

# PROCESSING, STRUCTURE AND PROPERTIES OF PITCH-BASED CARBON-CARBON COMPOSITES

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## INTRODUCTION

The potential of carbon-carbon (CC) composites as materials for high temperature applications was recognised at a very early stage, leading to their development in the 1960's as materials for thermal protection during space vehicle re-entry. By the early 1970's, two basic approaches to the formation of the carbon matrix were established, namely through chemical vapour deposition from a hydrocarbon gas (CVD) (1) and through carbonisation of a carbon-bearing resin or pitch (2). Fundamentally, little has changed since those early years with respect to these basic methods of CC composite fabrication. Further developments have, however, involved the introduction of multidirectional fibre architectures in order to reduce the mechanical anisotropy present in unidirectionally and bidirectionally reinforced composites caused by poor mechanical properties in the unreinforced directions. The strategic importance of several aerospace applications of CC composites, including military rocket nozzles and nose cones, the NASA space shuttle nose cone and leading edge protection surfaces, aircraft brake discs and gas diverter fins, ensured their continued development during the 1970's and 1980's.

The technique of liquid impregnation is now a major procedure for the densification of CC composites (3). Despite nearly 30 years of development, however, the utilisation of fibre strength in densified CC composites is still only around 65 % (3). There is, therefore, a need for a comprehensive understanding of the factors giving rise to this lost potential so that improvements in properties may be achieved. Furthermore, new applications of CC composites are currently emerging which exploit some of the thermal characteristics of the composite structure as manifest in the graphite crystal structure. There is thus a need to further understand the ways in which the composite microstructure may be controlled during the fabrication process. This paper reviews the principal microstructural features of interest in CC composites produced with pitch precursors to the carbon matrix and illustrates the influence of fibre-matrix interactions on the microstructure and properties.

## MICROSTRUCTURE OF CC COMPOSITES

The microstructures of CC composites may be very complex, involving various degrees of crystallinity and texture on differing scales of magnitude, and several types of interfaces, pores and microcracks, conceivably all in the same specimen (4). Both fibre and matrix undergo significant microstructural changes during fabrication; the fibre and matrix may interact, thus producing unique microstructural features that cannot be obtained by identical processing of the separate constituents (5).

The orientation of the outer turbostratic sheath of carbon fibres has been observed to increase on graphitisation compared with that of a fibre graphitised independently of a composite (6). This increased alignment is thought to arise from an interfacial stress effect. Fibres may thus undergo a substantial increase in modulus of elasticity during thermal processing of a CC composite (7). Such stresses, caused by strong fibre-matrix coupling and matrix shrinkage during carbonisation of the composite, have also been claimed to damage the fibre (8).

Although the overall texture of CC composites is dominated by the structure and architecture of the fibre reinforcement, the existence of preferred orientation (texture) in the microstructure of the matrix is significant. Texture in the matrix is established primarily from two sources, namely the chemistry of the organic matrix precursor and fibre-matrix interfacial effects. Matrix carbons derived from pitches tend to be structurally anisotropic, a product of the development of layers during the growth and coalescence of mesophase spheres in the initial stages of pyrolysis. If unhindered and mechanically undisturbed, the coalesced mesophase produces a coarse microstructure (9). Plastic deformation during this stage, due to externally applied stresses or the formation of gaseous by-products of pyrolysis, may disrupt long range ordering of the mesophase resulting in a finer microstructure. Similar effects are caused either by the application of pressure during carbonisation or by

chemical cross-linking of the structure (10, 11). Controlled alteration of the matrix microstructure may be achieved by the blending of various fractions of pitches (12).

Texture has been observed to initiate in previously structurally isotropic matrices on heat treatment to graphitising temperatures (13). This effect has been ascribed to a concentration of stress developing along the fibre-matrix interface, arising from the combined actions of matrix densification (volume shrinkage) and thermal expansion mismatch between the fibre and the matrix. A second form of fibre-matrix interfacial effect, characteristic of structurally anisotropic matrices, involves the development of carbon atoms arranged in planar layers oriented parallel to the fibre surface (14). A full understanding of this effect has not been reached. The "matrix sheath" may result from fluid flow rather than from wetting (15), though forces acting on the disc-like molecules by the surface do produce a strong anchoring effect, as detected by the resistance to orientation induced by a magnetic field (16). Disruption of the sheath can be produced by the application of pressure during carbonisation and the effects of chemical cross-linking of the structure (10, 11). Given the potential anisotropy in properties conferred by the structure of graphite, the ability to control the texture of the matrix is clearly important in order to allow complete control over the properties of the composite.

Graphitisation of anisotropic matrix carbons causes further structural changes to occur. These changes include "fold-sharpening" and "polygonisation". The former appearing to constitute the first point at which the process of graphitisation becomes microscopically evident (17); shrinkage cracking tends to break a sheet or fold into segments at fairly regular intervals, and these segments sharpen to decreasing radii of curvature. Polygonisation is evidenced by the formation of mosaic block type structures, and has the effect of relaxing the compressive stresses generated by the tendency to shear the layers into graphitic registry (17).

