

The Surface Characterization of Polyacrylonitrile-based Carbon Fibres by Electrochemical Techniques

S. J. PORTER, C. L. DEARMITT, R. ROBINSON, J. P. KIRBY & D. C. BOTT

ABSTRACT Carbon fibre surface properties have been studied by measuring the electrochemical behaviour of the hexacyano ferrate(III)/ferrate(II) couple using carbon fibre brush electrodes. Courtaulds Grafil polyacrylonitrile (PAN) based fibres have been studied that have been subjected to different extents of a proprietary wet oxidative surface treatment varying from 0 to 500% of the standard treatment. Analysis of the cyclic voltammograms gives information on the electroactive surface area, a parameter related to the conductivity perpendicular to the fibre surface and rate of electron transfer across the surface of the fibres. The electrochemical data are correlated with other surface properties such as the surface area determined by oxygen chemisorption, surface energy components and some adhesion parameters, such as interlaminar shear strength and critical fragment aspect ratio of epoxy matrix composites.

1. BACKGROUND

In order to optimize/control the translation of fibre properties into composite materials performance, a greater understanding of the fibre-polymer matrix interactions in the interphase region is required. Much work has already been done in investigating the role of the surface properties of fibres in controlling adhesion [1]. In particular, a good correlation is found between the fibre/matrix interlaminar shear strength measured on composites of Courtaulds Grafil 33-600 fibres and a variety of other surface properties such as the chemically active surface area (determined by oxygen chemisorption) or the polar component of the solid surface energy (determined by wetting angle measurements) [2].

The purpose of these experiments was to investigate the use of electrochemistry in determining the active surface area of a variety of carbon fibre types. In this study Courtaulds Grafil PAN-based 33-600 and 43-750 fibres have been used. Data were obtained using cyclic voltammetry to calculate the electrochemically active 'surface area', and the electrochemical transfer product, αN [3, 4]. These data are correlated with available data relating to fibre surface area and surface energy as well as fibre-matrix adhesion values for the two fibre types in thermosetting resins.

Although data on the two fibre types are here presented together, we wish to make it clear that we are not drawing any comparisons between the two fibres. The preliminary nature of this work means that direct comparisons of data obtained on different fibres must await the development of a suitable calibration technique.

2. EXPERIMENTAL

In these experiments the carbon fibre is simply used as a working electrode. By comparing the redox behaviour of the hexacyano ferrate(III)/ferrate(II) couple [3] at carbon fibre electrodes that have been subjected to different levels of Courtaulds Grafil proprietary wet oxidative surface treatment, the evolution of the surface properties with increasing surface treatment can be measured. The degree of treatment found to give the optimum adhesion to epoxy resin matrices is arbitrarily described as 100% surface treatment. All other degrees of treatment are described as fractions or multiples of the '100%' surface treatment level.

The carbon fibre tows consisted of 12,000 filaments, with filament diameters of 7 μm for the 33-600 and 5 μm for the 43-750 fibres. The tow (4 cm) was attached to a copper wire, using electrically conductive graphite adhesive (LIET-C). The graphite adhesive was sealed with Araldite glue, to ensure that any electrochemical properties of the graphite adhesive would not appear in the results.

The experiments were performed by immersing the carbon fibre brush in a 4 mM solution of potassium hexacyanoferrate(III) in 2 M KCl. The brush was the anode and a platinum cathode was employed. All potentials were measured with respect to a Ag/Ag⁺ reference electrode (saturated KCl salt bridge). New carbon fibre electrodes and fresh electrolyte (4 mM hexacyanoferrate(III) in 2 M KCl) were used for each set of voltage scans, on each fibre sample. The data presented here represent an average of three sets of experiments on each fibre with a different surface treatment level.

All electrochemical experiments were performed without resistance compensation using a Princeton Applied Research Model PAR 273 potentiostat/galvanostat with a Hewlett Packard 9000 series microcomputer for control and data acquisition. Measurements of the critical fragment aspect ratios are based on the single filament fragmentation tests as carried out by Drzal [1] using a single filament of fibre set in a DGEBA type epoxy resin. The chemisorption, interlaminar shear strength and surface energy measurements are described in detail elsewhere [2].

