

# Mechanical Properties of Unidirectional Carbon-carbon Composites as a Function of Fiber Volume Content

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## Abstract

Unidirectional polymer composites were prepared using high-strength carbon fibers as reinforcement and phenolic resin as matrix precursor with keeping fiber volume fraction at 30, 40, 50 and 60% respectively. These composites were carbonized at 1000°C and graphitised at 2600°C in the inert atmosphere. The carbonized and graphitised composites were characterized for mechanical properties as well as microstructure. Microscopic studies were carried out of the polished surface of carbonized and graphitised composites after etching by chromic acid, to understand the effect of fiber volume fraction on oxidation at fiber-matrix interface. It is found that the flexural strength in polymer composites increases with fiber volume fraction and so does for the carbonised composites. However, the trend was found to be reversed in graphitised composites. In all the carbonized composites anisotropic region has been observed at fiber-matrix interface which transforms into columnar type microstructure upon graphitisation. The extension of strong and weak columnar type microstructure is function of fiber volume fraction. SEM microscopy of the etched surface of the sample reveal that composites containing 40% fiber volume has minimum oxidation at the interface, revealing a strong interfacial bonding.

**Keywords :** Carbon fibers, fiber volume fraction, carbon-carbon composites, Interface, Mechanical properties

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## 1. Introduction

Carbon-carbon composites have become one of the most important materials because of their light weight coupled with the unique thermal, mechanical, chemical and biomedical properties, which can be tailored to give large number of applications in the modern era of science and technology [1, 2]. The performance of these composites depends upon the fiber-matrix interface, type of fiber and the matrix [3, 4] and stress transfer capability of the interface. In the carbon-carbon composite materials, different type of interfaces exist, such as those between fibers and matrix, between different layers or phases within the matrix, and within fiber bundles [5]. In addition to this, strain to failure of matrix and of carbon fiber plays an important role in realizing full potential strengthening effect of carbon fibers in these composites [6,7]. Whereas in case of polymer matrix composites, properties of composites mainly get influenced by the reinforcing fiber properties, in carbon-carbon composites properties get influenced by the properties of reinforcing fibers as well as of carbon matrix. In the earlier study authors have reported that, how different carbon fibers and its surface functional groups effect on the development of interface and its influence on the mechanical properties of carbon-carbon composites [8]. It has been found that high-strength carbon fiber makes strong interactions, intermediate-modulus fiber makes

neither too strong nor too weak interactions while high-modulus fiber makes weak interactions with resol-type phenolic resin. As a result, high-strength carbon fiber derived composites develop a laminar texture with strong extinction lines or well defined columnar type texture, intermediate-modulus fiber composites develop laminar texture with lesser number of extinction lines whereas high-modulus fiber composites develop laminar texture at the fiber-matrix interface when heat treated at 2600°C [9]. In the present investigation study has been extended to understand the effect of different volume fraction of high-strength carbon fibers on the mechanical properties and microstructure of carbon-carbon composites.

## 2. Experimental

Unidirectional polymer composites were prepared by wet winding and match mold die technique [10] with fiber volumes of 30, 40, 50 and 60% respectively at polymer stage. PAN based T-300 carbon fibers were used as reinforcement (T. S. 3.5 GPa, T. M. 230 GPa and strain to failure 1.4%) and resol type phenolic resin was used as matrix precursor. The composites prepared with different fiber volume content (Fv) were coded as;

Composites A; fiber volume fraction at polymer stage

30% and at carbonized stage 45%.

Composites B; fiber volume fraction at polymer stage 40% and at carbonized stage 53%.

Composites C; fiber volume fraction at polymer stage 50% and at carbonized stage 62%.

Composites D; fiber volume fraction at polymer stage 60% and at carbonized stage 69%.

These composites were carbonized at 1000°C and graphitised at 2600°C under inert atmosphere. The polymer, carbonized and graphitised composites were characterized for mechanical properties i.e. flexural strength, flexural modulus and interlaminar shear strength by three point bending method on Universal Instron Testing machine model 4411 as per ASTM standard (D-790-80). The microstructure of carbonized and graphitised composites was analyzed using polarized light microscope. To elucidate the effect of fiber volume content on the microstructure of matrix, surface of composites were observed under SEM after etching the polished surface of the composites with chromic acid for four hours.