Few studies have been reported concerning the characterisation of porosity in CC composites. Jortner (18) distinguishes between "pores" and "cracks". Pores primarily arise from processing problems. Examples of these include pores formed by incomplete filling by the matrix (perhaps due to poor wetting of the fibres, or incomplete compaction of prepregs resulting in dry zones within the composite) and by the entrapment of gases produced during solvent removal, curing or pyrolysis while a matrix precursor is still liquid or plastic (18). Cracks, comprising "shrinkage", "cooldown" and "thermal stress heating" cracks, arise from stresses due to structural rearrangements during heat treatment or thermomechanical effects.

The geometry of the fibre architecture and nature of fabrication of CC composites generate a number of interfaces present on both the "mini-mechanical" and "micro-mechanical" scales (18). Interfaces that occur on the mini-mechanical scale include fibre tow-fibre tow, bundle-bundle, bundle-matrix and layer-layer interfaces. On the micro-mechanical scale exist fibre-matrix and matrix-matrix interfaces (18). The strength of the fibre-matrix interface is critical to the behaviour of CC composites under mechanical loading. A good fibre-matrix coupling is required to maximise energy transfer from the matrix to the fibre, though it must not be so strong as to cause brittle failure of the composite (19). Matrix-matrix interfaces also have importance as they may limit the ability of the matrix to distribute the load equally between fibre-matrix units or to redistribute the load around individual unit failures (20). In pitch-based carbon matrix composites, the structure of the interfacial zone is monopolised by the presence of matrix sheath, described above. This sheath may actually be a source of debonding of the interface due to the actions of fold-sharpening and polygonisation during graphitisation (11).

The exact nature of "bonding" at the interfaces in CC composites, and hence what controls the bond strength, is not fully understood. Various types of interaction across the interface may exist, including strong and weak chemical bonds, mechanical interlocking and friction (4). Full characterisation and control of interfaces remains one of the most elusive aspects of the technology of CC composites.

## EXPERIMENTAL

Model unidirectional CC composites comprising continuous PAN-based fibres and petroleum pitch-based matrices were fabricated by wet-winding and moulding in a heated press, followed by heat treatment. Several types of PAN fibre were used. These included a surface treated standard modulus fibre (SMS) and an untreated high modulus fibre (HMU). Two main temperatures were chosen for the routine

heat treatment of composites. These were a "carbonisation" temperature of 900 °C and a "graphitisation" temperature of 2250 °C. The porous composites so formed were densified by means of pitch-melt impregnation. Composites were studied by optical and scanning electron microscopy and X-ray diffraction. Various properties were studied including electrical resistivity and mechanical behaviour.

#### STRUCTURAL AND PHYSICAL CHARACTERISATION

A major characteristic of the initial establishment of CC composite structures during carbonisation and graphitisation was the creation of a large number of voids due to matrix shrinkage. After initial carbonisation of the HMU-pitch composites, point counting revealed only ~ 20 % of the fibre surface to be contiguous with matrix. Cracks had developed which were mainly located at the fibre-matrix interface. These cracks, however, were extensively interconnected and enabled very efficient densification of the structure by pitch-melt impregnation. Cracks in the SMS composite, conversely, were generally located within the matrix and tended to have a thin lath-like morphology. This reflected the greater strength of the fibre-matrix interface due to the surface treatment of the fibre, and also revealed the matrix to be prone to failure due to cleavage of the anisotropic structure along planes of weakness. Densification of the SMS composites was not very efficient due to the "bottle-shape" nature of the voids. The location of shrinkage cracks was thus strongly influenced by the combination of the fibre-matrix interface strength and the strength and texture of the matrix (Figure 1). In turn, the void shapes and their degree of interconnectivity governed the efficiency of densification by liquid impregnation.

X-ray diffraction (002) profiles of the green and carbonised composites were largely dominated by the fibre (002) profiles. On graphitisation, marked changes in the composite (002) profiles occurred as they became matrix dominated. Deconvolution of the (002) intensity profiles into separate fibre and matrix profiles enabled  $d_{(002)}$  and  $L_c$  to be determined for each constituent (Figure 2). The matrix  $L_c$  values were greater with respect to similarly heat treated bulk raw materials, indicating the effects on structure of fibre-matrix interactions during graphitisation.