3. RESULTS

3.1 Electrochemical Surface Area of Carbon Fibre Electrodes

A representative series of voltammograms of the hexacyanoferrate(III)/ferrate(II) couple at different scan rates are shown in Figure 1. The electrochemically active surface area of the electrode may be determined by measuring the peak height (here of the reduction scan), i_{red} , and using the Randles/Sevcik equation:

$$i_{\text{red}}/[2.69 \times 10^5 n^{3/2} \cdot D^{1/2} C v^{1/2}] = A \text{ (cm}^2\text{)}$$

where D is the diffusion coefficient of hexacyanoferrate(III) ion ($6.29 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), A is the surface area of the electrode (cm^2), C is the concentration of hexacyanoferrate(III) ion ($4 \times 10^{-6} \text{ mol cm}^{-3}$), n is the number of electrons transferred (1) and v is the scan rate (volt s^{-1}). Greater accuracy for the surface area value is achieved by plotting a graph of i_{red} against $v^{1/2}$ (not shown). Scan rates between 1 mVs^{-1} and 50 mVs^{-1} were used to calculate the electroactive surface areas. Under these conditions reversibility is maintained; the areas under the oxidation and reduction peaks, representing the charge involved, are essentially equal for both fibre types at all treatment levels. The specific surface area is obtained by dividing the area value obtained from the slope of these lines by the weight of the fibre used (10 mg).

The variation of the electrochemically active surface area with surface treatment

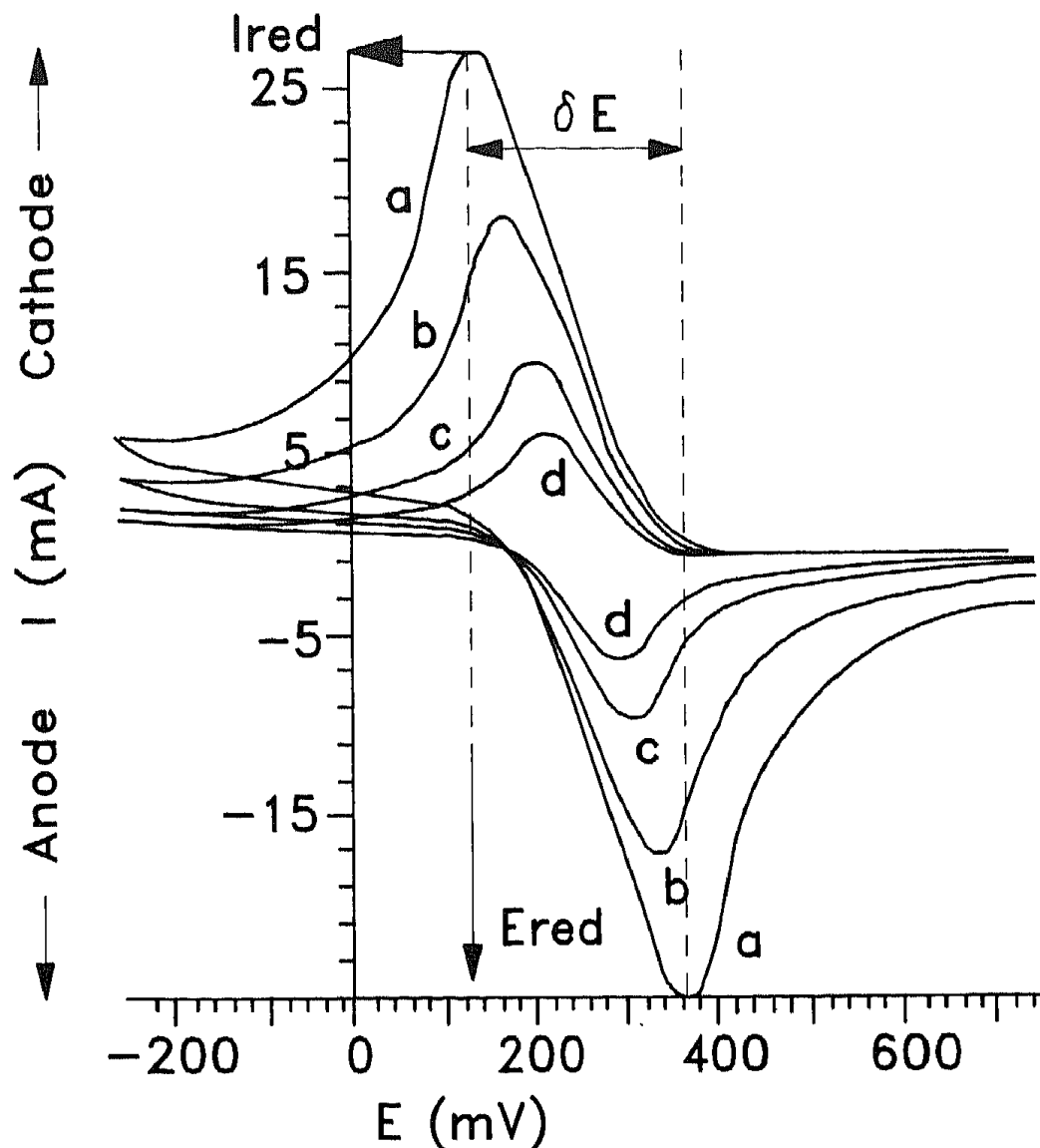


Figure 1. Cyclic voltammograms of $\text{Fe}[\text{CN}]_6^{3-}$ at 33-600 fibre brush electrode at a: 100 mV s^{-1} ; b: 50 mV s^{-1} ; c: 20 mV s^{-1} and d: 10 mV s^{-1} .

