphitizeble carbon derived from mesophase pitch that gives the average interlayer spacing value 0.34326 nm. On heat treatment at 2500°C, the asymmetric peak transforms in to symmetric peak possessing average interlayer spacing (d_{002}) 0.33944 nm. This value of interlayer spacing is higher

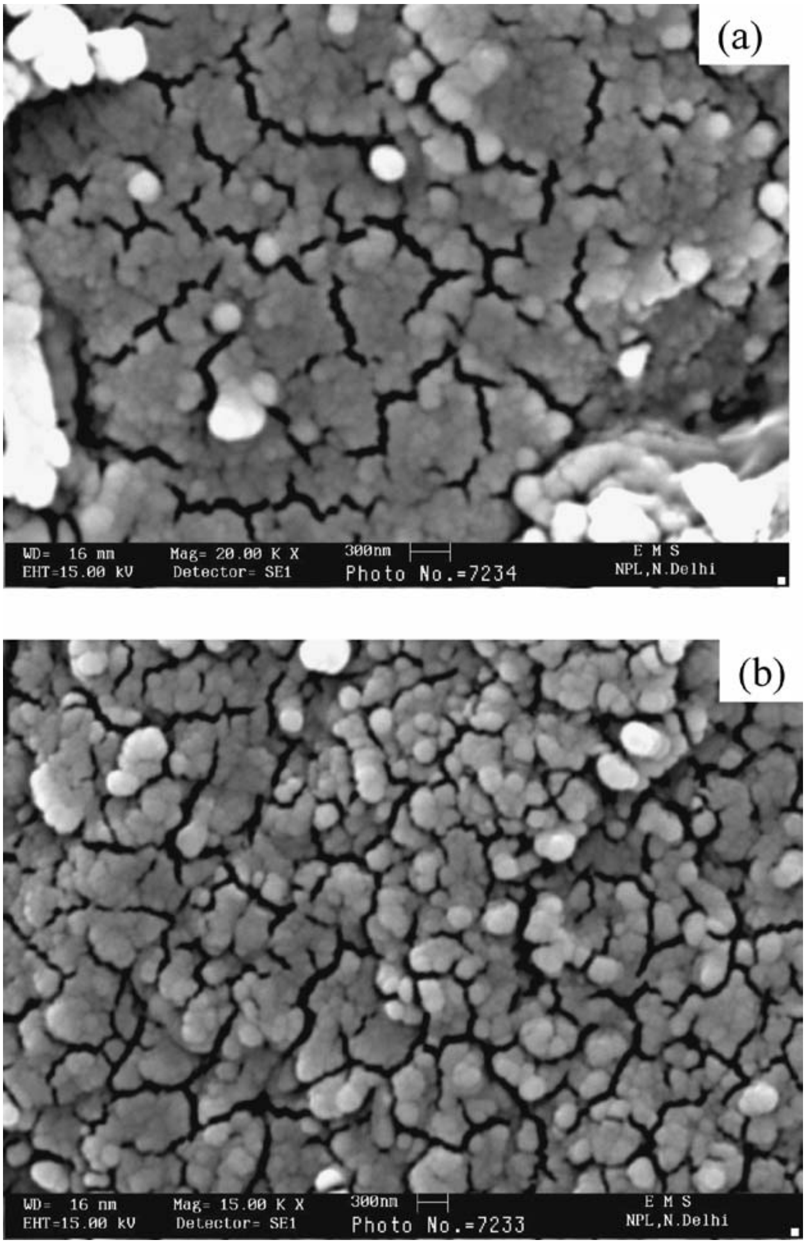


Figure 4 SEM micrographs of C/C composites heat treated at 2500°C. (a) Parallel to moulding direction, (b) Perpendicular to moulding direction.

than as such heat treated VGCF at 2500°C. It is interesting to note that, as received VGCF possess the degree of graphitization 12.5% and after heat treatment at 2500°C, degree of graphitization increases and it is 80%. But on the other hand, degree of graphitization of composites heat treated at 1500°C is 8% and of 2500°C heat treated composite is 53% even the graphitizeble mesophase pitch used as carbon matrix. The degree of graphitization of VGCF fibers based composites is lower than the as received fiber heat treated at same temperature. This shows that the graphitization of VGCF fibers in composites are restricted by development of large number of inter crystalline boundaries due to the different types of bonding in composites.

