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X-ray photoelectron spectroscopic studies of carbon fibre surfaces

Part 6 Pilot plant surface treatment and epoxy resin composites

JOHN HARVEY
Materials and Structures Department, Royal Aircraft Establishment, Farnborough, Hants GU14 6TD, UK

CAROL KOZLOWSKI, PETER M. A. SHERWOOD*
Department of Inorganic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Carbon fibres were anodically surface treated by passing them continuously through an electrochemical bath, thus simulating a possible industrial surface-treatment process. Composites were made from these fibres with an epoxy resin and their interlaminar shear strength (ILSS) tested. The surfaces of the fibres were examined by X-ray photoelectron spectroscopy after treatment. Both galvanostatic and potentiostatic cell control led to treated fibres that produced composites with high interlaminar shear strengths (80 to 90 MPa). The effect of potential, reaction time, electrolyte and subsequent heating of the fibres in a vacuum on the ILSS of the composites is reported. The rise in ILSS with surface treatment is not dependent upon the O–1 s : C–1 s ratios or the amount of carboxyl functionality present on the surface. This supports the view that mechanical keying of the resin to the fibre surface plays an important role in forming the fibre–resin bond.

1. Introduction

The nature of the surface of carbon fibres is of considerable relevance to the mechanical properties of composite materials made from the fibres. Various surface sensitive methods have been used to examine the fibre surfaces, including X-ray photoelectron spectroscopy (XPS). There have been a number of XPS studies of carbon fibre surfaces ([1] and the references therein). We have reported a series of studies [1–6] in this area, and in this paper we examine the effects of oxidative surface treatments, carried out on a pilot-plant scale, on the X-ray photoelectron spectrum of the fibres and the properties of the resulting epoxy resin composites.

It is well known that oxidative surface treatment of fibres prior to their incorporation into epoxy resins increases the interlaminar shear strength (ILSS) of the resulting composities. Many workers [e.g. 3] have examined fibres that have been commercially treated, but details of process conditions were unknown or confidential. We (amongst others) have shown [1–6] that anodic oxidation of fibres in different electrolytes can produce a variety of changes in the chemical and physical nature of the fibre surfaces. All these treatments were carried out in the laboratory where the cell was extremely clean and electrolyte solutions were almost pure. On an industrial scale these stringent conditions are neither practical nor economical. The use of a commercial cell enables a continuous tow of fibres to be treated in sufficient quantities for composites to be made. We have treated fibres in a pilot-plant "commercial-type" cell which allows the effect of a known commercial-type surface treatment on the ILSS of the composite to be studied.

The electrochemical conditions can be carried under galvanostatic and potentiostatic control. Our study used both methods of control to determine optimal treatment conditions.

2. Experimental procedure

Type 2 carbon fibres (heated to a maximum of 1500° C in manufacture) were used in these experiments.

The electrochemistry was carried out using a specially built pilot plant. This plant was able to treat the relatively large amounts of carbon fibres needed to prepare composites; about 7 g are needed to make a 1 cm × 0.2 cm × 8 cm composite bar. Fig. 1 shows a schematic diagram of the pilot plant. The cell (Fig 2) consisted of a tow of fibres acting as the working electrode (anode) and two graphite plates as the counter electrode. There were about 3000 fibres (of a diameter between 2 and 5 μm) in the tow, and the cell was constructed so that there was a 60 cm total length of immersed fibre. The fibre was pulled through the cell at a constant rate. For some treatments the cell current was kept constant by means of a power supply (galvanostat). For constant-potential treatments, a reference electrode (saturated calomel electrode

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**Present address*: Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, USA

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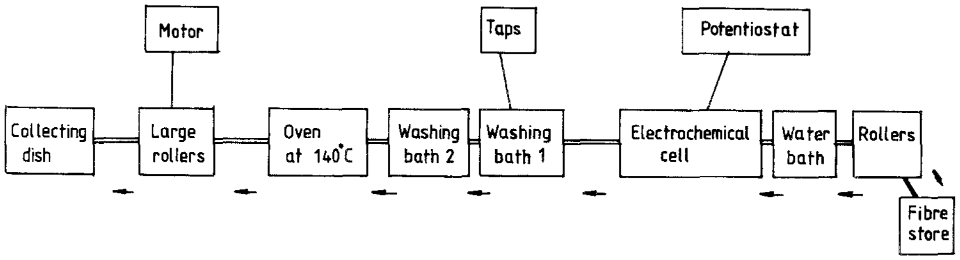


Figure 1 Schematic diagram of the pilot plant.

