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Structure and properties of unidirectionally reinforced PAN-resin based carbon–carbon composites

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A study has been made of the structure and properties of in-house fabricated, unidirectionally reinforced polyacrylonitrile (PAN) fibre-phenolic plus furfuryl alcohol matrix carbon/carbon (C/C) composites comprising surface-treated (ST) as well as non-surface-treated (NST) carbon fibres. The composites are subjected to a final heat treatment of 1000 or 2000 °C. Mechanical properties of the composites were found to be sensitive to the process parameters (particularly the final heat-treatment temperature) as well as fibre surface condition (ST or NST). For the composites comprising ST fibres, flexural strength and modulus of those heat treated at 2000 °C were higher than those treated at 1000 °C. For the composites comprising NST fibres, the results were the opposite. At the carbon fibre-reinforced plastic (CFRP) stage, strength and modulus of ST fibre composites were higher than those of NST composites by 400% and 100%, respectively, due to the stronger fibre–resin bonding in the ST composite. After the first carbonization treatment, the ST composites always possessed higher strength and modulus values than NST composites, whether the final heat treatment temperature was 1000 or 2000 °C. In the ST series of composites, the improvement in strength and modulus became significant from the third densification cycle, while in the NST series, both second and third cycles were effective. Microstructure, particularly fibre–matrix interface morphology, has been studied using polarized light microscopy, scanning electron microscopy, and transmission electron microscopy, to help interpret the process–structure–property relationships.

1. Introduction

It is well known that mechanical properties of carbon/carbon (C/C) composites are sensitive to the bonding nature between carbon fibres and carbon matrix. Some relationships between surface condition of fibres and mechanical properties of C/C composites have been pointed out by several researchers [1–9]. For example, Fitzer *et al.* [5, 6] have reported that a strong bond between a surface-treated (ST) fibre and matrix precursor resin was formed by a chemical reaction. Such a strong bond could be maintained even after being carbonized at 1000 °C, resulting in a brittle C/C composite with poor mechanical properties. In contrast, for a non-surface-treated (NST) fibre, a weak bond was formed due to a lack of chemically reactive surface functional groups on the fibre surface. Instead of a catastrophic failure which occurred in ST fibre composites, such NST fibre composites showed better mechanical properties with a moderate fibre pull-out at failure [5, 6].

Manocha *et al.* [7] have recently reported the influence of composite heat treatment on the relationship between fibre surface treatment condition and the composite strength. Similar to that observed by Fitzer *et al.*, the carbonized (1000 °C) C/C composites comprising ST fibres were found to fail in a brittle manner and possess lower strengths, compared to the carbonized composites comprising NST fibres. However, the graphitized (3000 °C) composites comprising ST fibres, exhibited higher strengths, compared to the graphitized composites comprising NST fibres, presumably due to a weaker fibre–matrix bond caused by the graphitization treatment.

Although the relationships between fibre surface condition, process parameters and composite properties have been studied by Fitzer and co-workers,

TABLE I Characteristics of carbon fibres

Fibre type	Surface treatment	Sizing agent	Density ($g\,cm^{-3}$)	Tensile strength (MPa)	Tensile modulus (GPa)	Fracture strain (%)
Torayca M40	Yes	Epoxy resin	1.81	2746	392	0.6
Besfight HM40	No	No	1.83	2550	392	0.7

Manocha and co-workers, and others, the existing data are still very limited, considering the existence of a wide range in choices of fibre, matrix, and process technique and variables for fabrication of C/C composites. The present study attempted to provide more fundamental information in this area, using two types of composites (ST and NST fibre composites) fabricated in-house at Kawasaki Steel Corporation, Japan. Some detailed microstructural information, particularly the fibre–matrix interface and local basal plane alignment which was not obtained previously, is provided by transmission electron microscopic study in this report.

2. Experimental procedure

ST PAN-based Torayca M40 carbon fibre (Toray Co.), and NST PAN-based Besfight HM40 carbon fibre, (Toho Rayon Co.), were used as reinforcement in this study. As shown in Table I, density, strength, and modulus of these two fibres are similar, although their cross-sectional shapes are quite different. Besfight HM40 fibre has a circular shape, while Torayca M40 fibre has an irregular shape. As shown in Table II, a commercial resole-type phenolic resin (Dainippon Ink and Chemicals Co.), was used as the starting matrix precursor, and a furfuryl alcohol resin (Hitachi Chemicals Inc.), was used as the densification precursor.

TABLE II Characteristics of resins

	Phenolic resin	Furfuryl alcohol resin
Non-volatile content (%)	60 ± 2	46–54
Viscosity (cP)	140–300	850–1430
Solvent	Ethanol	–

Unidirectional C/C composites were fabricated in-house according to the flow chart shown in Fig. 1. Individual prepregs were first made by uniformly mixing fibres and the phenolic resin of a controlled composition by a drum winding machine. The prepregs were then stacked, moulded, and cured in an autoclave to form a CFRP, which was subjected to subsequent carbonization and further treatments. The CFRPs were carbonized to 1000 °C at a heating rate of $10\,°C\,h^{-1}$ under a pressure of 9 atm nitrogen. The carbonized samples were densified by liquid furfuryl alcohol resin due to its lower viscosity than for phenolic resin. The carbonization–densification cycle was repeated up to three times. Some of the carbonized composites were subjected to a final heat treatment of 2000 °C. Tables III and IV list, respectively, some properties measured at different stages in the process of ST and NST fibre composites.

TABLE III Process parameters and properties of C/C composites containing surface-treated carbon fibres

Specimen	Condition	Final HTT (°C)	V_f (%)	Density ($g\,cm^{-3}$)	Porosity (%)	Flexural strength (MPa)	Flexural modulus (GPa)
1	CFRP	–	57.9	1.47	1.1	1324.9	195.2
2	First carbonized	1000	64.1	1.51	6.0	361.9	183.4
3	First carbonized	2000	65.1	1.58	7.0	385.4	169.7
4	Second densified	1000	65.5	1.60	2.1	356.0	187.3
5	Second densified	2000	64.4	1.58	3.5	364.8	109.8
6	Third densified	1000	64.9	1.53	5.6	203.0	152.0
7	Third densified	2000	61.5	1.56	10.6	541.3	208.9

TABLE IV Process parameters and properties of C/C composites containing non-surface-treated carbon fibres