Measurements of electrical resistivity were made both parallel and perpendicular to the fibre axes. Of the densified composites, the carbonised SMS composites exhibited the lowest electrical anisotropy (~ 6). This reflected both the lower structural anisotropy of the SMS fibre and matrix structures (cf. graphitised fibres / matrices) and the high degree of fibre-matrix contiguity present in the composite. Departures from one or more of these conditions resulted in greater anisotropy. Matrix resistivity in the axial direction was calculated by considering the composite as a sequence of parallel resistors, together with knowledge of the longitudinal fibre resistivities,  $V_f$ ,  $V_m$  and  $V_c$ . The carbonised matrix resistivity averaged  $1.64 \times 10^{-6} \Omega m$ , reducing to  $4.02 \times 10^{-6} \Omega m$  on graphitisation. The axial resistivity of the graphitised pitch matrix thus approximately matched that of highly oriented Amoco P-100 pitch-based fibres after individual heat treatment to 2500 °C (21). These measurements clearly illustrate the potential of the matrix sheath regarding control of composite properties; alignment of matrix carbon basal planes parallel to the fibre axis greatly enhanced composite electrical conductivity in the longitudinal direction.

#### MECHANICAL PROPERTIES

Flexural strengths were measured at span-to-depth ratios of 80:1. The strength of the fibre-matrix interface strongly influenced the mode of fracture during flexural testing. A range of fracture behaviour was observed, from "brittle-catastrophic" to "pseudo-ductile", depending on the fibre-matrix combination and fabrication history. The carbonised SMS composites failed by a brittle failure mechanism; only 25 % of the fibre strength was utilised. Failure of the carbonised, densified HMU composite was evidently by means of multiple matrix cracking followed by fibre failure and fibre pull-out. In this case 60 % utilisation of fibre strength was achieved (assuming the contribution of the matrix to strength to be negligible). Graphitisation may give rise to changes in the mode-of-failure due to changes in the nature of the interface and matrix texture. Similarly, low temperature oxidation, in which the oxidation reaction clearly takes place preferentially at the fibre-matrix interface may weaken the fibre-matrix interface enabling debonding and fibre sliding. Increases in utilisation of fibre strength may thus occur as a result of the greater strains at which maximum load occurs.

## CONCLUSION

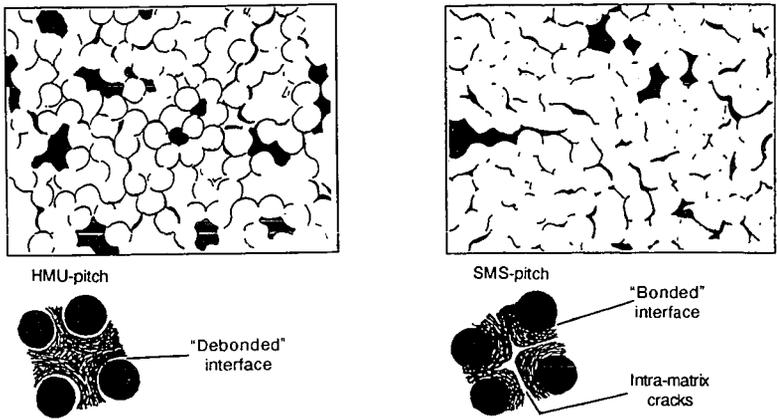
Successful control of fibre-matrix interactions at each stage of fabrication is key to the control of properties of CC composites. The void network established during the initial heat carbonisation has a large effect on the efficiency and effectiveness of subsequent densification processing. The influence of matrix texture on the electrical properties of CC has been illustrated; as the lattice properties of anisotropic carbons are similarly reflected in the properties of modulus of elasticity, thermal expansivity and thermal conductivity, an ability to control matrix texture is clearly of great importance. These properties are of especial importance regarding an emerging application of CC composites, namely the packaging of electronic systems. Finally, if improvements in utilisation of fibre properties are to be achieved, it is imperative to advance understanding of the various structural features influencing modes-of-failure.

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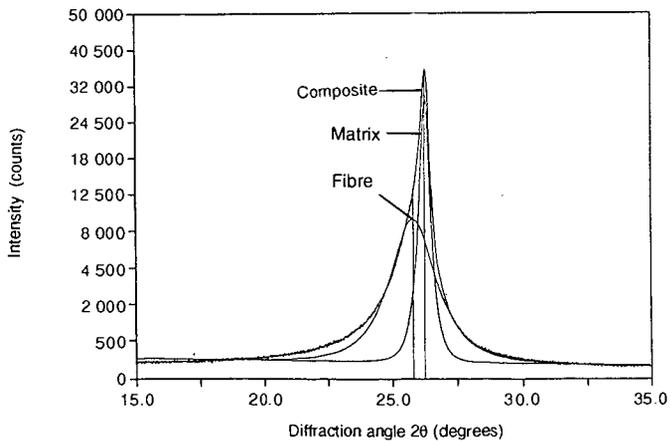
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**Figure 1**  
 Schematic illustrations of the different void network structures arising from the different fibre-matrix interactions that occurred in HMU-pitch and SMS-pitch composites on carbonisation.



**Figure 2**  
 X-ray diffraction profile given by HMU-pitch composite (carbonised, re-impregnated with pitch and then graphitised) with component fibre and matrix profiles obtained by computational deconvolution of the intensity profile.