Fiber/Matrix Interface in Carbon/Carbon Composites
— Effect of Surface Morphology of Carbon Fibers —

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Carbon/carbon composites have been made with three kinds of carbon fibers having irregular shape, bean shape and circular crosssections as reinforcements and coal tar pitch as matrix precursor with low pressure pyrolysis. The microstructure of the matrix at the fiber/matrix interface is found to be influenced by the surface morphology of the fibers. This is further found to influence the fracture behaviour and mechanical properties of the ultimate carbon/carbon composites.

KEYWORDS: Carbon fiber, Interface, Surface Morphology, C/C Composite, Mechanical properties.

1. INTRODUCTION

Interface science has key role to play in hybrid materials specially in fiber reinforced composites. Development of high performance fibers boosted the research in adhesion science. Studies have been made to develop surface treatment procedures for carbon fibers 1)-3) and on fiber/matrix interface in carbon fiber reinforced composites 4). But most of the studies have been made with aim to improve the mechanical behaviour of carbon fibers in fiber reinforced plastics. No doubt most of the carbon fiber consumption is in polymer composites, but these fibers are the sole fibers to be used for advanced high temperature composites i.e. carbon/carbon composites. Over past two decades, there has been growing interest in the area of carbon/carbon composites. This material which was initially built to withstand the flammig heat of rocket nozzles and re-entry vehicles, has reached the common man in form of biomaterials5). The unsubstituted application of carbon/carbon composites had necessitated the basic as well as applied research in this field. Like in all composites system, fiber/matrix interface will have a dominating role in carbon/carbon composites too. It will be rather more critical in these composites than in polymer composites since in former case fibers as well as matrix both are ceramics. In polymer composites good adhesive bonding is required for maximum stress transfer to the fibers to achieve the best mechanical properties of the composite3),6), whereas, in ceramic composites some form of energy absorbing interface interactions are needed for high fracture toughness7). Fiber/matrix interface in carbon/carbon composites is important from one another point of view as well since in these composites, the matrix is undergoing structural changes with heat treatment temperature and the adhesion of the matrix with the fibers influences the structural changes in the matrix as well as the microstructure of the ultimate carbon matrix8, 9). Carbon matrix is derived by different methods e.g. CVD, pyrolysis of carbon yielding materials using low pressure and high pressure pyrolysis etc. Though in all cases fiber/matrix interface will have its role to play, the present paper will be limited to carbon/carbon composites made by pyrolysis of carbon yielding materials at normal pressure.

2. FACTORS INFLUENCING THE FIBER/MATRIX INTERFACE IN CARBON/CARBON COMPOSITES

The first step in fabrication of carbon/carbon composites by liquid infiltration technique is the development of rigid composites with carbon fibers and carbon yielding polymer matrix
(thermoset resins or thermoplastic pitches). These polymer composites are then pyrolysed to give carbon/carbon composites. The fiber/matrix interface in the resulting carbon/carbon composites is to a large extent dictated by the fiber/matrix interface in parent polymer composites, which in turn are affected by
1) Orientation of graphite crystals near the fiber surface
2) Functional Groups on the carbon fiber surface produced by surface treatment of the fibers
3) Geometrical arrangement of the fibers
4) Morphology of the fiber surface.

In previous papers authors have studied the effect of first three factors on the fiber/matrix interface in carbon/carbon composites at different stages of development and the mechanical properties of these composites. It has been established that strong fiber/matrix bonding in polymer composites achieved either through the functional groups on the carbon fiber surface or through the active carbons at the surface of the fibers in high strength fibers persists during carbonisation and results in increased strength of the polymer composites but decreased strength of the carbon/carbon composites heat treated to 1000°C or so. In these composites the identity of the fiber/matrix interface is lost and the crack propagates normal to the carbon fibers resulting in catastrophic failure of the composites at low ultimate breaking load. The strong fiber/matrix interface in such composites influences the orientation of the graphitic planes of the matrix near the fiber surface too. In graphitised composites the columnar type graphitic micro-structure of the matrix is obtained with increased mechanical properties of the graphitized composites. These findings have been summarised in a diagram shown in fig. 1.

The following sections will concentrate on the effect of the surface morphology of the carbon fibers on the fiber/matrix interface and the mechanical behaviour of these composites.

3. EXPERIMENTAL

Carbon/carbon composites were made with three kinds of high modulus carbon fibers.
1. Rayon based carbon fibers having irregular surface morphology
2. PAN based carbon fibers having bean shaped surface (M40)
3. PAN based carbon fibers having circular crosssection (Besfite)

All the fibers were without any surface treatment or sizing. Composites were made by multiple impregnation/carbonization technique with normal pressure pyrolysis. Two types of coal tar pitches were used as matrix precursor. The characteristics of these pitches are compiled in table 1. Pitch I was used for making the skeleton composites while pitch II was used for impregnation purposes. Composites were heat treated to 1000°C and 2700°C. These were characterised for density and mechanical properties at intermediate densification levels as well as at the final stage.