levels up to 400% for 33-600 fibres, and up to 200% for the 43-750 fibres, is shown in Figure 2. In general, the 43-750 fibres have a slightly smaller electrochemically active surface area than was observed for the 33-600 fibres. The observation that the

Table 1. Data for 33-600 Fibre

Surface treatment (%)	Electroactive surface area ($\text{cm}^2 \text{ g}^{-1}$)	Chemisorption surface area ($\text{cm}^2 \text{ g}^{-1}$)	Interlaminar shear strength (MPa)
0	934 ± 5	170	45
10	1234 ± 14	—	—
50	1637 ± 43	—	83
100	2221 ± 40	359	100
200	1560 ± 44	947	95
300	1751 ± 18	907	82
400	1433 ± 29	648	94

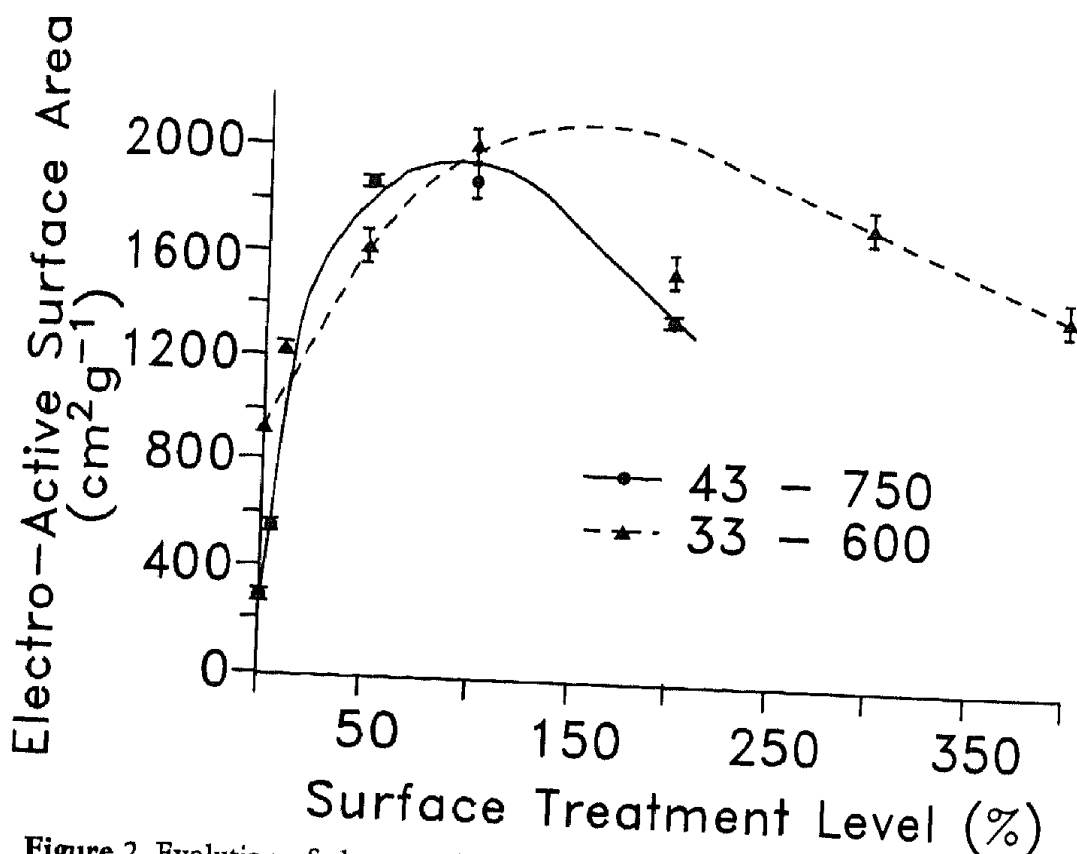


Figure 2. Evolution of electroactive surface area with surface treatment level.

Table 2. Data for 43-750 Fibre

Surface treatment (%)	Electrochemical surface area (cm² g⁻¹)	Chemisorption surface area (cm² g⁻¹)	Critical fragment aspect ratio
0	297 ± 13	156	179.0
5	545 ± 40	281	176.0
20	1854 ± 14	405	107.0
50	1873 ± 9	623	97.8
100	1887 ± 120	685	78.6
200	1376 ± 9	465	91.6

optimum fibre-matrix adhesion strength occurs at about 100% surface treatment is borne out by the observation of a maximum in the surface area for both fibres between 100 and 200% treatment levels.

The electrochemically active surface area is correlated against the 0° short beam shear strength in Figure 3 for 33-600 fibre samples at various surface treatment levels embedded in Courtaulds Grafil CG9101 matrix resin.