(SCE)) was placed as close as possible to the fibre by means of a Luggin capillary. The potential was controlled using a potentiostat. All solutions were made using distilled water and Analar grade chemicals. The reaction time of the fibres (i.e. the time during which the fibres were immersed in the electrolyte solutions) was 9 sec, unless otherwise stated.

Unidirectional fibre–resin composites were made in the following way: a mould was treated with ROCOL(PTFE) release agent and preheated to 60° C. A resin mixture was prepared, consisting of Shell Epikote 828(2,2-diphenyl propane-*p*,*p*′-diglycidine ether), 100 parts by weight; nadic methyl anhydride, 90 parts by weight; and Shell Epikure K618, 4 parts by weight, and warmed to 60° C. Thirty lengths (this quantity of fibre was sufficient to give a volume fraction of 60% in the final unidirectional composite) of treated carbon fibre was impregnated by placing in the resin mix for 5 min at 60° C. The bundle of tows was then removed, the excess resin drained off and the bundle of tows placed in the mould which was clamped in position with 2 mm spacers. The bar was then cured at 120° C for 2 h and post cured at 180° C for 16 h. The mould was allowed to cool, the bar removed, and the edges and ends trimmed. It was then cut into eight specimens (about 12 mm in length) for interlaminar shear testing.

The ILSS was measured by using a short beam shear test with a span–depth ratio of approximately 6. The load was applied and measured with an Instron testing machine.

Samples of fibre for XPS analysis were prepared by washing thoroughly in triply distilled water and drying in an oven at 100° C. All sample transfers were made in air.

XPS spectra were obtained using an AEI (Kratos) ES200B X-ray photoelectron spectrometer operated in the FRR mode using MgK_α X-radiation (240 W). Data were collected using an Apple II microcomputer linked to an IBM 370/168 computer, the latter being used for most of the data analysis [7]. The base pressure in the sample chamber was in the range 10^{-8} to 10^{-9} torr.

The curve fitting was carried out by using a non-linear least-squares curve-fitting program with a Gaussian–Lorentzian product function [7, 8]. The C–1 s binding energy of the graphitic peak was taken as 284.6 eV for calibration purposes. This peak overlapped directly with the signal one would expect from the hydrocarbon contamination often used in XPS for calibration, though we would expect that there is little, if any, hydrocarbon contamination on the fibres.

3. Results and discussion

We have not shown an overall XPS spectrum for any of these fibres, since they are all essentially similar showing only a C–ls peak and an O–ls peak in the case of oxidized fibres. No N–ls peak could be observed. Checks were made for any fibre-surface decomposition [4], but no significant decomposition occurred during the collection time of the spectra reported here.

3.1. The effect of galvanostatic oxidation on the fibre surface

Fibres were treated in each of several different electrolytes using a series of currents. These treated fibres

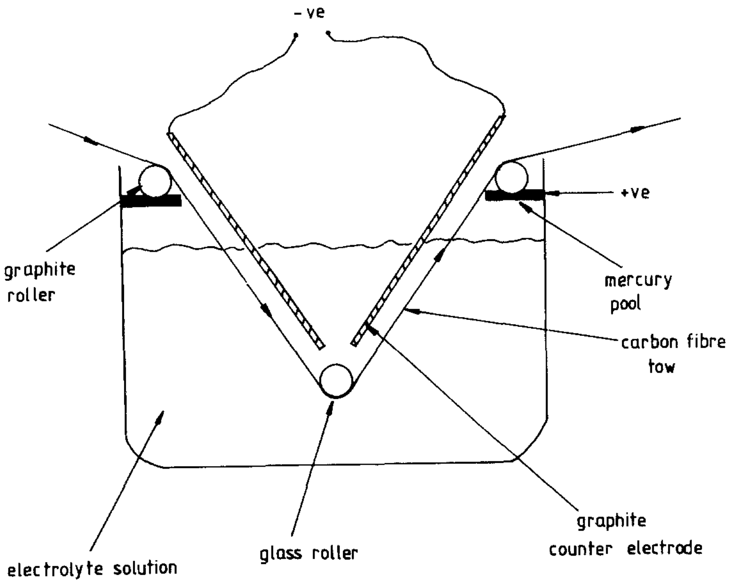


Figure 2 Industrial type electrochemical cell.