Specimen	Condition	Final HTT (°C)	V_f (%)	Density ($g\,cm^{-3}$)	Porosity (%)	Flexural strength (MPa)	Flexural modulus (GPa)
1	CFRP	–	60.2	1.43	5.6	304.5	78.5
2	First carbonized	1000	–	–	–	–	–
3	First carbonized	2000	–	–	–	–	–
4	Second densified	1000	53.5	1.43	5.6	233.4	104.9
5	Second densified	2000	47.0	1.42	5.0	104.9	24.5
6	Third densified	1000	53.4	1.56	3.7	342.3	131.4
7	Third densified	2000	53.4	1.56	11.4	193.2	124.5

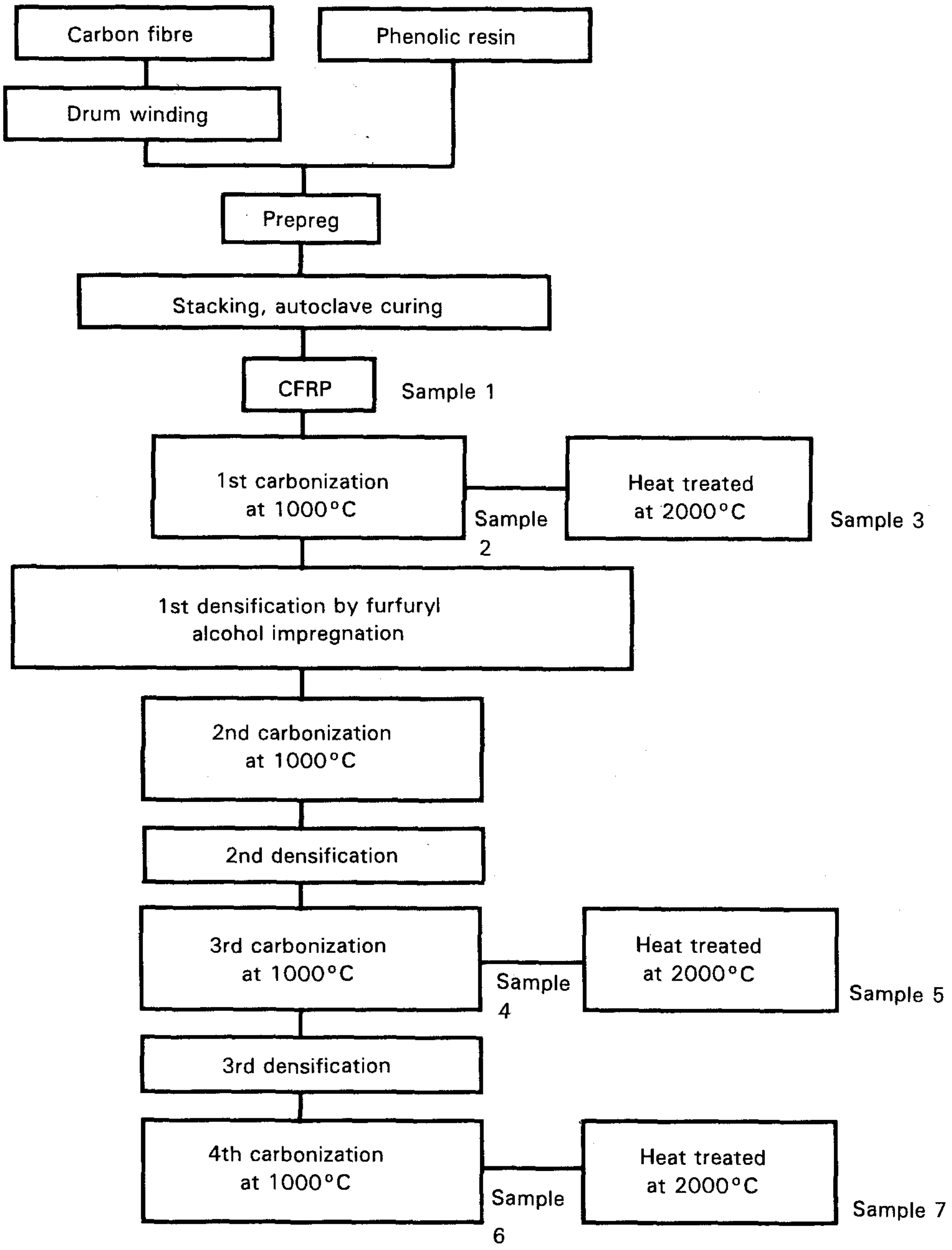

Figure 1 Process of carbon/carbon composite production used in this study. The process stages where samples were taken for characterization are noted.

The flexural strength of the composites was measured by a three-point bending test, and the Young's modulus was calculated from the linear regions in stress–strain diagrams. The dimensions of the specimens were 10 mm wide, 2 mm thick and 50 mm long. The span of the bending test was 40 mm and the crosshead speed was 0.2 mm min^{-1}. The porosity was measured using an image analyser which was connected to a Nikon Microphoto optical microscope and an IBM personal computer. It should be kept in mind that, in using the image analysis technique to measure porosity, the numerous submicrometre-sized pores/cracks which were shown by TEM could not be resolved. Such porosity data could only be considered as relative ones.

The overall microstructural feature of the composites was characterized using the same Nikon Microphoto polarized light microscope at magnification in a range × 100 to × 800. Fracture surfaces of the tested composites were examined by SEM, and detailed interfacial morphology between carbon fibres and carbon matrix was examined by TEM. The C/C thin foils for TEM were prepared by a technique involving mechanical dimpling followed by argon atom milling [10].

3. Results

3.1. Mechanical properties

Flexural modulus and strength data of the composites at different fabrication stages using ST and NST fibres are given in Tables III and IV, respectively, and plotted in Figs 2 and 3. The first impression in these data was that, in the CFRP stage (Sample 1), the ST fibre composites had much higher flexural modulus (more than twice) and strength (more than four times) than

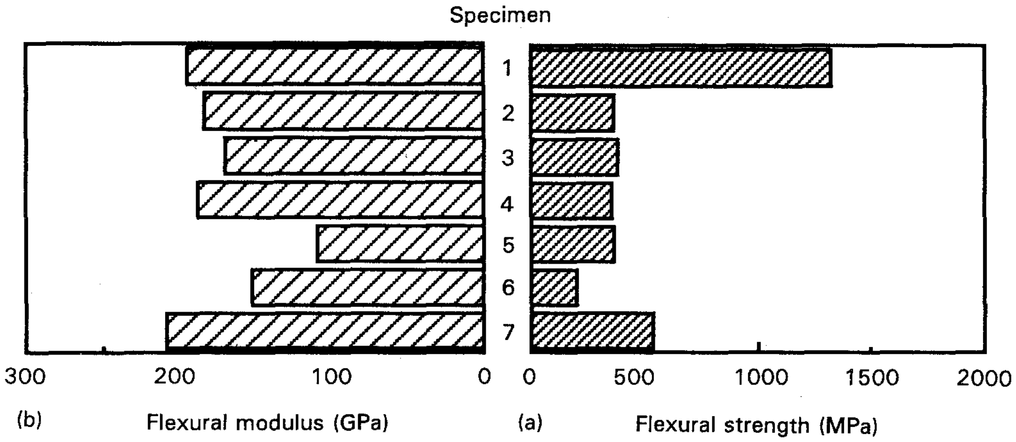

Figure 2 (a) Flexural strength and (b) modulus of surface-treated fibre composites at different process stages.