A strong correlation between the oxygen chemisorption surface area and the matrix adhesion strength has been reported for 33-600 carbon fibres [2]. The correlation between the electrochemical surface area of the 43-750 fibre and the oxygen chemisorption surface area is shown in Figure 4. Obviously the values for the surface area determined by the two techniques are different. The oxygen chemisorption experiment,

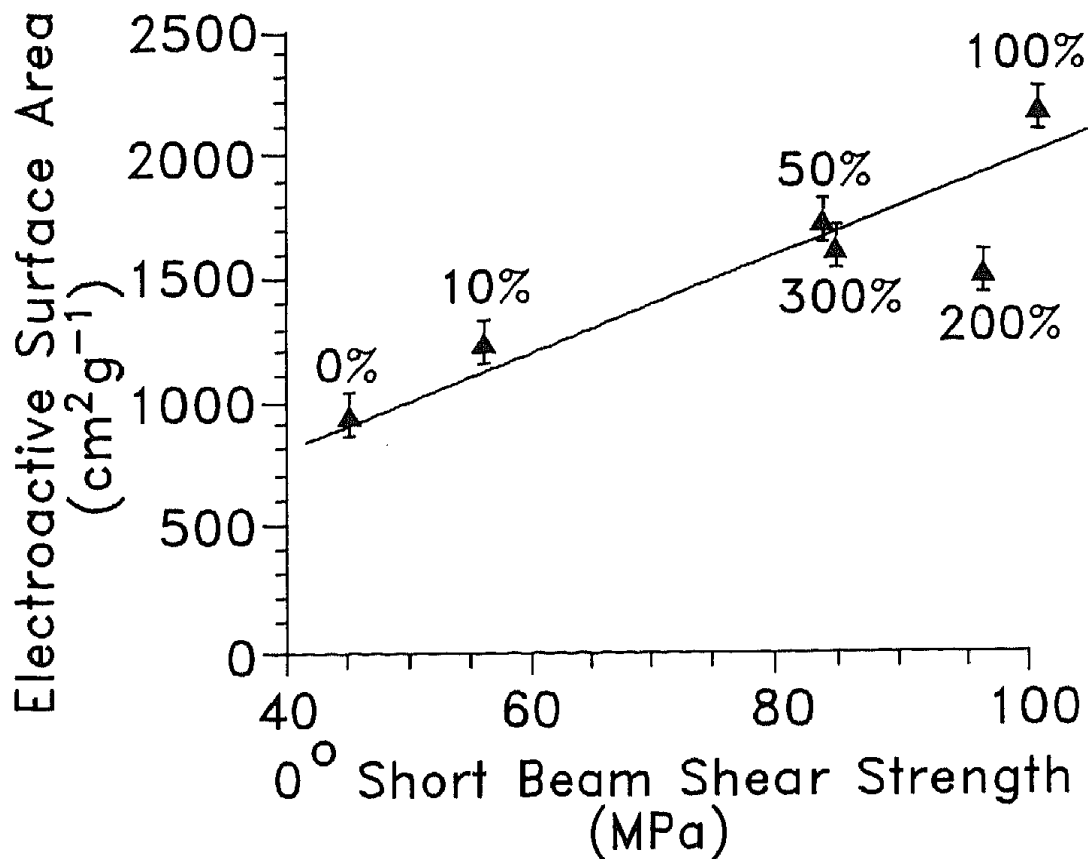


Figure 3. Correlation of electroactive surface area for 33-600 fibres with the 0° Short Beam Shear Strength for 33-600 fibre embedded in CG9101 epoxy resin.

conducted in the gas phase, determines area based on specific chemically reactive surface states. The electrochemical method determines areas which the hexacyanoferrate(III) ion can reach (obviously a smaller electroactive probe may give a greater surface area) and at which electron transfer is a facile process. However, the trend is the same as the surface treatment level increases.

The correlation between the electroactive surface area of 43-750 fibre and the reciprocal of the critical fragment aspect ratio (proportional to the strength of bonding between the fibre and the epoxy resin matrix) determined by the single filament fragmentation tests [1], is demonstrated in Figure 5. These data are summarized for 33-600 and 43-750 fibres in Tables 1 and 2, respectively.