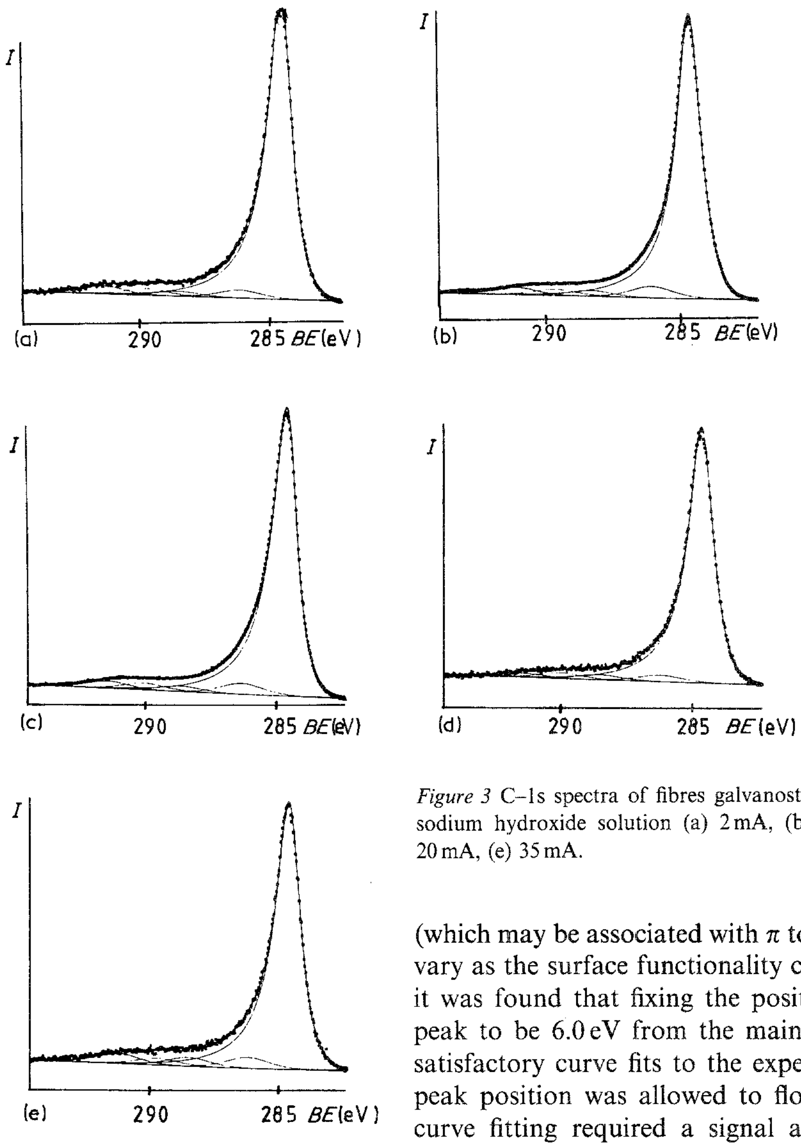


Figure 3 C–1s spectra of fibres galvanostatically treated in 0.5 M sodium hydroxide solution (a) 2 mA, (b) 5 mA, (c) 10 mA, (d) 20 mA, (e) 35 mA.

were incorporated into the resin. A series of fibre samples treated in sodium hydroxide and another treated in potassium dichromate were chosen for examination using XPS. The results of this study are discussed below.