### 3. Results and Discussion

#### 3.1. Mechanical properties of the composites

Figure 1 shows the total volume shrinkage in composites A, B, C and D after carbonization and graphitisation. The shrinkage occurring during carbonization depends upon fiber-matrix interactions and bulk matrix contribution. It is noticed that the volume shrinkage is inversely proportional to the Fv. The maximum volume shrinkage i.e. 34% is for composite A and only 13% in composite D. This is due to the higher volume fraction of matrix in composite A and minimum in composite D. However, almost same volume shrinkage is noticed in all the composites during graphitisation.

The flexural strength of polymer, carbonized and graphitised composites as a function of Fv is shown in figure 2a. In polymer composites, flexural strength increases from com-

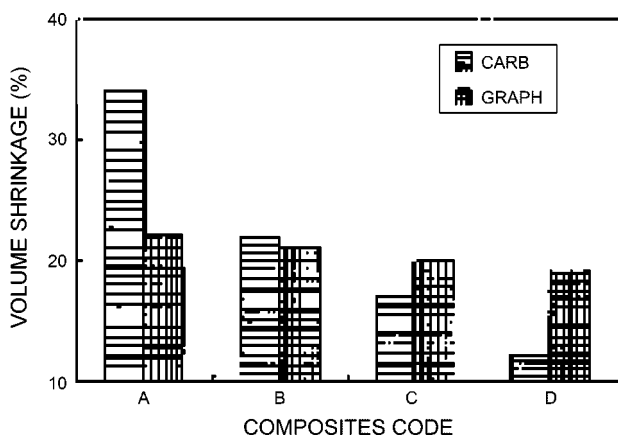


Fig. 1. Total volume shrinkage during carbonization and graphitisation of composites.

posites A to D which indeed follows the rule of mixture. In composite A due to higher contribution of matrix, there is only a limited stress transfer capability and with increasing the fiber volume fraction stress transfer capability of composites increases because of more uniform distribution of fibers in the matrix. On the other hand, the flexural strength in composite D is only 900 MPa, which is much less than theoretical value of flexural strength as per rule of mixture. This is due to much lower volume fraction of the matrix and the interfaces existing in composite D between fiber and matrix and within fibers. As a consequence stress transfer