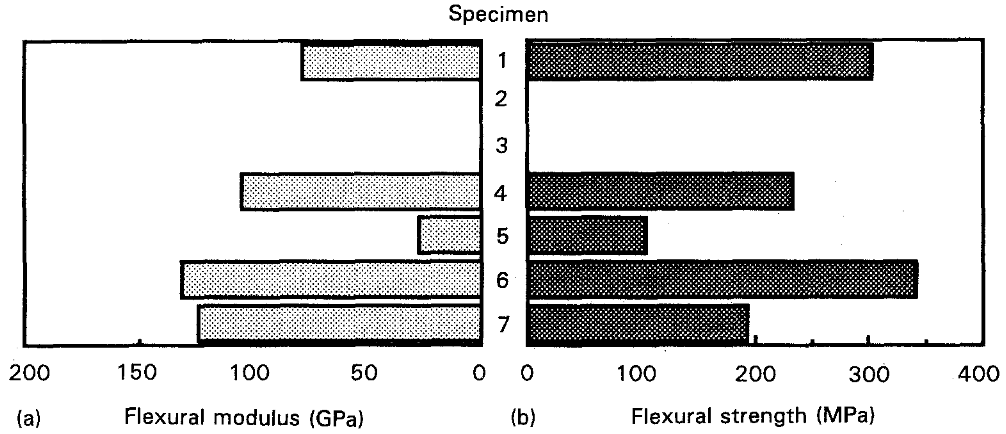

Figure 3 (a) Flexural strength and (b) modulus of non-surface treated fibre composites at different process stages.

the NST fibre composites, although both fibres had similar strength and modulus values (Table I). Obviously the surface treatment applied to the M40 fibres had made the difference by enhancing the fibre–resin interfacial bonding, as is widely known in the plastics industry. The large porosity difference between the two composites also indirectly confirmed this (Tables III and IV).

After the first carbonization treatment (1000 °C), the flexural strength of the ST composite (Sample 2) dropped drastically to about 27% of its CFRP precursor, which is not uncommon for C/C composites. Microscopic study showed that large pores/cracks are developed at this stage. The flexural modulus, which is generally not as sensitive to porosity as for strength, however, was not much affected. The following two densification cycles did not improve either strength or modulus of the ST composite. The third densification followed by carbonization and a final heat treatment at 2000 °C (Sample 7), however, significantly improved the strength by about 48%, compared with the second densified sample followed by the same heat treatment (Sample 5). Another thing to be noted is that the flexural strength of the composite heat treated at 2000 °C was much higher than those treated at 1000 °C. In the ST series, Composite 7, which had been densified three times and heat treated at 2000°C, showed the highest strength, while the strength of Composite 6, densified three times and treated at 1000 °C, showed the lowest. The stress–strain curves showed that the composite (Sample 6) failed in a much more brittle manner than that of Composite 7. Like flexural strength, flexural modulus of the high-temperature (2000 °C) treated composite (Sample 7) was higher than that of the low-temperature (1000 °C) treated composite (Sample 6). The data for the first-carbonized composites (Samples 2 and 3) and the second densified composites (Samples 4 and 5), however, showed the opposite trend, although not drastically. This indicates that mechanical properties of the composites are not determined simply by a final heat-treatment temperature. The microstructural variation as well as micro- and macro-porosity development which were found different in each process step, should be carefully taken into account. Also shown in Fig. 2, the flexural strengths and moduli of both (1000 and 2000° C) composites did not vary significantly with their density/porosity values.

Compared to the ST composites, the NST composites almost always exhibited lower modulus and strength, whether the final HTT was 1000 or 2000 °C. The second and third densification cycles were effective in improving the composite strength and modulus (the first densified samples were not tested). In the NST series of composites, the flexural strength and modulus of the carbonized (1000 °C) composites were consistently higher than those heat treated at 2000 °C. As an example, the flexural strength of Composite 6 was higher by 76% than that of Composite 7. The modulus of Composite 6 was also higher, although not significant. Obviously for the NST composites, the flexural strength and modulus of the carbonized composites were degraded by the final high-temperature treatment at 2000 °C. Their stress–strain curves, however, showed that both (1000 and 2000 °C) composites failed in a non-brittle manner. Again, their flexural strengths and moduli did not vary directly according to their density or porosity data.

3.2. Microstructural characterization

Fibre surface condition and composite heat treatment were found to have a great influence on the microstructure of the composites. Optical microscopy showed that, in all our composites, except CFRPs, an anisotropic carbon structure was more or less developed in the matrix adjacent to carbon fibres as well as to internal cracks. The degree of this anisotropy was clearly higher in such composites heat treated at 2000 °C than those heat treated at 1000 °C, as shown in the example of Fig. 4.

Scanning electron micrographs of fracture surfaces showed that, for ST series of composites, the fracture surface of the low-temperature (1000 °C)-treated composites was quite flat, whereas significant fibre pull-out was observed in the high-temperature (2000 °C) treated composites. An example was given in Fig. 5. For the NST series of composites, the fracture surface of the low-temperature treated composites was generally flat, although fibre pull-out had been observed in a few local regions (marked by arrows in Fig. 6a). The fracture surface of high-temperature treated NST composites depicted an extensive pull-out of fibres (Fig. 6b). Examination of these two (1000 and