3.1.1. The C–1s spectra of treated fibres

From laboratory-treated fibres [1–5] it is known that certain types of functional groups give rise to signals in the photoelectron spectrum with a particular range of binding energies. It has already been shown that functional groups giving rise to chemically shifted signals at 1.6, 2.1 and 4.0 eV from the main carbon signal can be produced from a variety of chemical treatments. There are also plasmon and satellite signals present in the spectra with kinetic energies 6.9 eV (plasmon) and 6.0 eV (satellite) less than this main peak. The spectra in this study were fitted to a graphitic peak and combinations of signals at 1.6, 2.1 and 4.0 eV from the main graphitic signal, together with a fourth peak. The graphitic peak had an exponential tail and a Gaussian–Lorentzian mix that were fixed at 0.0275 (360 points) and 0.840, respectively. A plasmon signal was included fixed at 6.9 eV from the graphitic peak.

One would expect the position of a satellite peak (which may be associated with π to π^* phenomena) to vary as the surface functionality changes, and indeed it was found that fixing the position of the satellite peak to be 6.0 eV from the main peak did not give satisfactory curve fits to the experimental data. The peak position was allowed to float and in all cases curve fitting required a signal at between 5.1 and 5.9 eV from the main graphitic signal. This contrasts with results from laboratory-treated fibres [1–5]. The solutions used for this commercial-type treatment have not been deaerated. This may lead to dissolved oxygen reacting with carboxyl groups already present on the fibre surfaces to give carbonate, which would explain the fourth peak. Carbonate is said to have been produced in potassium hydroxide solutions using other types of carbon [9].

3.1.2. Sodium hydroxide results

Fig. 3 shows the C–1s spectra of fibres treated in sodium hydroxide (0.5 M) using several cell currents. It can be seen that very little surface oxidation has taken place compared to fibres treated under laboratory conditions [1]. This is most probably due to the short reaction times (9 sec). The variation in relative areas of the component peaks with respect to the main graphitic signal are given in Table I.

It can be seen that for higher currents the amount of carboxyl/ester groups (4.0 eV) is almost double the relative amount (with respect to the graphitic peak) produced using lower currents. The relative intensity of alcohol groups (1.6 eV) varies from 0.036 to 0.058, although there seems to be no relationship between their amount and cell current. The relative intensity of the signal at 5.4 eV remains almost constant (0.035 to 0.032).

TABLE I The relative area ratios (with reference to the graphitic peak) of chemically shifted species in the C–1s spectra of fibres galvanostatically treated in sodium hydroxide (0.5 M)

Current (mA)	Area ratios (eV)			
	1.6	4.0	5.4	6.9
2	0.038	0.024	0.032	0.039
5	0.058	0.030	0.032	0.038
10	0.053	0.028	0.033	0.035
20	0.036	0.029	0.032	0.022
35	0.052	0.046	0.035	0.054

The plasmon intensity decreases with current applied (with the exception of that corresponding to 35 mA). This is to be expected because this plasmon is a feature of the main fibre lattice and, as the surface oxygen concentration increases, less of the bulk fibre structure is present in the sampling depth of the photoelectrons. (The reason for the exception is not known.)

3.1.3. Potassium dichromate results

The results obtained from curve fitting the C–1s spectra from fibres treated in potassium dichromate (0.02 M) and the area ratios with respect to the main graphitic signal are shown in Table II. As the current increases, the area ratio of the carboxyl groups (4.0 eV) also increases from 0.017 at 0 mA to 0.069 at 50 mA. The alcohol (1.6 eV) intensity varies with current, and in general there appear to be more alcohol-type groups produced at low currents than at high currents. At 10 mA and above, the carboxyl intensity is greater than the alcohol intensity. This is unlike the sodium hydroxide case where the number of carboxyl groups is always greater than the alcohol groups. This may be due to potassium dichromate being a good oxidizing agent, well known to be able to oxidize alcohols to carboxylic acids. The potassium dichromate was known to be reduced during treatment because the solution in the washing baths turned green due to the presence of Cr(III) aqueous ions. No chromium remained on the fibre after washing, as it was not detected in the spectrometer.

