**Introduction**

The commercial exploitation of carbon fibres rests on the discovery of effective methods of increasing the interfacial shear strength between the surface of the cylindrical fibre and the compatible material with which they are combined to form a composite material.

Since the structural characteristics of carbon/epoxy composites are usually evaluated by measuring the short beam shear strength (a measure of interlaminar shear strength), it is important to correlate the shear with the bonding between the fibres and the matrix material.

Knowledge of the atomic structure of the surfaces of carbon fibres is therefore essential and the surface structure has recently been studied by photomicroscopy and low temperature adsorption of N\textsubscript{2} and Ar by M\textregistered{ö}ller and Fort, Jr (1). The atomic composition of the external surface of carbon fibres has also been investigated by the application of high energy photoelectron spectroscopy (ESCA) by Barber, Swift, Evans and Thomas (2) and with Auger electron spectroscopy by Connell (3).

**Experimental**

Six types of polyacrylonitrile-based fibres were examined viz. Torayca T300A, Torayca M40A, Torayca T200A, Courtaulds HM-S, Courtaulds A-S, Courtaulds HT-S. They can be divided in three groups, named Type 1, Type 2 and Type 3 depending on their mechanical properties. Type 1 are the high modulus carbon fibres Courtaulds HM-S and Torayca M40A. Type 2 are the high tensile strength carbon fibres Courtaulds HT-S and Torayca T300A. Type 3 are the high strain carbon fibres Courtaulds A-S and Torayca T200A. A tow of carbon fibres consists of 2000, Torayca, and 100000, Courtaulds, individual parallel filaments each only 8-9 μm. A hemicylindrical mirror analyzer (Vacuum Generators 950 CMA) fitted with a microfocus electron gun (LEG 52) was used for Auger studies. In order to minimize possible intensity variations of the Auger-signals due to the geometrical extensions of the carbon fibres, the electron beam (8-5 μm) was allowed to scan with high velocity across a large area. Thus all Auger spectra shown, are average results from a surface area equal to 2x2 mm. Concentration gradients were studied by simultaneous ion-etching of the samples. For this purpose an argon-ion beam was used with an ion current density of 20 μA/cm\textsuperscript{2} and an acceleration voltage of 2 keV (3.2*10\textsuperscript{-16} J). The profile studies were made to a depth of 30 nm (300 Å). All measurements were performed at a pressure of 10\textsuperscript{-7} Pa. This pressure was attained without any bake-out of the vacuum chamber.

**Results and Discussion**

The Auger spectroscopy examination gave the concentration gradients for oxygen, sulfur and chlorine to a depth of 30 nm (300 Å) for the six carbon fibres. The concentration gradients for oxygen in the six carbon fibres are present in fig 1a for sulfur in fig 1b and for chlorine in fig 1c. It may be noted that the oxygen content of Torayca type 1 and type 2 carbon fibres increases with the depth in the carbon fibres. Type 3 fibres have a high oxygen concentration on the fibre surface and the concentration decreases with depth to a depth of 5 nm (50 Å) in the fibre. This might be because these fibres have large surface roughness. They are not so well crystallized and so they have a larger surface area than the other four carbon fibres. The concentration of chlorine in the six fibres is nearly constant. The chlorine comes probably from oxidation of the fibres with hypochlorite. It is of interest that sulfur is present in all the carbon fibres. On the surfaces there is no sulfur except for the Torayca type 3 fibre. In all the other carbon fibres the sulfur concentration increases with depth in the fibres to about 10 nm (100 Å) and is then constant. Sulfur has been found in PAN-based carbon fibres earlier by Kalnin (4) 0.2-0.3 %, Liberman and Moles (5) found about 0.05-0.1 % in three different types of PAN-based carbon fibres. Sodiumthiocyanate solution is used as solvent for the polymerisation of the acrylonitrile. It seems likely that the use of this solvent results in some residual sulfur in the carbonised fibres. Such a hypothesis would also suggest a constant sulfur concentration within the fibre. The present Auger examination confirms this as is demonstrated by fig 1b. The low sulfur concentration at the surface of the fibres especially for Type 1 and Type 2 probably arises from their heat treatments during manufacture. Removal of sulfur and chlorine is difficult if the sulfur and chlorine atoms are situated between the graphite basal planes and not in cavities. The distances between graphitic basal planes in carbon fibres are between 0.341 to
0.348 nm (6,7) compared with 0.335 nm in graphite. C-S bond distances are between 0.155 and 0.181 nm and C-Cl bond distances between 0.1635 and 0.1767 nm. Thus there could be a carbon-sulfur-carbon cross-link between the layers perpendicular to the axis of the microfibrils.

References

Fig. 1. The concentration gradient for (a) oxygen, (b) sulfur, (c) chlorine in carbon fibres deduced from Auger electron spectroscopy examination.