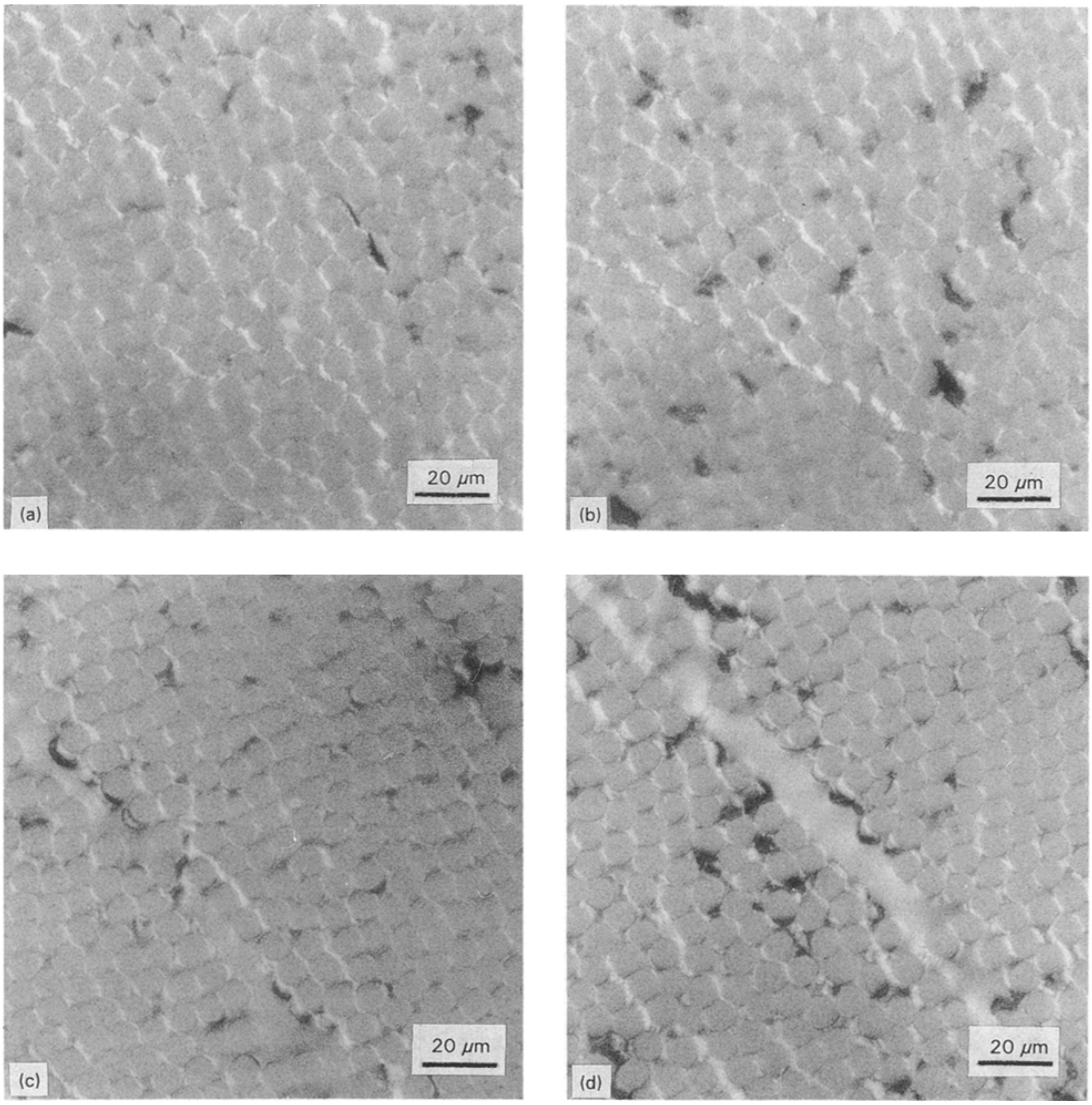

Figure 4 Optical micrographs of composites. (a) 1000 °C, surface-treated fibre, (b) 2000 °C, surface-treated fibre, (c) 1000 °C, non-surface-treated fibre and (d) 2000 °C, non-surface-treated fibre.

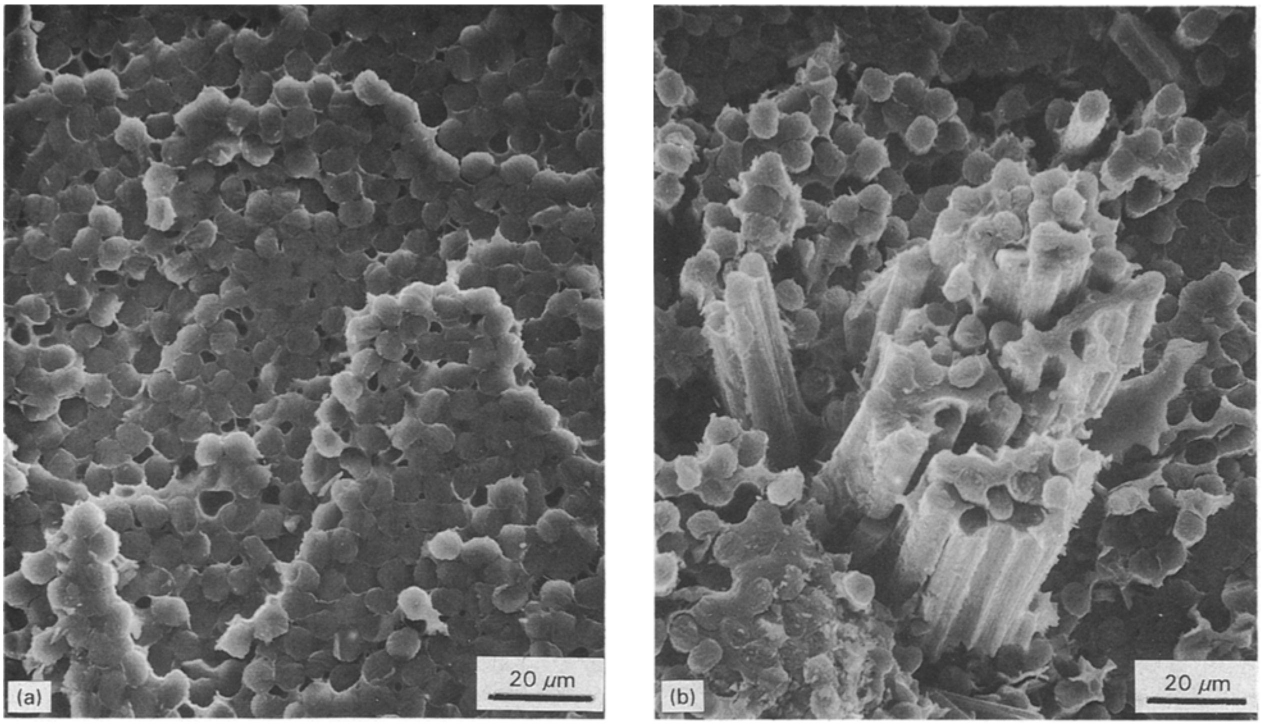

Figure 5 Scanning electron micrographs showing fracture surfaces of composites comprising surface-treated carbon fibres heat treated at (a) 1000 °C and (b) 2000 °C.

