

THE SURFACE PROPERTIES OF CARBON FIBRES AND THEIR INFLUENCE ON THE VOID STRUCTURE OF CARBON/CARBON COMPOSITES

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Introduction

The interactions at the interface between the fibres and matrix are crucial in determining the mechanical properties of carbon/carbon composites. A compromise between strong and weak bonding at the interface is necessary to optimise the efficiency with which fibre properties are utilised and the fracture toughness of the composite[1-2]. Studies of interfacial/mechanical property relationships are relatively straight-forward in the case of a unidirectional reinforced structure. However, for multi-directional composites, the various fibre directions introduce different types of interface and voids which also affect the mechanical properties of the composites. Hence, in these structures many more interfacial and processing parameters must be considered in order to achieve optimum mechanical properties. This work was focused on woven fibre reinforced laminate structures and has investigated the surface properties of three types of carbon fibre and the pore structure of their carbonised preforms.

Experimental

The materials investigated comprised three types of carbon-fibre cloth and their carbonised laminates. Laminates were produced from the fibre cloths using a 0/90° layup impregnated with a phenolic resin and carbonised to 1000 °C. The three types of cloth studied were produced from polyacrylonitrile (PAN), rayon, and mesophase pitch based carbon fibres. The PAN and pitch based cloths were woven in a five harness satin weave, whilst the rayon material had an eight harness weave. The PAN fibre was a medium modulus type and the other two types of fibres were of low modulus. The rayon fibres were heated to graphitisation temperature during the fibre processing.

The samples of the rayon and pitch fibres for surface investigations were unsized. The PAN fibres were only available in prepregged form. Dichromethane was used to remove the resin from the PAN cloth prior to the investigation of surface morphology.

The surface morphology of the carbon fibres was studied using polarised-light and scanning force microscopy (PLM & SFM). The SFM system used was a Nanoscope III STM-SFM made by Digital Instruments Inc. In the experiment, the samples were scanned at a constant force in the range of 10^{-8} to 10^{-9} N. The scanning rates were 1 to 10 Hz depending on the samples and magnifications.

The surface composition of the fibres was measured using X-ray photoelectron spectroscopy (XPS). This measurement was carried out on a VG ESCALAB MK1 using Al K α x-rays of energy 1486.6 eV at a power of 200 W. All peaks were referenced to the major C-C/C-H 1s peak at 284.4 eV. Surface composition was calculated using the areas of the respective photoelectron peaks after background correction.

The void structure of the carbonised preforms was studied using a water penetration techniques [3] for the measurements of open and closed porosities. Image analysis of optical microscopic images of polished cross-sections of the composites was used for characterisation of pore geometry, location and area fraction (voidage). Details of this method have been published elsewhere [4].

Results and Discussion

The carbonised preforms produced from the three types of fibre all have a similar total porosity of approximately 23 vol%. In the pitch and rayon based preforms closed porosity makes up less than 5% of the total porosity. However, in the PAN-based preforms the closed porosity is considerably higher at 28% of total porosity.

Further studies by image analysis indicate that the PAN-based preforms show an increase in a type of porosity which takes the form of larger cracks which are mostly transverse matrix cracks similar to those observed in woven polymer composites[5]. Cracks of this type predominate at the inter-layer and inter-

bundle interfaces[4,6]. The difference in the porosity associated with the small voids within fibre bundles, between the three types of preform, is not as significant as that of the larger cracks.

These results suggest that stronger bonding at the fibre/matrix interface has occurred in processing of the PAN based preforms. Such bonding leads to the formation of the closed porosity which is so marked in the PAN based composite. In addition, the generation of higher thermal stresses during carbonisation resulting from shrinkage of the matrix phase causes the larger transverse matrix cracks observed in this material. Little interaction at the fibre/matrix interface has occurred in processing of the pitch- and rayon-based preforms.

The bonding at the fibre/matrix interface could be associated with either chemical interactions or mechanical locking between the fibres and matrix. In order to find which factor has played a more important role, the surface properties of the carbon fibres were investigated using PLM, SFM and XPS. Polarised-light microscopy of polished cross-sections of the fibres has shown that the circumference of the PAN and pitch fibres is smooth. The rayon fibres, however, have a crenellated surface.

Further details on the surface morphology were obtained by SFM with higher magnification. The crenellated surface of the rayon fibres is not noticeable at higher magnification and the surface of all the three types of fibres appeared to be similar up to a magnification of $10^6\times$. At higher magnification significant differences between the different types of fibre were distinguishable. The pitch fibres had the roughest surface which appeared to be composed of large grains. The PAN fibre was similar, however, the grain size was much smaller. Many ridges on the surface of the PAN fibres were visible and were orientated in the fibre direction. The rayon fibre had the smoothest surface at this magnification, however, grains on the fibre surface were just visible. The root mean square average roughness (R_{ms})^[7] of the fibre surface, measured in both longitudinal (R_{msL}) and circumferential (R_{msT}) directions, is given in Table 1. The magnitude of the roughness in the table follows such a sequence: Pitch>PAN>Rayon, which agrees with the above observations.

The microscopic studies of the fibre surface in both micro- and nano-metric regimes indicates a lack of correlation between the surface roughness of the carbon fibres and bond quality at the fibre/matrix interface in C/C composites. Chemical interactions

may play a more important role. This has been confirmed by the measurement of surface composition of the three fibre types using XPS. The results of this work are shown in Table 2. The data on the PAN fibres in the table were not obtained from the PAN fibres studied. It is reasonably assumed that the data on the PAN fibres studied should be between the range of those data obtained from high and low modulus PAN based carbon fibres shown in the table. The surface oxygen content of the PAN fibres appears higher than that of the pitch and rayon fibres. It is postulated that the surface oxygen groups may first bridge the carbon atoms between the fibres and matrix and then form carbon-carbon bonds by the release of either CO or CO₂ during pyrolysis, resulting in strong chemical bonding at the fibre/matrix interface.

Table 1. The root mean square average roughness of the fibre surface measured by SFM

	Pitch	PAN	Rayon
R_{msL} , nm	12.215	5.921	3.354
R_{msT} , nm	18.819	10.746	4.753

Table 2. Surface composition of the carbon fibres

Fibre Type	C, mol%	O, mol%	N, mol%
Pitch	98.2	1.8	0
Rayon	99.1	0.9	0
PAN*	92.0-96.5	3.2-4.7	0.3-3.3

* Based on the measurements of various high and low modulus PAN-based carbon fibres

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