For high current (10 to 50 mA) treatments a signal at 5.8 eV from the main peak was present. This peak position does suggest that it arises from satellite processes (see section 3.1.1 for a discussion of the variable position of this peak). For lower currents (0 to 5 mA) a peak at 5.1 eV was present which corresponds to carbonate.

TABLE II The relative area ratios (with reference to the graphitic peak) of chemically shifted species in the C–1s spectra of fibres galvanostatically treated in $K_2Cr_2O_7$ (0.02 M)

Current (mA)	Area ratios (eV)				
	1.6	4.0	5.1	5.8	6.9
0	0.067	0.017	0.047	–	0.028
2	0.061	0.031	0.034	–	0.022
5	0.139	0.009	0.057	–	0.035
10	0.033	0.044	–	0.028	0.037
20	0.032	0.056	–	0.023	0.042
35	0.041	0.066	–	0.032	0.035
50	0.049	0.069	–	0.031	0.035

TABLE III Curve-fitting results and relative areas for O–1s spectra of fibres galvanostatically treated in sodium hydroxide (0.5 M)

Current (mA)	Binding energy (eV)	Fraction of total O–1s area
2	532.4	0.719
	533.9	0.281
5	532.7	0.855
	533.8	0.145
10	532.6	0.723
	533.7	0.277
20	532.4	0.669
	533.7	0.331
35	532.4	0.874
	534.2	0.126

3.1.4. The O–ls spectra

3.1.4.1. Sodium hydroxide results. Table III shows the curve-fitting results from the O–ls spectra of these fibre samples. These spectra consist of two resolvable oxygen species with binding energies around 533.9 eV and 532.4 eV.

The higher binding energy component corresponds to –O– type groups (in agreement with studies of laboratory-treated samples). The lower binding energy value is about one volt higher than that for =O character in laboratory-treated samples, and may have both =O and –O– character. Such an interpretation is supported by the greater intensity of the lower binding energy component (see Table III), which must have some –O– character since the C–ls spectra shows more alcohol groups than carbonyls.

3.1.4.2. Potassium dichromate results. The fitted O–ls spectra for samples treated in potassium dichromate are shown in Fig. 4. The binding energies and area ratios are given in Table IV. At currents below 20 mA only two oxygen species are produced, but above this cell current an additional peak, perhaps due to absorbed water [1] is present on the fibre surface. The binding energies for both =O and –O– decrease with increasing current, while the intensity of the former component increases relative to the latter component with increasing current.

3.1.4.3. Oxygen/carbon intensity ratios. For fibres treated in sodium hydroxide the O–ls : C–ls ratio varies for different cell currents, there being no observable

TABLE IV Curve-fitting results and relative areas for O–1s spectra of fibres galvanostatically treated in $K_2Cr_2O_7$ (0.02 M)

Current (mA)	Binding energy (eV)	Fraction of total O–1s area
0	532.6	0.819
	533.9	0.181
2	532.3	0.756
	533.8	0.244
5	532.5	0.788
	533.7	0.212
20	532.1	0.562
	533.4	0.370
	536.0	0.068
35	531.8	0.514
	533.3	0.389
	536.0	0.097