3.2. Physical properties of C/C composites

Fig. 6(a and b) shows the variation in bulk density and apparent density of VM1 and VM2 composites with HTT. Initially at green stage (moulded composites) density of VM1 composites is higher than VM2 where the fiber volume (30 ± 2%) is same in both the composites. But on carbonization (at 1000°C) density of VM2 composites increase due to the higher shrinkage as a cause of strong fiber-matrix interactions and compactness of sample. If we see the shrinkage behavior, there is nearly 4% higher shrinkage in VM2 composites than VM1 (Fig. 7a). The two pitches (MI and M2) used in this study possessing different carbon yield (Table II). The carbon yield of M2 pitch is higher than M1 pitch. In general higher the carbon

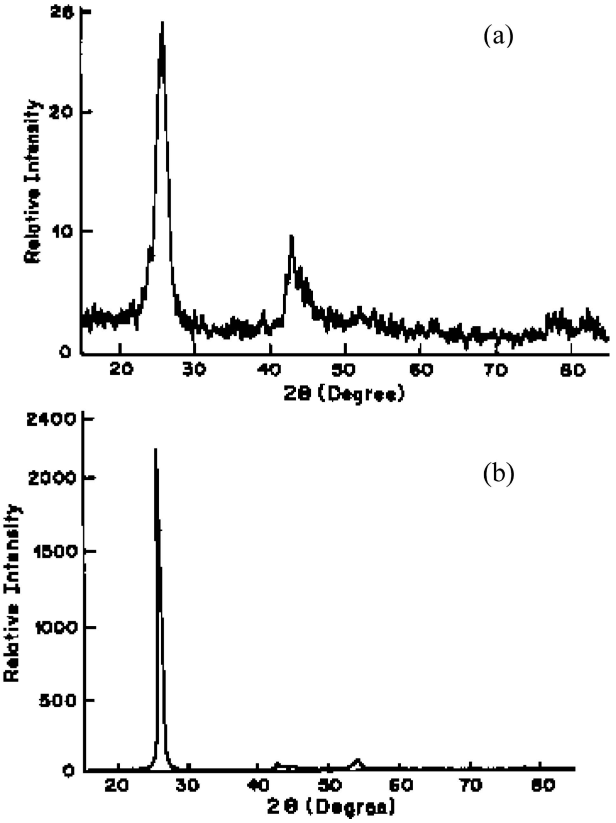


Figure 5 XRD pattern of C/C composites: (a) HTT 1500°C, (b) HTT 2500°C.