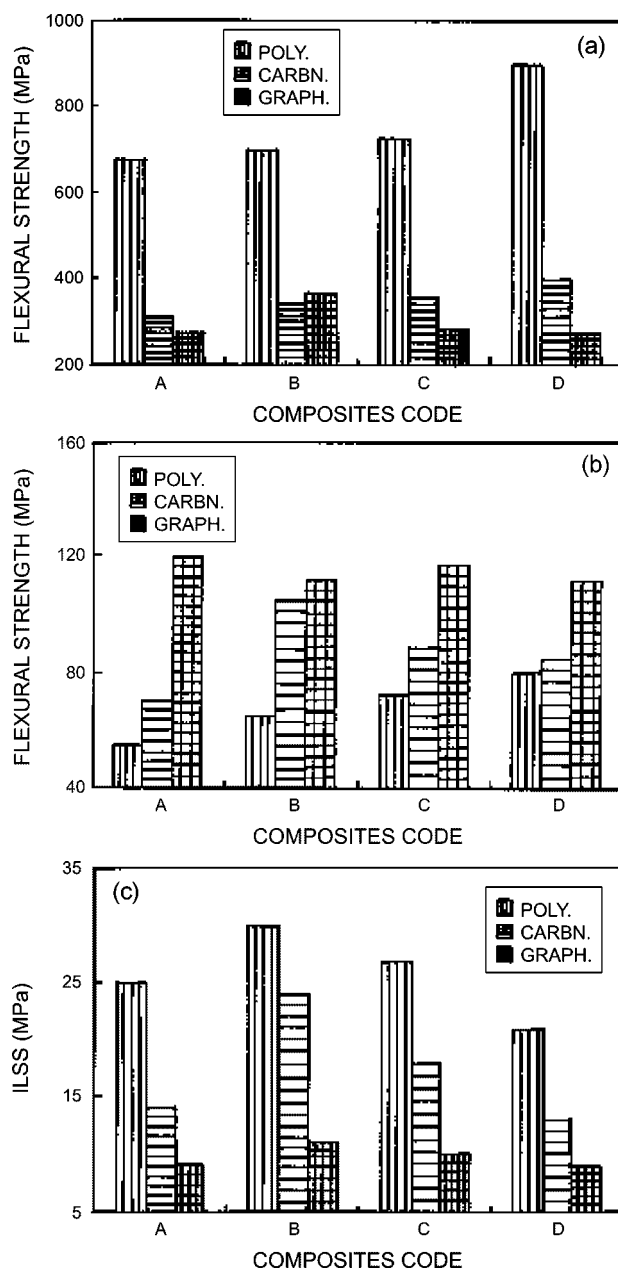


Fig. 2. (a) Flexural strength (b) Flexural modulus and (c) ILSS of composites as a function of fiber volume fraction.

capability is comparatively lower.

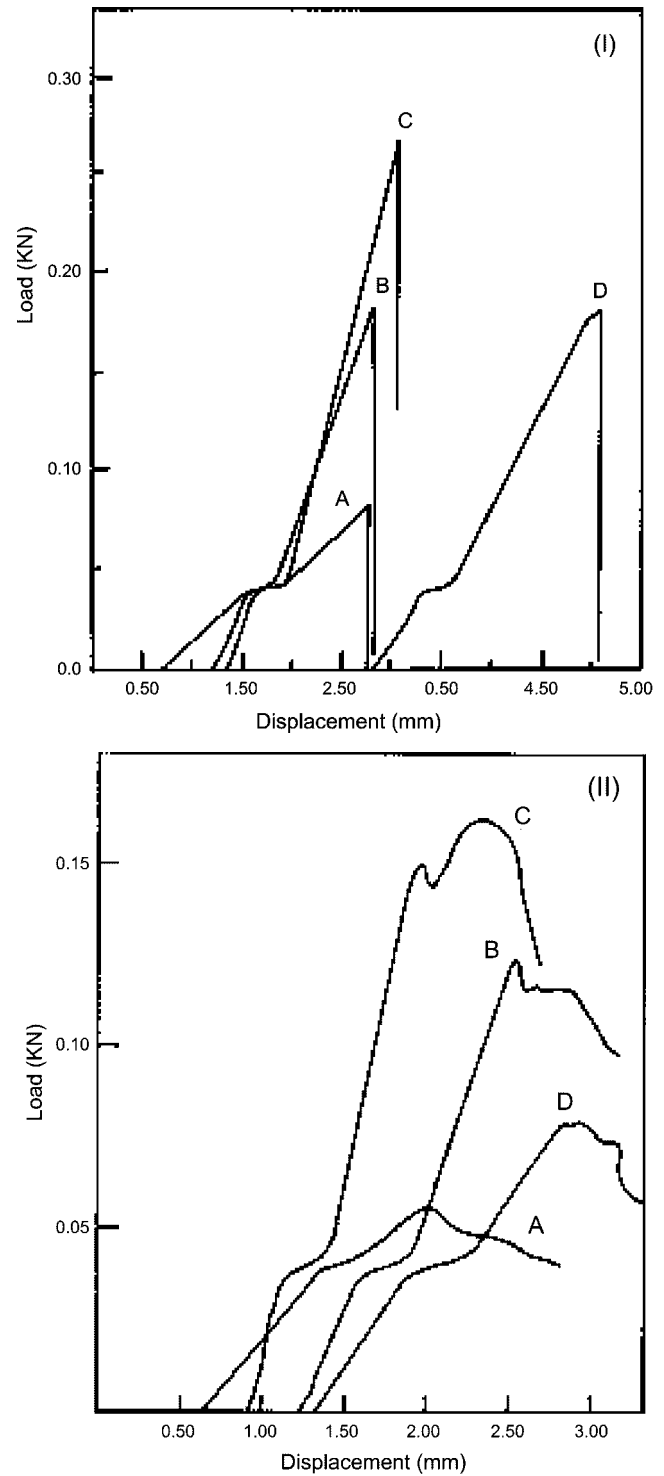
On carbonization, flexural strength of all the composites fall drastically. Due to significant shrinkage of the matrix during carbonization, the shrinkage stresses developed during pyrolysis lead to microcracking in the composites [11]. On the application of external load, even at small stress levels, crack tips developed during pyrolysis initiate cracks which propagate continuously through fibers, without any deviation and damages the fiber structure. As a result drastic drop in the mechanical properties of carbon-carbon composites is observed in all the cases. However, the relative flexural strength of carbonized composites increases with increase in the Fv though it is still short of theoretically expected value. This is normally the case with brittle materials where rule of mixture is not followed strictly. The flexural strength goes up from 300 MPa for composite A to 400 MPa for composite D. It is found that upon graphitisation, flexural strength of the composites decreases as compared to that of carbonized samples except for the composite B.