![Diagram](image-url)
The microstructure of the matrix around carbon fibers was studied with polarised optical microscope and scanning Electron Microscope (SEM).

4. RESULTS AND DISCUSSION

4.1. Density of carbon/carbon composites

The density of carbon/carbon composites depends on the density distribution made by the reinforcing carbon fibers and the packing of the carbon matrix within and around the carbon fiber bundles. In case of fabrication of composites by low pressure pyrolysis, latter depends on the fiber/matrix adhesion. Figure 2 shows the density of carbon/carbon composites at different stages of densification made with different carbon fibers. As seen in the figure, composites made with rayon based carbon fibers, though initially have very low density of the carbon/carbon skeleton, exhibit more increase in density during densification than those made with M40 or Besfite fibers. This is because of the reason that the fibers having irregular surface lead to better fiber/matrix adhesion than those having regular bean shape or circular cross-sections. Initial low density of the composites is due to low density of the fibers itself. Moreover, in composites made with rayon based fibers, the impregnated pitch gets blocked within the space bounded by the surface of the fibers resulting in high yield, whereas in case of composites made with PAN based carbon fibers, a part of the impregnated pitch melts out of the large gaps in between the fibers during carbonisation. However, after certain impregnation cycles, the entrants to the space in between the fibers gets narrowed down and further impregnation of the composites becomes difficult in former composites. That is why former composites achieve a plateau in the densification curves at comparatively lower impregnation cycles.

4.2. Microstructure of carbon/carbon composites

In carbon/carbon composites made with coal tar pitch as matrix precursor, the graphitic structure forms at low temperature (450–600°C) while the pyrolysing pitch is still in the liquid crystalline phase (mesophase). The extent and orientation of the crystallographically aligned regions depend on the processing conditions such as pressure, rate of heating etc. and the carbon fiber surface. Figure 3 shows the optical micrographs under polarised light and fig. 4 shows the SEM micrographs of the crosssections of various carbon/carbon composites. As seen in figs 3 and 4, the carbon matrix surrounds the filaments with graphitic layers laid circumferentially to the filament surfaces. The structure of the matrix becomes more distinct after graphitization of the composites. The carbon matrix in the composites can be classified into two categories: (i) carbon matrix just near the fiber surface called sheath and (ii) bulk carbon in between the filaments called bulk matrix. The structure of the sheath matrix is governed by the adhesion of the pitch with the fiber surface. Therefore the structure of these two phases varies to some extent depending on the fiber surface. The variation increases as the surface of the fibers deviates from regular to irregular ones. As seen in fig. 4c, the microstructure of the sheath in composites made with rayon based fabric is quite different than the bulk matrix. In sheath the graphitic layers are sharply kinked as per the contour of the fibers while the bulk matrix consists of curved
Fig. 3 Optical micrographs of various Carbon/Carbon Composites under polarised light. (a) and (b) Composites made with Rayon based fibers (c) and (d) Composites made with M40 fibers and (e) and (f) Composites made with circular fibers.

Fig. 4 SEM micrographs of various Carbon/Carbon Composites. (a), (b) and (c) Composites made with Rayon based fibers (d), (e) and (f) Composites made with Bean shape fibers and (g), (h) and (i) Composites made with circular fibers.
graphitic layers. In composites made with M40 fibers, the sheath consists of graphitic layers having bent at the polar edges while that in composites made with Besfite fibers is made of regular curved planes. The microstructure of the bulk matrix in latter two composites is almost similar. The observations made from the optical and SEM micrographs of these composites are drawn schematically in fig. 5.

**Fig. 5** Schematic representation of matrix microstructure in Carbon/Carbon Composites made with (a) Rayon based fibers (b) PAN based bean shaped fibers and (c) PAN based circular carbon fibers.

### 4.3. Mechanical Properties of carbon/carbon composites

The microstructure as well as adhesion of the matrix in carbon/carbon composites will affect the crack propagation and hence the mechanical properties of the composites.

Figure 6 shows the stress/strain behaviour of various carbon/carbon composites made with three types of carbon fibers. The mechanical properties of the carbon/carbon composites under study are compiled in table 2. Table also includes the fiber translation factor calculated by dividing the experimental strength of the composites with theoretically expected value assuming that all the reinforced fibers contribute towards the strength of the composites. The factor is also indicative of the failure mechanism in the composites. As evident from the table, carbon composites made with circular fibers exhibit highest fiber translation factor. Composites made with M40 bean shaped fibers also exhibit very high translation of fiber properties. However, on graphitization, the flexural strength of these composites drops to about 50% or less. The interlaminar shear strength also drops appreciably. Composites made with rayon based carbon fibers exhibit very low strength at even carbonized level. However, on graphitization, these composites show lesser decrease in flexural strength as compared to the former composites. Similar trends are observed for compressive strength of the composites in directions parallel as well as perpendicular to the fibers.