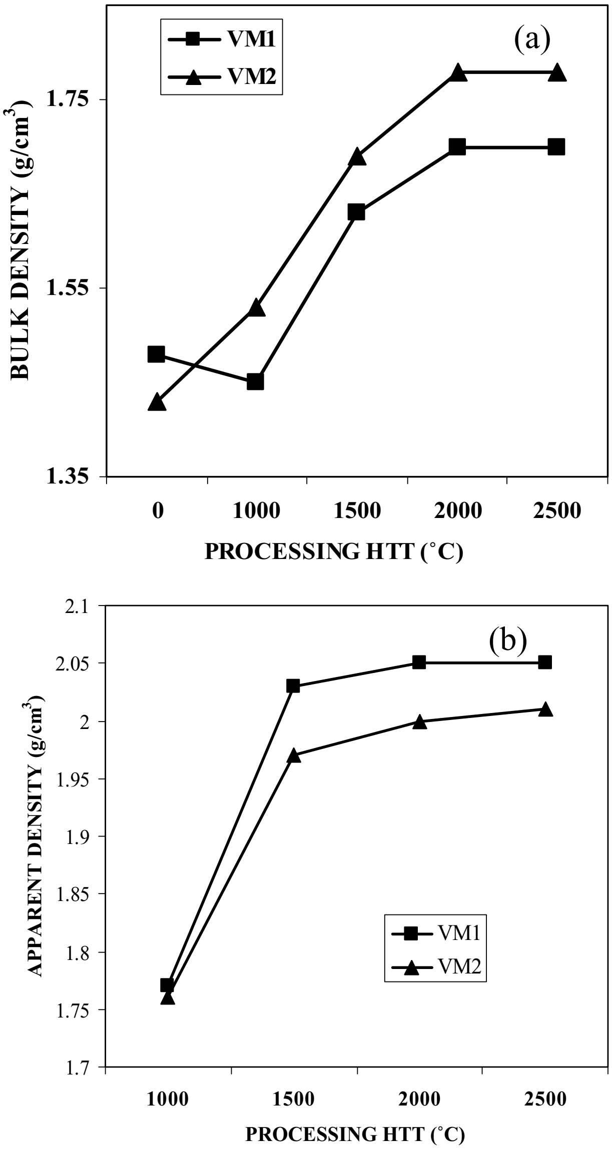


Figure 6 Variation in (a) bulk density, (b) real density of VM1 and VM2 composites with HTT.

yield lower is shrinkage and vice-versa. Therefore, the higher shrinkage of VM2 composite is due to the stronger fiber-matrix interactions. With increasing the heat treatment temperature (HTT) above 1000°C, bulk density continuously increases in both types of composites and at HTT 2000°C density of VM1 and VM2 composites are registered 1.70 and 1.78 g/cm^3 respectively. But further on HTT 2500°C, the bulk density in both the cases does not increases. As well as there is only small incremental shrinkage at this temperature range Fig. 7a. Fig. 6b shows the apparent density and total porosity of C/C composites. The apparent density at 1000°C is in the order of 1.76–1.77 g/cm^3 and with increasing the HTT, apparent density suddenly increases from 1.76–1.77 to 2.01–2.03 g/cm^3. Further with increasing the temperature, density increases moderately up to 2000°C and above 2000°C, more or less no increase in apparent density in both types of composites. This suggests that the heat treatment at 2500°C is not made any physical changes in the composite. This might be due fact that, as observed in Fig. 4(a and b), the creation of nano-width cracks at fiber-matrix interface as a cause of fibers shrinkage and change in fiber morphology. This resulted in to the cracks and porosity throughout the sample cross section, but on the same time there are regions of well bonded fiber phases. This type of composites morphology is might be responsible for yielding high density composites. However, the porosity is in the order of 32–36% at HTT 1000°C and with increasing the HTT, porosity decreases in both the type of composites, this is due to self sintering of fibers. The porosity suddenly decreases at temperature 1500°C, thereafter with increasing HTT up to 2500°C; porosity increases in small increment (Fig.7b). The small incremental increase in the porosity is due to the creation of interfacial cracks at fiber-matrix interface. This is completely different observations than the continuous fiber reinforced carbon/carbon composites where the bulk density varies within limit with the HTT and porosity increases [24, 25] with HTT. Because it is well known that the graphitization in C/C composites initiated in this temperature range (>2000°C) [26], due to this process porosity increases in C/C composites with HTT.

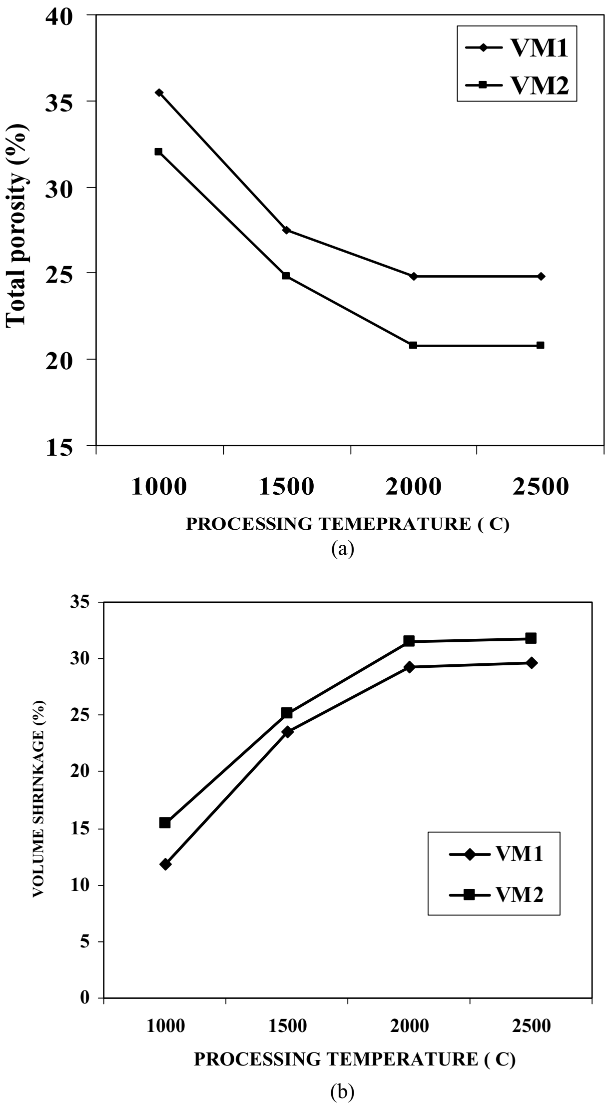
3.3. Mechanical properties C/C composites