3.2 Other Electrochemical Properties

Data related to the ease of electron transfer across the fibre-electrolyte interface can be obtained by plotting the peak reduction potential, E_{red} (see Figure 1), against $\log_{10}[v]$ (not shown), where v is the scan rate in volts s^{-1} . At low scan rates the value of E_{red} is invariant of the scan rate. This is indicative of a fully reversible electron transfer reaction. These scan rates were used in the calculation of electroactive surface areas in section 3.1. At higher scan rates the value of E_{red} becomes dependent on the scan rate as the electrochemical reaction becomes more irreversible and can be expressed by the relationship [5]

$$E_{\text{red}} = E_{\text{const}} - 2.303 \cdot RT \cdot \log[v] / 2\alpha NF \quad \text{at } 25^\circ\text{C}, v \gtrsim 100 \text{ mVs}^{-1},$$

where E_{const} is a constant, F is Faraday's constant, R is the gas constant and N is the

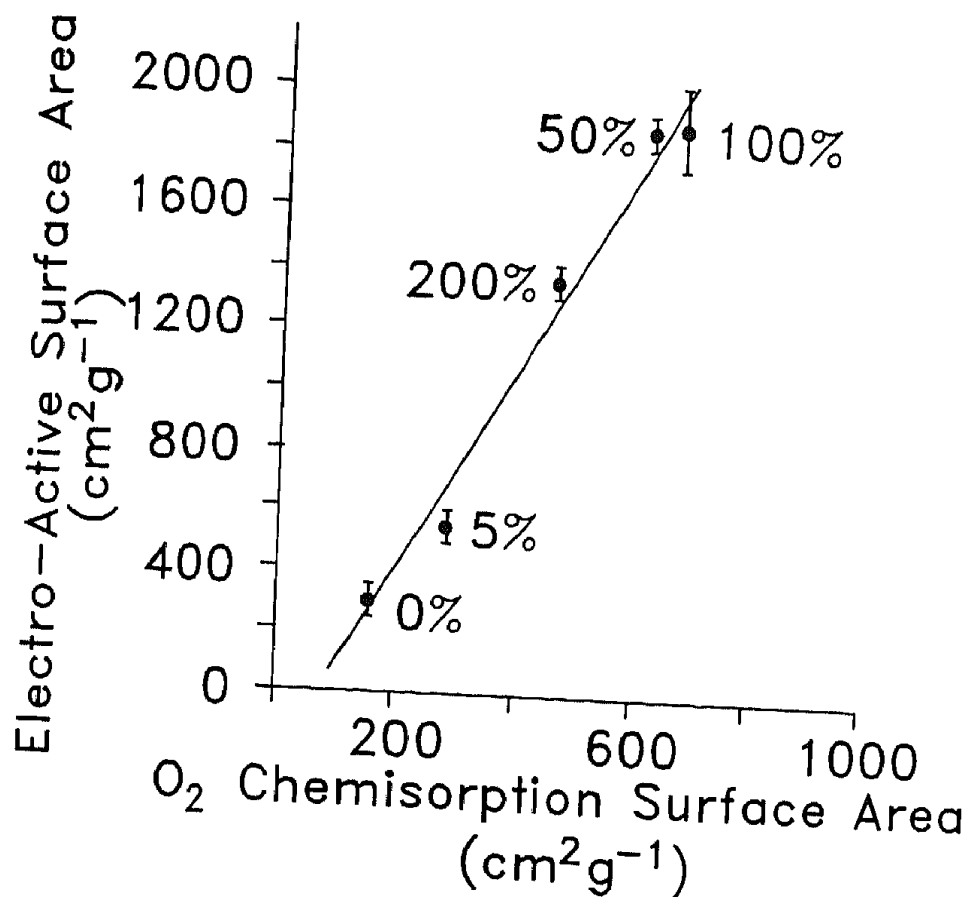


Figure 4. Correlation of electroactive surface area with surface area determined by oxygen chemisorption for 43-750 fibres.

number of electrons transferred in the rate limiting step. The term α is the transfer fraction related to the effect that the applied potential has on the activation energy of the rate limiting step. Application of an external voltage, $\Delta\Phi$, such that a reduction reaction is favoured, drops the Gibbs free-energy of activation for the reduction reaction process by a value $-\alpha NF\Delta\Phi$. A fall in αN means that the reduction reaction becomes a more activated process, or more difficult to achieve. The value of αN calculated for both 33-600 and 43-750 fibres is plotted as a function of surface treatment level in Figure 6. The value of αN decreases to a plateau at 100-200% treatment for the 33-600 fibre and at 100% treatment for 43-750 fibres. In general the αN values for the 33-600 fibres are higher than those measured for the 43-750 fibres indicating the electron transfer reaction to be a far more facile process at the former fibre. This may be due in part to the larger active surface area at 33-600 fibres. The causes of the change in αN may be related to changes in the reduction mechanism of the hexacyanoferrate(III) ion or changes in the adsorption mechanism of the ion in the proximity of the fibre electrode surface.