The flexural modulus of polymer composite increases with increase in the Fv as shown in figure 2b. In polymer composites, contribution of matrix is negligible because of the fiber modulus is always much greater than that of matrix modulus. Flexural modulus on the other hand shows entirely different behaviour than the flexural strength with increasing Fv in carbonized composites. The flexural modulus is maximum in composite B where Fv is 53% and with further increase of the Fv the flexural modulus goes down. Higher modulus in case of composite B is not only due to the fiber modulus but also the carbon derived from phenolic resin matrix which also contributes to the modulus of composites. In composite B the contribution of fiber and matrix at carbonized stage is nearly same, therefore the interface developed in these composites is mainly between fiber and the matrix. Due to the strong fiber-matrix interactions, interface does not allow carbon matrix to fail at higher strain (figure 3). On graphitisation of these composites, flexural modulus increases in all the composites because of stress graphitisation of matrix and fiber surface also.

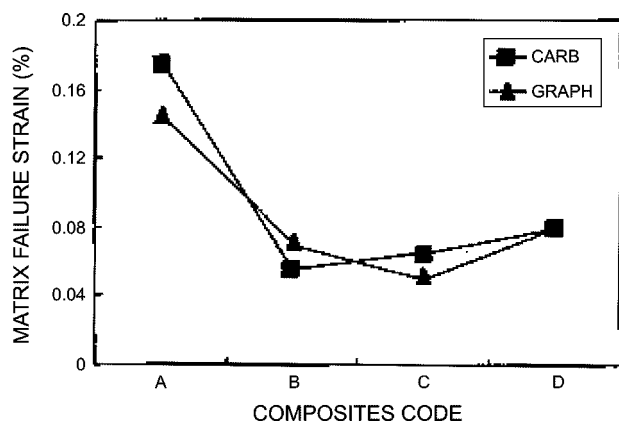
Figure 2c shows the interlaminar shear strength of composites. As expected, ILSS is maximum in composite B as compared to composites A, C and D in polymer stage. The higher value of ILSS in composite B, establishes the presence of strong fiber-matrix interactions as compared to composites A, C and D respectively. The behaviour of interlaminar shear strength of the composites at polymer stage is similar as observed for their carbonized counterparts. This clearly indicates that in composite B, strongest fiber-matrix interactions are established at polymer stage which persist after carbonization. After graphitization, ILSS of the composites decreases but is still higher comparatively in composite B. The study shows that in all the composites, fiber-matrix interactions established are strong but magnitude is different. During graphitisation, the fiber-matrix

interface gets modified by weakening of bonds and as a result ILSS values are lowered.

### 3.2. Effect of fiber volume content on matrix failure strain



**Fig. 3a.** Load-displacement curve of (I) carbonized and (II) graphitised composites



**Fig. 3b.** Change in matrix failure strain in carbonized and graphitised composites as a function of fiber volume fraction.