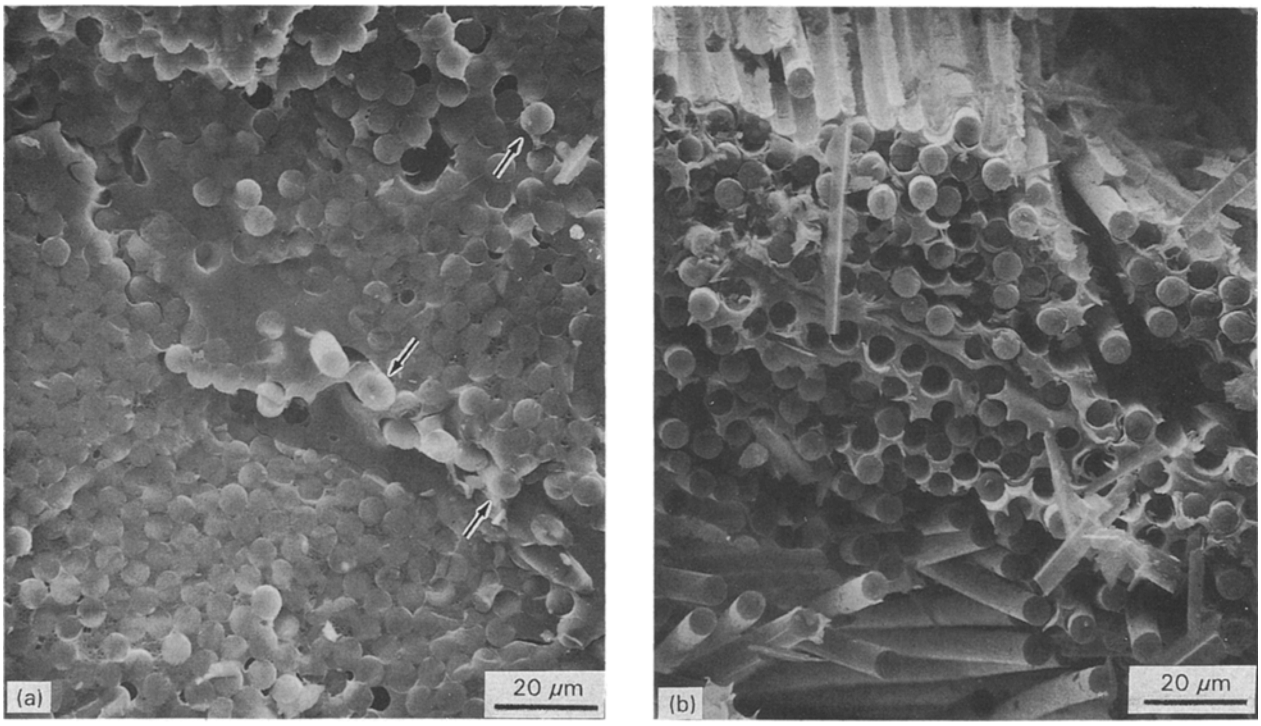

Figure 6 Scanning electron micrographs showing fracture surfaces of composites comprising untreated carbon fibres heat treated at (a) 1000 °C and (b) 2000 °C.

2000 °C) composites at higher magnification (Fig. 7) revealed that, in both composites, large crescent-shaped pores existed around fibres, which had possibly formed due to matrix shrinking away from the fibre surface during carbonization. The matrix structure of the high-temperature (2000 °C) treated composite was preferentially orientated, as evinced by the fringes surrounding fibres (Fig. 7b). Such fringes were not observed in the low-temperature (1000 °C) treated composite (Fig. 7a).

TEM examination showed that, in ST series, the fibres and the matrix in the carbonized (1000 °C) composites were well bonded, in spite of the few small pores existing along the fibre–matrix interface (Fig. 8a). In the higher temperature (2000 °C) treated composite, the fibre–matrix interface appeared much

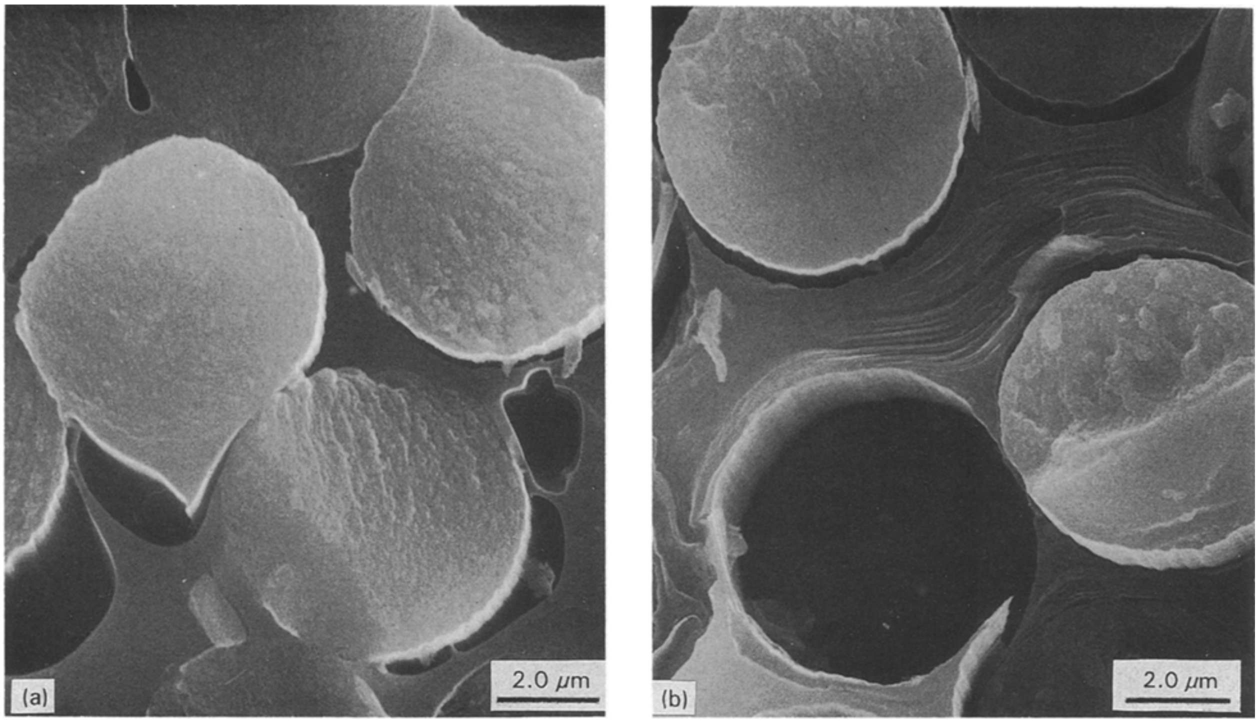

Figure 7 Scanning electron micrographs showing fracture surfaces of composites comprising untreated carbon fibres heat treated at (a) 1000 °C and (b) 2000 °C.