4. DISCUSSION

One possible interpretation of these results is that the surface treatment initially erodes surface irregularities. This erosion process possibly leads to the generation of 'chemically reactive' carbon fragments that are revealed as an increase in chemically and electrochemically active surface states. The adhesion of a matrix resin to the carbon fibre surface depends, in part, on these active surface areas as shown by the good

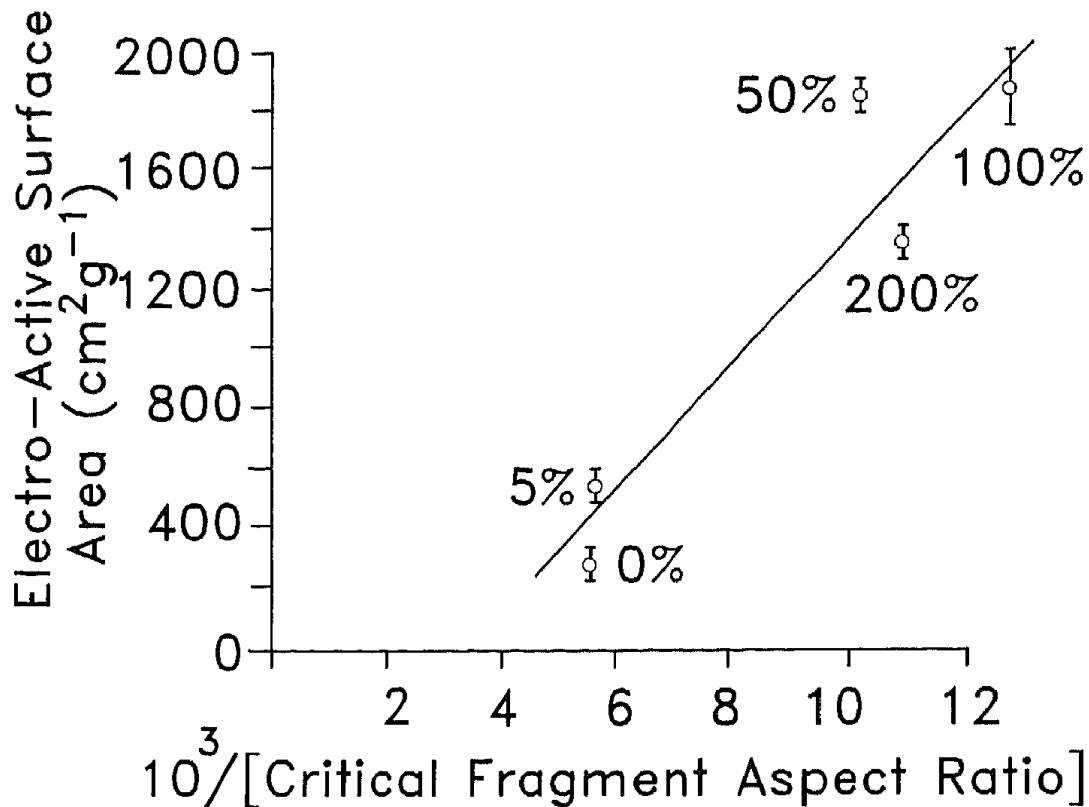


Figure 5. Variation of electroactive surface area with the reciprocal of the critical fragment aspect ratio for 43-750 fibres.

correlation between electroactive area and matrix adhesion parameters (Figures 3 and 5).

Beyond the 100% surface treatment level even the active surface carbons are eroded, possibly smoothing the surface but leaving it predominantly populated by basal-plane graphitic structures at very high surface treatment levels. These are not chemically or electrochemically as active as edge-plane structures. The anisotropic electrical conductivity of single crystal graphite is known. The conductivity along the basal-plane is some four orders of magnitude higher than the conductivity perpendicular to it [6].

The drop in reversibility above 100% surface treatment could be explained by the formation of surface oxygen groups (carboxylic acid and phenolic groups) that are known to be added during surface treatment. These oxygen groups attain a maximum population at the 100-200% treatment level [2]. These could have either a blocking effect on the transfer of electrons across the fibre-electrolyte interface or an effect on the ion adsorption at the interface.

Changes in the ionic adsorption at the fibre-electrolyte interface are backed up by the various surface energy data available. The adsorption of ions at the electrode surface will be affected by changes in electrode surface energy [7]. Previous studies on 33-600 fibres have shown that the surface energy rises as the surface treatment level rises, but becomes invariant above 100% treatment levels [2]. The resolved polar component of the surface energy rises with increased surface oxygen levels caused by increased surface treatment (Table 3). At the same time the resolved dispersive component of the fibre surface energy decreases slightly. Figure 7 shows the evolution of αN with the polar component of the fibre surface energy, γ_s^p , for different surface treatment levels. Obviously the increase in surface oxygen levels (causing a rise in