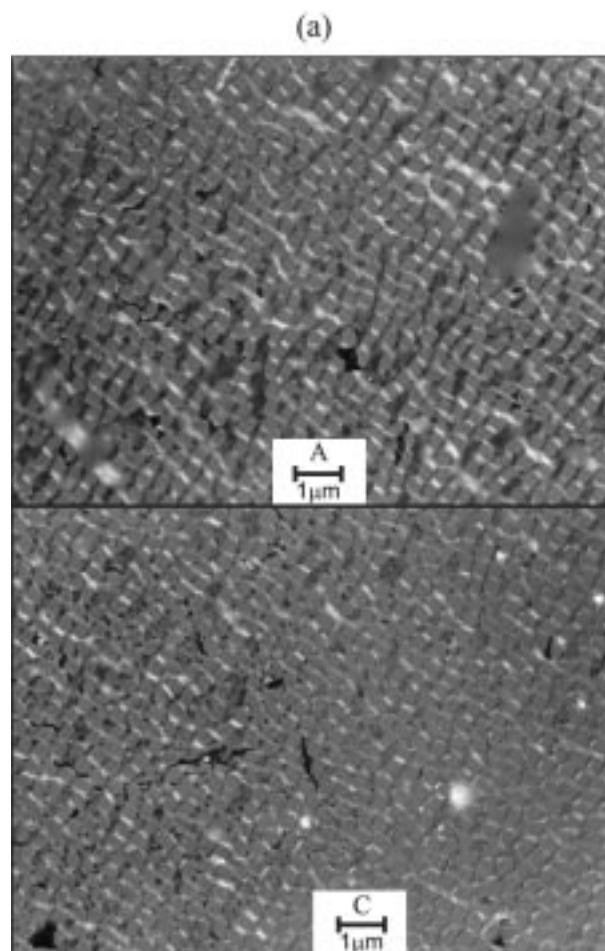
Figure 3a (I and II) shows the load-displacement curve of carbonized and graphitised composites obtained on Instron machine. It is observed that, in all the composites matrix failure load is nearly same but at the same load matrix failure displacement is different. In all the cases, the composites exhibit brittle fracture leading to catastrophic failure (figure 3a I). The matrix failure strain is maximum in composite A and minimum in composites B at carbonized stage while after graphitisation, matrix failure strain is maximum in composite A and minimum in composite C (figure 3b). This could be due to different nature of fiber-matrix interactions within samples. After graphitisation, all the composites show mixed mode of failure with initial matrix carbon microcracking and as a result composites fracture in shear mode (figure 3a II). During graphitisation of the composites, the residual stresses at the fiber-matrix interface generated during carbonization get relaxed in process of matrix graphitisation and fiber-matrix bonding gets modified in all the composites resulting into crack branching at the fiber-matrix interface [12]. As a result composites do not show catastrophic failure.

Figure 3b shows the change in matrix failure strain with Fv in carbonized and graphitised composites. The matrix failure strain is maximum in case of composites A and minimum in case of composite B. The difference in matrix failure strain and stress is due to different type of matrix microstructure and interface existing in composites A, B, C and D respectively. It is well known that the matrix failure strain in composites decreases due to the shrinkage of matrix and fiber-matrix interactions during processing. If we see the volume shrinkage during carbonization, maximum shrinkage is seen in case of composite A and minimum in case of composite D, but matrix failure strain is maximum in composite A and minimum in composite B due to different matrix structure present in these composites. This observation is also confirmed from the results of ILSS. After graphitisation, strain to failure of carbon derived from matrix however

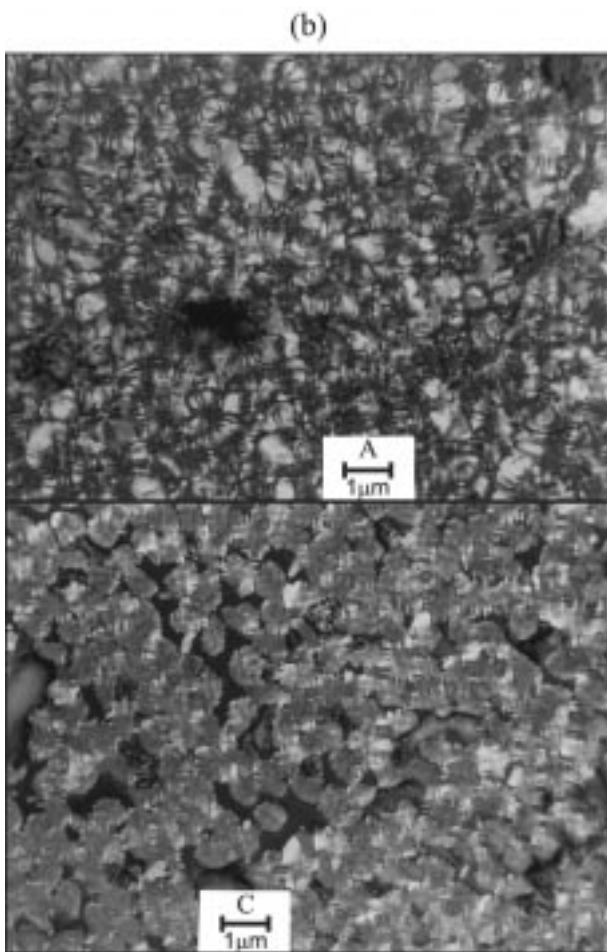
shows different trend. In graphitised composites maximum matrix failure strain is shown by composites A while it is minimum in case of composite C. Surprisingly, matrix failure strain is same in both carbonized and graphitised stage in composites D.