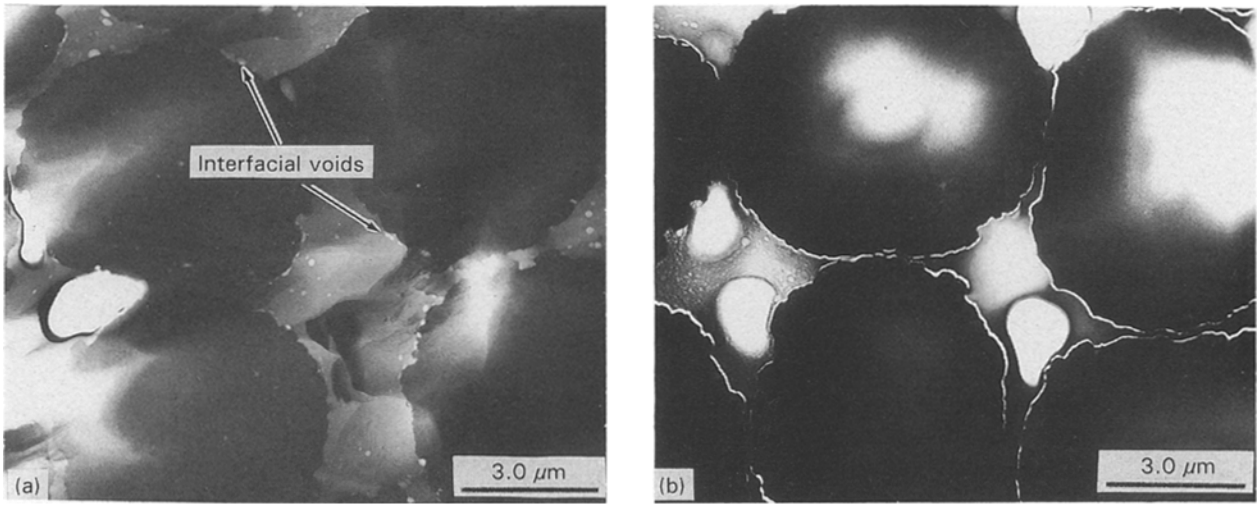

Figure 8 Bright-field transmission electron micrographs of composites comprising surface-treated fibres heat treated at (a) 1000 °C and (b) 2000 °C.

more discontinuous. Actually, a major portion of the fibre surfaces was entirely separated from the matrix (Fig. 8b). Selected-area diffraction (SAD) showed that the basal plane orientation in the majority of this matrix appeared random, except in the narrow matrix regions between individual fibres where the basal planes were preferentially aligned to the fibre surface (Fig. 9). This preferential alignment of basal planes was, as expected, more developed in the high-temperature (2000 °C) treated composites (Fig. 10). Again, in such preferentially oriented regions, the basal planes were predominantly parallel to the fibre surface.

In the NST series, even in the carbonized (1000 °C) stage, the fibres were almost entirely separated from the surrounding matrix (Fig. 11a). This is very different from the carbonized ST composite shown in Fig. 8a. As in the ST composites, large crescent-shaped pores surrounding each fibre were developed, and the matrix in the high-temperature treated composites, especially between narrowly spaced fibres, was highly preferentially oriented.

4. Discussion

Results in this study indicate that both strength and microstructure of the unidirectional, in-house fabricated C/C composites can be significantly affected by surface treatment of the fibres and heat treatment of the composites. While this general statement is consistent with that previously made by Fitzer *et al.*

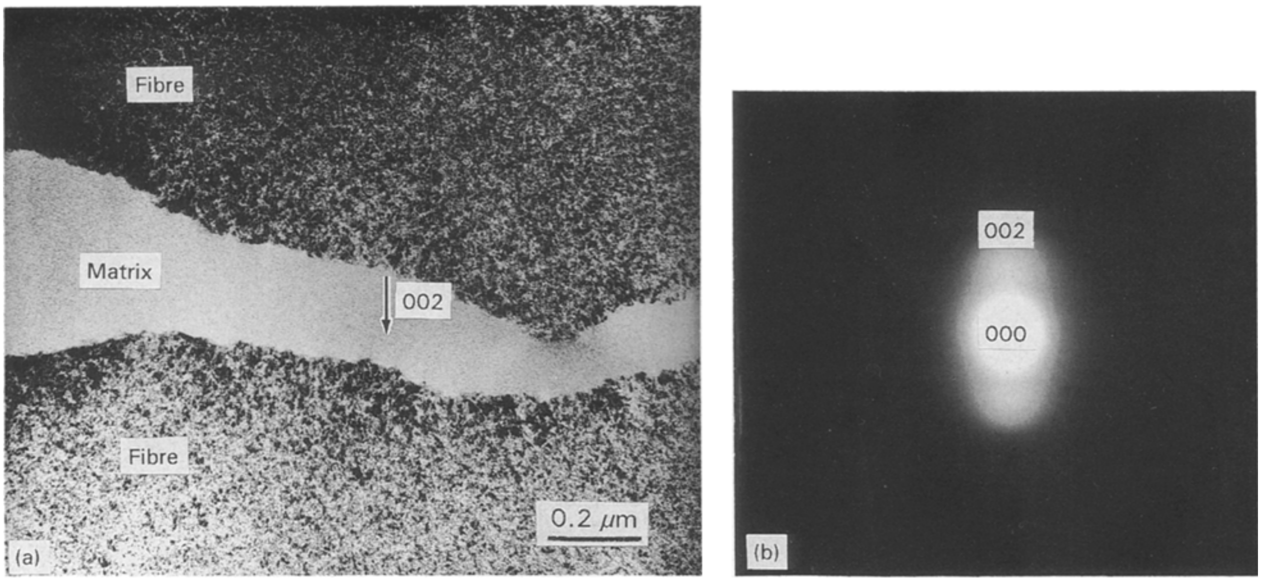

Figure 9 (a) Bright-field transmission electron micrograph and (b) SAD pattern showing fibre–matrix interfacial morphology and basal plane orientation in the matrix region between two closely spaced fibres in a composite comprising surface-treated fibres heat treated at 1000 °C.