TableIII shows the compressive strength and Scleroscopic hardness of composites after HTT at 1500 and 2500°C.

TABLE III Mechanical properties of VGCF based composites

Composites	Compressive strength (MPa)		Scleroscopic hardness	
code	HTT 1500°C	HTT 2500°C	HTT 1500°C	HTT 1500°C
VM1	90	98	87	80
VM2	97	105	85	75

At 1500°C compressive strength of VM2 composites is higher than VM1 composites and at 2500°C strength increases slightly in both the type of composites. The increase is related to increases in bulk density. On the other hand, even there is development of nano width cracks at fiber-matrix interface but compressive strength does not decrease. This shows that, the interfacial cracks developed at fiber-matrix interface due to fiber shrinkage above HTT 1500°C does not influence the compressive strength of both the types of composites, while instead of decreasing the compressive strength, it increases. This value of compressive strength of C/C composite is comparable to that of high density isotropic graphite. Ishiyama *et al.* [27] reported the bulk density and compressive strength of isotropic graphite (IG-110), 1.78 g/cm^3 and 76.8 MPa respectively. This shows that the value of compressive strength of VGCF based composites is higher but the degree of graphitization is lower (discussed in Section 3.1). The scleroscopic hardness of 1500°C heat treated VM1 and VM2 composites is in the range of ~85 and on HTT 2500°C it decreases to 75–80. The decrease in the scleroscopic hardness is due to the increase in the degree of graphitization of C/C composites on HTT 2500°C as discussed in Section 3.1.



(a)

(b)

Figure 7 Variation in (a) total porosity and (b) volume shrinkage with HTT of composites.

4. Conclusions

By applying iso-static pressure one can able to developed VGCF based C/C composites possessing the very high bulk density (1.80 g/cm^3) and apparent density (2.01 g/cm^3) only by heat treatment up to 2500°C without any densification cycle. This might be due to the strong physical compaction between the fiber and the matrix as a cause of strong fiber-matrix interactions and self sintering between the fibers. The SEM study of 1500°C heat treated composites reveals that there is strong fiber-matrix interactions and sintering between the fibers. On heat treatment at 2500°C, microstructure of composites changes, there is formation of well defined interfacial cracks at fiber-matrix interface, crack width in the range of 100 nm scale. This type of uniform nano width crack at the fiber-matrix interface is due to the shrinkage in fiber cross section and decreases in fiber diameter. On the other hand, there are no cracks or porosity in the self sintered fibers region and the cracks developed at fiber-matrix interface are not propagating through the self sintered fiber interface. As a reason the compressive strength of 2500°C does not decreases even there is well defined uniform cracks in whole cross section of composites. However, hardness decreases due to the increase in the degree of graphitization of composites on 2500°C. The physical and mechanical properties of 1500°C heat treated composites are comparable to that of high density isotropic graphite. Therefore, VGCF based composites may be useful material for certain applications where the bulk density, compressive strength and hardness are the desired properties. Also by controlling processing condition and the dispersion of VGCF fibers in the matrix phase, it can be possible to develop nano size porosity at fiber-matrix interface. This may be one of the promising materials for gas storage application.

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