### 3.3. Change in microstructure of the matrix with fiber volume

Figures 4a and b show the optical micrographs of the composites A and C. In the carbonized composites anisotropic regions are observed at the fiber-matrix interface due to stress accumulation which is caused by the large volume shrinkage during carbonization (Figure 4a). Although the relative shrinkage in the composites is different as shown in figure 1, there is no noticeable difference in the anisotropic region at the fiber-matrix interface as observed in the respective optical micrographs of the two composites. However, distribution of fibers in the matrix is different in all the composites. Whereas in composite A, the fibers are not closely packed, the packing is more compact in composite C with



**Fig. 4.** Optical micrographs of (a) carbonized and (b) graphitised composites.

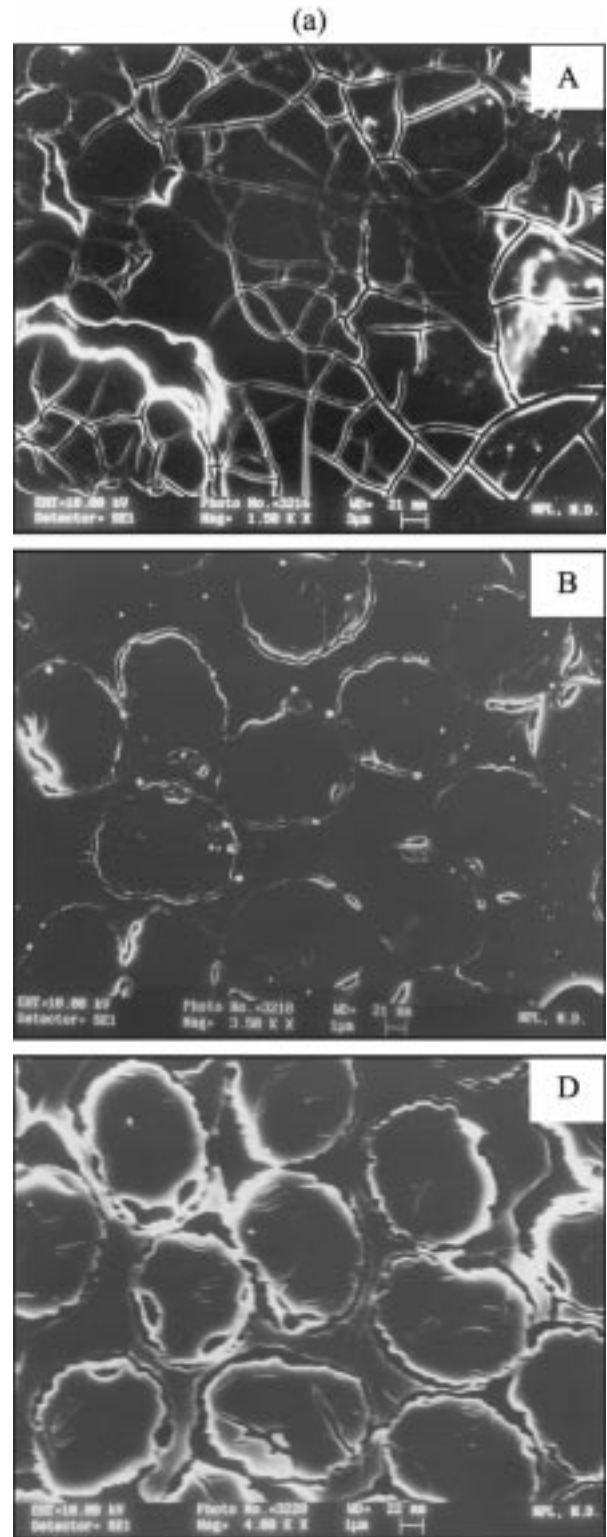


**Fig. 4.** Continued.

well defined interface between fibers and matrix.