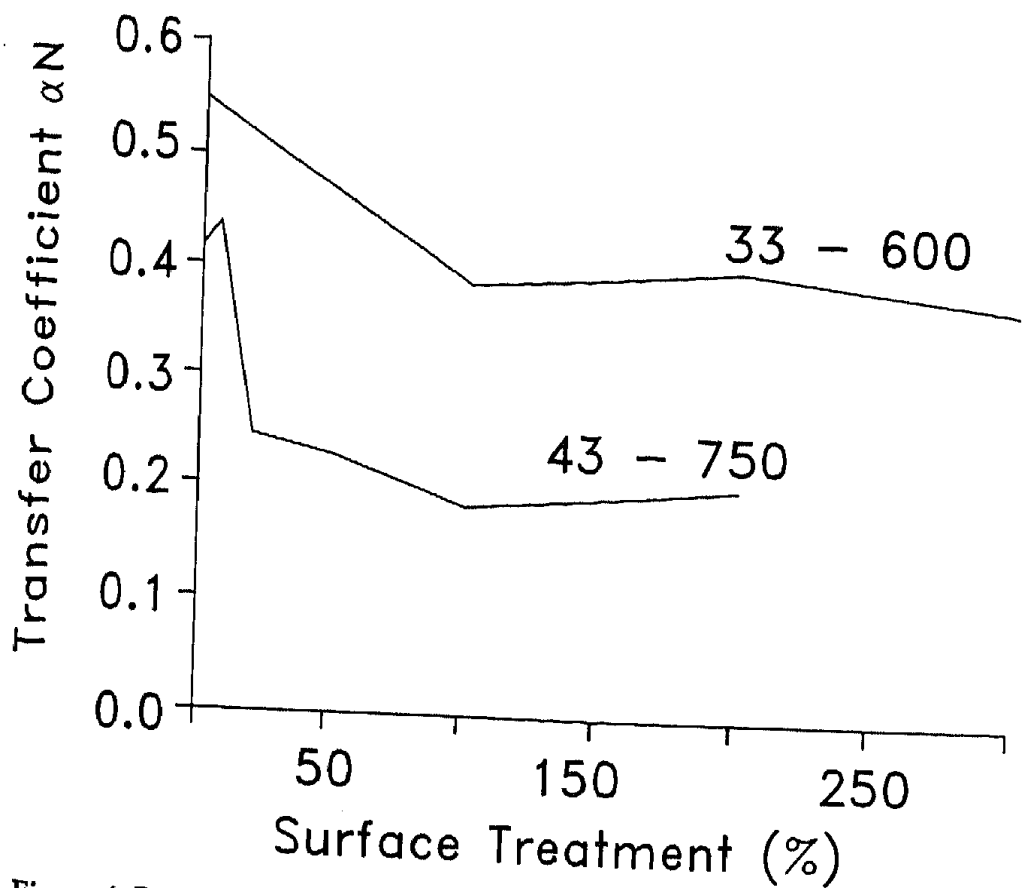


Figure 6. Evolution of the transfer coefficient, αN , with surface treatment level.