In case of carbonized composites made with rayon based fibers, the low absolute value of the flexural strength is due to the low strength of the fibers themselves. The translation factor for these composites is also low. This is attributed to their failure mechanism. The sharp kinks in the matrix around the fiber corners are the points of heavy stress concentrations. The microcrack initiation takes place at these points. Good fiber/matrix adhesion favours the cracks to propagate in direction perpendicular to the fibers resulting in tensile type failure (fig. 6a) at low load. In graphitized composites, the matrix exhibits columnar type microstructure. Strength of the graphitized composites is lower than that of the carbonized composites due to inplane shearing of the matrix. Crack arresting slits are also observed near the sheath. Under combination of these two factors, graphitized composites fail in tensile cum shear mode (fig. 6b) with fiber pullout.

As discussed above, in case of carbonized composites made with M40 and Besfite fibers, the sharp kinks are not present. Therefore the amount of points of stress concentrations decrease from composites made with M40 fibers to Besfite fibers. Therefore, these composites fail in tensile cum shear mode (figs. 6c and 6e) and exhibit higher translation of fiber properties. In graphitized composites, the matrix around these fibers exhibit lamellar type microstructure.

Table 2 Mechanical properties of various Carbon/Carbon composites.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Carbon Fiber Type</th>
<th>Composite Type</th>
<th>Fibre Volume (%)</th>
<th>Flexural Strength (N/m²)</th>
<th>Fibre Translation (%)</th>
<th>ILSS (MN/m²)</th>
<th>Compressive Strength (MN/m²)</th>
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<tr>
<td></td>
<td></td>
<td>Carbonized</td>
<td>34.0</td>
<td>280</td>
<td>60</td>
<td>22.9</td>
<td>85</td>
</tr>
<tr>
<td>1. Rayon</td>
<td>Graphitized</td>
<td>35.4</td>
<td>210</td>
<td>43</td>
<td>13.3</td>
<td>67</td>
<td>17</td>
</tr>
<tr>
<td>2. M40 Carbonized</td>
<td>37.0</td>
<td>820</td>
<td>110</td>
<td>27.3</td>
<td>102</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>3. Besfite</td>
<td>Graphitized</td>
<td>38.6</td>
<td>415</td>
<td>54</td>
<td>15.9</td>
<td>62</td>
<td>18</td>
</tr>
<tr>
<td>3. Besfite Graphitized</td>
<td>39.0</td>
<td>945</td>
<td>120</td>
<td>20.4</td>
<td>108</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>4. Besfite Graphitized</td>
<td>40.3</td>
<td>386</td>
<td>47</td>
<td>12.7</td>
<td>70</td>
<td>20</td>
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Fig. 6 Stress/Strain plots of various Carbon/Carbon Composites.

(a) Carbon Composites made with rayon based fibers
(b) Graphitized Composites made with rayon based fibers
(c) Carbon Composites made with M40 fibers
(d) Graphitized Composites made with M40 fibers
(e) Carbon Composites made with Besfite fibers
(f) Graphitized Composites made with Besfite fibers

with long range of ordering being more for Besfite based composites than M40 based composites. Failure in these composites takes place via shearing of these graphite planes. Therefore these composites on graphitization exhibit mixed mode fracture with predominant shear component in their failure behaviour. (figs. 6d and 6f) and decreased flexural as well as interlaminar shear strength.

These studies demonstrate that the matrix microstructure and hence mechanical properties of the carbon/carbon composites are influenced by the fiber/matrix adhesion in the composites which in turn are controlled by the surface morphology of the reinforcing fibers.

5. CONCLUSIONS
1. In Carbon/carbon composites made with pitch as matrix precursor and low pressure pyrolysis conditions, the carbon matrix consists of two phases (a) Sheath matrix just surrounding the reinforcing fibers and (b) bulk matrix inbetween the filaments.
2. The microstructure of the sheath is controlled by the fiber/matrix adhesion which is influenced by the surface morphology of the fibers.
3. Composites made with irregular shape fibers contain stress concentration points in the sheath. These are responsible for ultimate low strength of these composites.
4. Composites made with circular fibers exhibit highest translation of fiber properties in carbon composites. However, due to lamellar type microstructure of the matrix surrounding circular fibers, the strength of the composites drops down appreciably on graphitization.

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