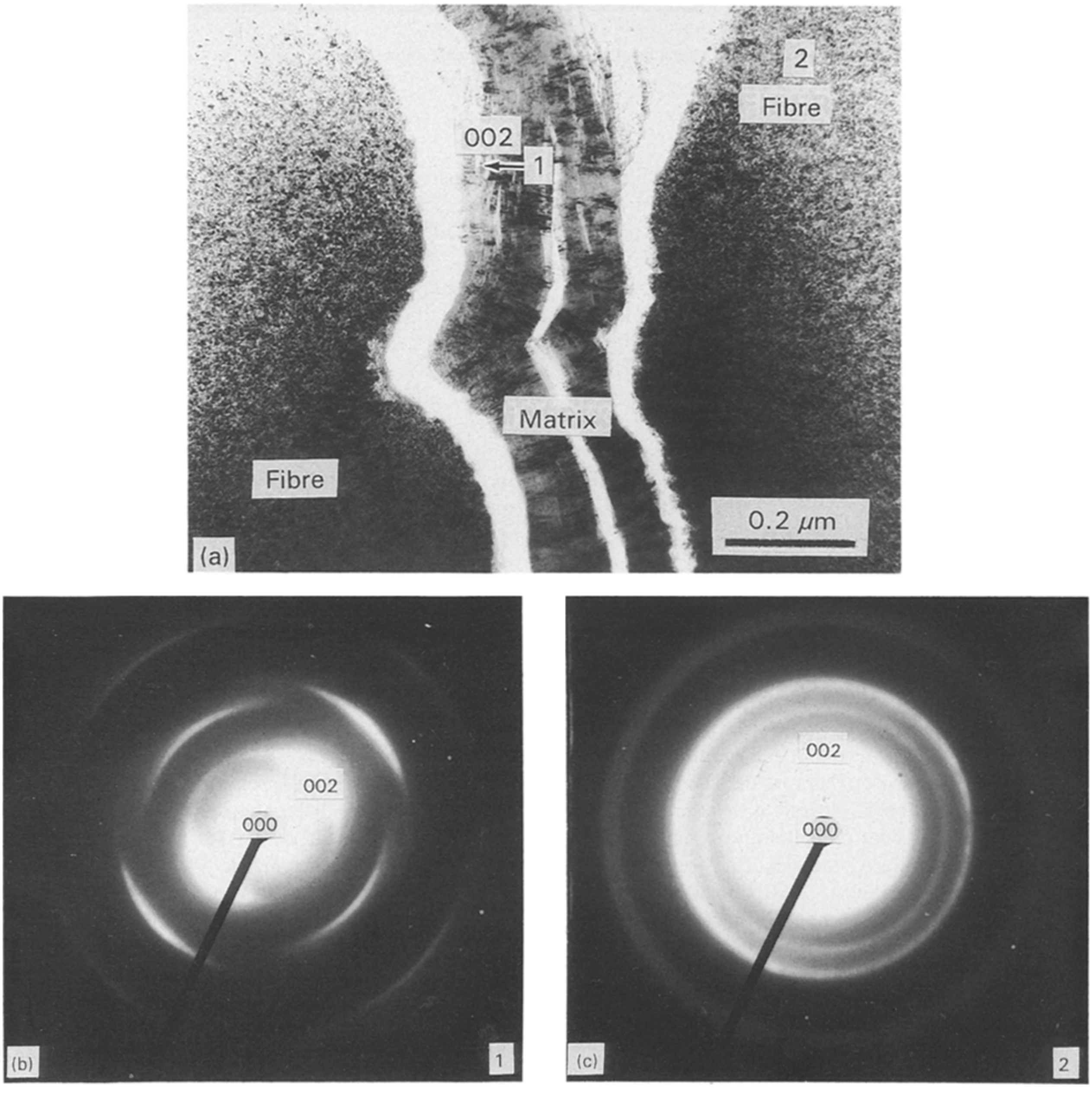

Figure 10 (a) Bright-field transmission electron micrograph, and SAD patterns of (b) matrix and (c) fibre in composite comprising surface-treated fibres heat treated at 2000° C.

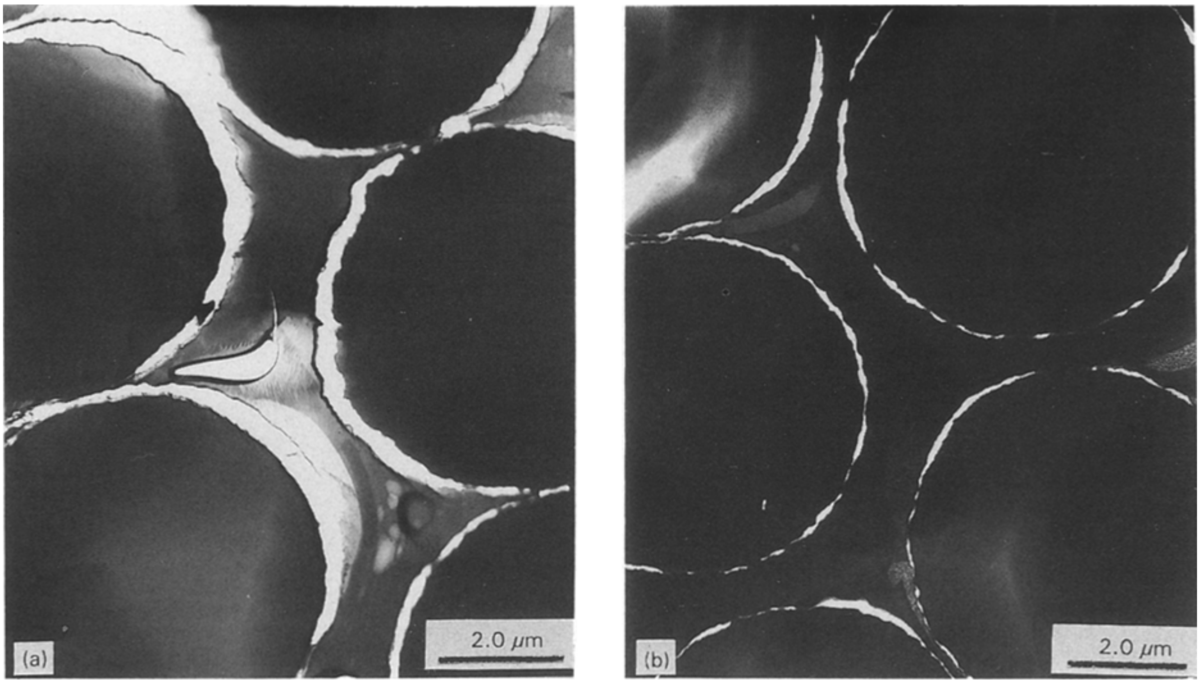

Figure 11 Bright-field transmission electron micrographs of composites comprising untreated carbon fibres heat treated at (a) 1000 °C and (b) 2000 °C.