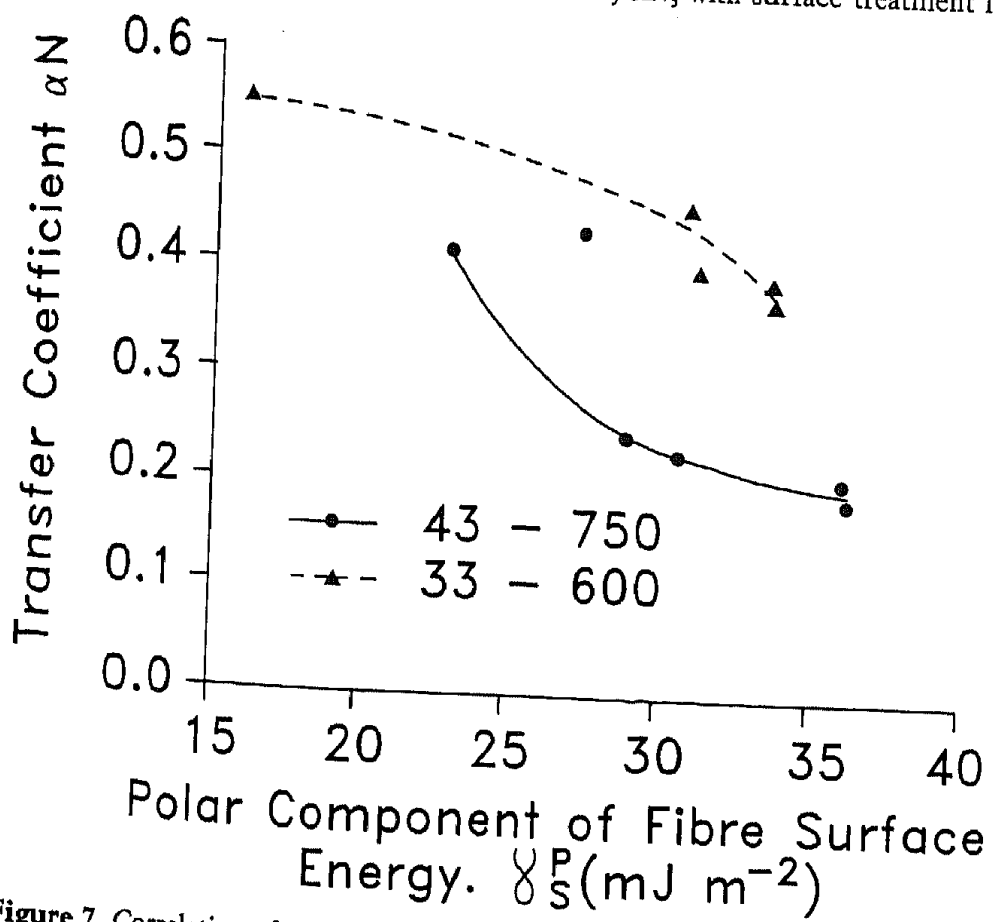


Figure 7. Correlation of transfer coefficient with polar component of the fibre surface energy.

Table 3.

Surface treatment (%)	33-600			43-750		
	Surface energy (mJ m^{-2})			Surface energy (mJ m^{-2})		
	αN	Polar γ_s^p	Total γ_s^t	αN	Polar γ_s^p	Total γ_s^t
0	0.548	15.9	41.5	0.412	22.87	47.2
5				0.434	27.39	49.0
20				0.243	29.05	51.4
50	0.459	31.0	52.9	0.229	30.75	52.3
100	0.385	33.7	55.3	0.187	36.14	56.9
200	0.401	31.2	53.1	0.206	35.97	56.3
300	0.375	33.6	54.8			

surface energy) causes a change in the ionic surface adsorption mechanism that is shown by the drop in αN . The rise in surface oxygen levels makes the transfer of electrons across the fibre-electrolyte interface a more activated process. The surface energy data tend to support the fact that on treatment, the surface becomes more polar in character suggesting that surface bound oxygen containing groups are the cause. These will tend to repel the hexacyanoferrate(III) anions giving the appearance of a less favourable electrochemical reaction (αN decreases). The values for αN are higher at 33-600 fibres than at 43-750 fibres, indicating a less activated more facile electrochemical reaction. The polar component of the fibre surface energy is lower for the 33-600 fibres (Table 4). However, the total surface energy values for the two fibre types are very similar.

This interpretation is of course still speculative. The important point is that the observed electroactive surface area correlates with the area calculated, from oxygen chemisorption studies. Obviously the electroactive surface area includes contributions from both surface area and surface chemistry, both of which are important in controlling composite performance [1,2].

5. CONCLUSION

In summary, cyclic voltammetry of external redox probes has been shown to be a viable technique for the study of carbon fibre electrode surfaces, yielding information relevant to the translation of the fibre properties to polymer matrix composite materials. The technique has highlighted an increase in active surface area by erosion during the oxidative surface treatment to a maximum at the 100% treatment level. However, at the same time, the electrochemical reaction is made more irreversible possibly due to surface oxygen containing species that reach a maximum population between 100% and 200% treatment. Beyond the 100% treatment level the electrochemical reaction becomes slightly less irreversible and the active surface area falls slightly. Further erosion of the surface (including the surface oxygen states) that leaves the surface populated by less active basal-plane graphitic structures is a possible explanation.

Of particular interest is the observed correlation between the measured electroactive surface area data and independently measured surface properties such as the O_2 chemisorption data and matrix adhesion data. Suitable calibration techniques are being

sought to aid in the full understanding and interpretation of these data in terms of ultimate composite performance.

References

- [1] L.T. Drzal, M.J. Rich and P.F. Lloyd, *J. Adhesion*, 16, 1 (1982).
- [2] R. Robinson, S. Lehmann, G. Askew, D. Wilford, C. Megerdigian and R. Papalia, in *High Tech—The Way into the Nineties*, Eds. K. Brunsch, H.-D. Gölden and C.-M. Herkert, Amsterdam Elsevier Science Publishers (Netherlands), 299 (1986).
- [3] R.N. Adams, in *Progress in Polarography*, Eds. P. Zuman and I.M. Koltoff, Interscience, New York, 1968.
- [4] F.J. Miller and M.E. Zittel, *Anal. Chem.*, 35, 1866 (1963).
- [5] H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, 59, 495 (1955) and L. Meites and Y. Israel, *J. Amer. Chem. Soc.*, 83, 409 (1961).
- [6] K.S. Krishnan and N. Ganguli, *Nature*, 144, 667 (1939).
- [7] D.M. Mohilner, in *Electroanalytical Chemistry*, Ed. A.J. Bard, Marcel Dekker (NY), 1, 241 and R.S. Perkins and T.N. Anderson, in *Modern Aspects of Electrochemistry*, Eds. J.O'M. Bockris and B.E. Conway, Marcel Dekker (NY), 5, 230 (1969).