Figure 4b shows the optical micrographs of graphitised composites A and C. A remarkable change is observed after graphitisation in all the composites. The anisotropic regions observed at the fiber-matrix interface converts into bulk matrix. A laminar type structure with strong extinction lines or well defined columnar type structure is observed at fiber-matrix interface suggesting a strong fiber-matrix interactions. In case of composite A, due to large volume shrinkage, carbon fibers loses their identity and only small core of the fiber is distinguishable from the carbon matrix and strong extinction lines between fiber and matrix are visible. With increasing Fv, both fiber and the matrix are quite easily distinguishable. In composites C, core of the fiber and fiber surface with extinction lines is clearly visible.

Figure 5 (a and b) shows the SEM micrographs of carbon-carbon composites which were etched by chromic acid. Chromic acid is known to preferentially oxidizes the sites within anisotropic carbon and appears to have relatively poor affinity towards isotropic carbon [13]. In carbonized composites minimum oxidation effect is seen at the interface in



**Fig. 5.** SEM micrographs of (a) carbonized and (b) graphitised composites after etching by chromic acid.

composites B where the fiber and matrix contribution is nearly same. However, in case of composite D, the cross

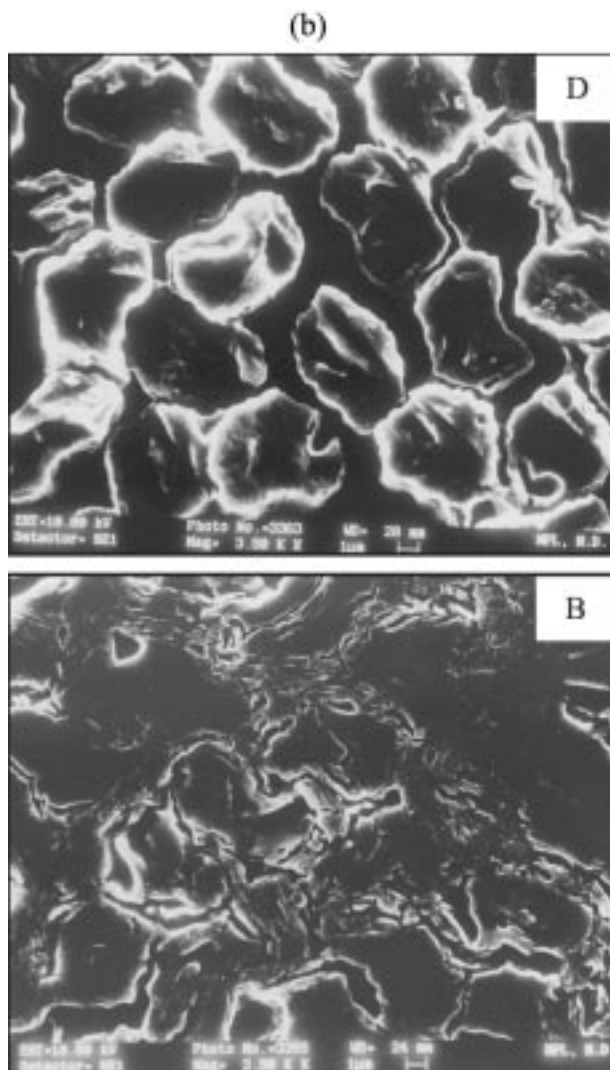


Fig. 5. Continued.

section of the fibers is also oxidized, showing voids between fibers and matrix interface. The micrograph corresponding to composite A shows bulk matrix cracking which is highlighted by etching effect through the cracks edge (figure 5a). Composites with higher Fv do not show this effect. Upon graphitisation, a different type of microstructure was observed after etching by chromic acid (figure 5b). In case of composites B selective etching effect was observed and the preferential oxidation fissures were developed at the fiber-matrix interface and along basal plane orientation between fibers. In composites D, the extent of preferential oxidation at the fiber-matrix interface is more due to the modification of fiber-matrix interactions during graphitisation as a consequence of magnitude of fiber-matrix interaction decreases due to the higher value of Fv.

#### 4. Conclusions

It has been found that there does not seem to be direct relationship in the mechanical properties of composites with fiber volume content, either at carbonized or graphitized stage. It is observed that the extent of strong or weak columnar type texture at the fiber-matrix interface depends upon the volume shrinkage during processing which is a function of Fv. Oxidation of composites through chromic acid increases with increasing fiber volume content and effect is minimum for composites possessing equal volume of fibers and the matrix. Strong bonding is also reflected in the strain to failure of matrix which is minimum for composite possessing equal volume of fibers and the matrix.

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