[1, 5, 6] and Manocha *et al.* [7] for their different composites and processes, it has been found in this study that, up to three densification cycles, the C/C composites comprising ST fibres almost always possessed higher strength and modulus than those comprising NST fibres, whether the final HTT was 1000 or 2000 °C. The properties variation after three cycles, however, remains unknown and difficult to predict.

Because fibre and matrix carbons are both inherently brittle, a relatively weak fibre–matrix bond is usually desired for C/C composites to avoid a catastrophically brittle failure, similar to that for ceramic matrix composites. The fibre strength utilization efficiencies for the present C/C composites were generally low. For example, the fibre strength utilization of ST Sample 7, the highest in the ST series, was only about 30%, while the utilization of NST Sample 6, the highest in the NST series, was only about 25%. While these low fibre strength utilization efficiencies are not uncommon for C/C composites, such low efficiency values indicate that the fibre–matrix bonding (should be poor) plays a critical role in determining properties of such composites. For this reason, a major focus of this study has been devoted to the study of fibre–matrix interfacial morphology.

In the current study, the flexural strength of ST composites heat treated at 2000 °C was higher than those heat treated at 1000 °C. SEM has shown that the carbonized (1000 °C) composites (Sample 6) failed in a brittle manner, presumably due to the strong bond existing between fibre and matrix, as shown by TEM. During bending, the propagating cracks could break the fibres because they were not deviated at such strongly bonded interfaces. Ease in this fibre breaking process resulted in a flat fracture surface and low strength for this type of composite. For the ST composites heat treated at 2000 °C, the fracture surface was rather rough, where pull-out of fibres was observed. TEM/SAD clearly showed that a large portion of fibre–matrix interface had been separated, supposedly due to the different shrinking tendency between fibre and matrix during cooling from 2000 °C, which generated large enough stresses at the fibre–matrix interfaces to crack them. A stress-enhanced preferential alignment of basal planes occurred in the matrix adjacent to the fibre surface, especially the matrix sandwiched between narrowly spaced fibres. Such preferentially aligned basal planes were found parallel to the fibre surface and are believed to be able to contribute to the modulus of such unidirectional C/C composites. Owing to the existence of the narrow gaps between fibres and matrix, crack deviation could occur at such interfaces during mechanical testing and, therefore, a higher strength was achieved. SEM has confirmed the pull-out of fibres in this type of composite, which was a direct result of a weak fibre–matrix bond.

In contrast to the ST series of composites, in the NST series, the flexural strength and modulus of the carbonized (1000 °C) composites were much higher than those heat treated at 2000 °C. One major difference between carbonized ST composites and carbonized NST composites, according to SEM examination, was that in the NST composites the fracture surface was much rougher and fibre pull-out was frequently observed. TEM showed that the fibre–matrix interface morphology of the two composites was apparently different. In the NST composites, a large number of fibres were entirely separated from the matrix and many crescent-shaped pores were formed around fibres. For such NST composites as heat treated at 2000 °C, the fibre–matrix interfacial morphology generally resembled that for the carbonized ones. The matrix basal planes, however, were much better aligned to the fibre surface, as evinced by TEM. Such alignment of basal planes to the fibre surface (and thus to the fibre axis) may contribute to the modulus of the composite. However, the modulus, strength, and other mechanical properties are determined not only by the basal plane orientation, but also by other critical microstructural parameters, such as fibre–matrix interface rigidity and extent of matrix porosity. TEM has shown that, in the preferentially oriented matrix of the NST composites heat treated at 2000 °C, extensive inter-basal plane microcracking was induced by the high-temperature treatment. Such extensive microcracking, combined with the large number of macrocracks and porosity developed during the high-temperature treatment, are believed to have largely weakened the matrix and result in even worse properties than those more brittlely failed 1000 °C treated NST composites.

As a final note, our study on the two-dimensional C/C composites using similar raw materials and processes has shown that the properties variation trends for the two-dimensional composites are different than the currently studied unidirectional composites, primarily due to the large differences in their contraction behaviour during processing [11]. The results from the unidirectional composites may not be accurately applied as a process guide to the more practical two-dimensional composites. Some basic information obtained in the current study, such as the near-interface microstructural information, however, has been found useful in developing our two-dimensional C/C composites.

5. Conclusions

1. Flexural strength and modulus of the in-house fabricated unidirectionally reinforced PAN-resin C/C composites were found sensitive to the process parameters (particularly the final HTT) as well as fibre surface condition (surface-treated or non-surface treated). For ST composites, the flexural strength and modulus of the composites heat treated at 2000 °C were higher than those treated at 1000 °C. For the NST composites, the results were just the opposite.
2. At CFRP stage, the strength and modulus of ST composites were higher than those of NST composites by 400% and 100%, respectively, due to the stronger fibre–resin bonding in the ST composite.
3. After the first carbonization treatment, the ST composites always possessed higher strength and modulus values than NST composites, whether the final HTT was 1000 or 2000 °C. In ST series of composites, the improvement in strength and modulus became significant from the third densification cycle, while in the NST series, both second and third cycles were effective.
4. Optical and electron microscopy showed that, in all composites, except for CFRPs, an anisotropic carbon structure was more or less developed in the matrix adjacent to fibres as well as to internal cracks. The degree of this anisotropy was much higher in the 2000 °C treated composites than the 1000 °C-treated ones. TEM/SAD showed that, in the preferentially oriented regions, the basal planes were predominantly parallel to the fibre surface.
5. SEM revealed a significant fibre pull-out in both 2000 °C-treated ST and NST composites, but a rather flat fracture surface in the 1000 °C-treated ones.
6. TEM showed that, in the ST series, the fibres and the matrix in the 1000 °C-treated composites were well bonded, while in the 2000 °C-treated composites, the fibre–matrix bonding was very loose. In the NST series, the fibres even in the 1000° C-treated composites were almost entirely separated from surrounding matrix. Large crescent-shaped pores surrounding fibres were developed in both ST and NST composites during processing.

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