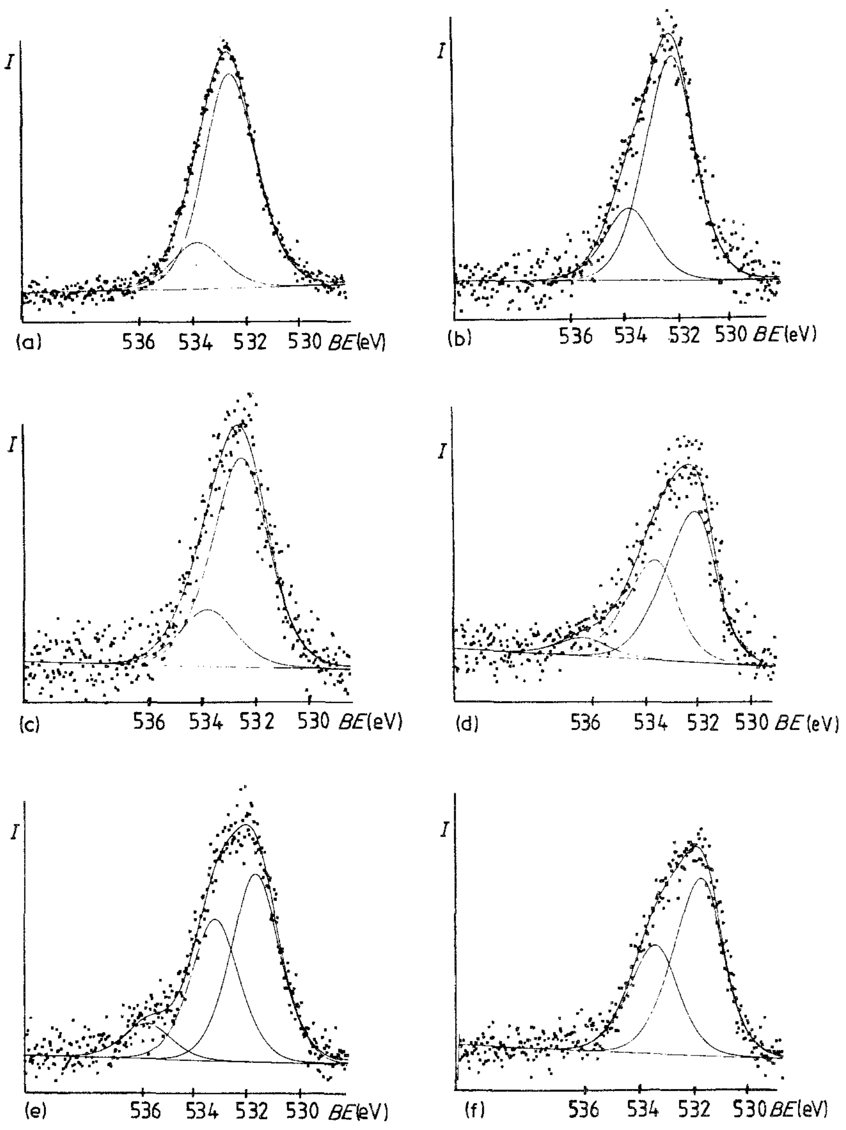


Figure 4 O-1 s spectra of fibres galvanostatically treated in 0.02 M potassium dichromate solution. (a) 0 mA, (b) 2 mA, (c) 5 mA, (d) 20 mA, (e) 35 mA, (f) 50 mA.

trend in the results (see Table V). These ratios were much smaller (approximately 1/4) than those found on laboratory-treated samples due, in part, to the limited reaction times.

For fibres treated in potassium dichromate this ratio generally increases with increasing current from 0.067 to 0.200 (see Table V). These ratios are higher than those for sodium hydroxide; this is not surprising because potassium dichromate is a good oxidizing agent in itself. In addition the pH of the solution is lower than for sodium hydroxide which would lead to more oxidation [1].

TABLE V O-1s:C-1s area ratios for galvanostatically treated fibres

Current (mA)	O-1s:C-1s area ratio	
	NaOH	$K_2Cr_2O_7$
0	–	0.067
2	0.054	0.096
5	0.049	0.079
10	0.061	–
20	0.071	0.085
35	0.088	0.184
50	–	0.200

3.2. The effect of galvanostatic surface treatment upon the ILSS of composites

Fig. 5a shows the IlSSs of composites made from fibres treated with sodium hydroxide and with potassium dichromate. Both plots show that the ILSS initially increases with increasing cell currents up to 20 mA, thereafter remaining constant at 86 MPa. This plateau in the ILSS could be due to several factors:

(a) all the reactive sites on the fibre surface having been utilized and the maximum possible ILSS therefore achieved using that particular electrolyte;

(b) the limiting strength of the resin; or

(c) the limit of the ILSS test itself.

The rise in ILSS occurs at the same cell current suggesting that the same reaction is involved in both cases. There also seems to be a slight dependence upon concentration in the sodium hydroxide case.

Fig. 5b shows a plot of ILSS against current for sodium chloride and oxalic acid treatments. The results for sodium chloride are very similar to those reported above. No chlorine was found on the surface. Oxalic acid, however, inhibited any increase in ILSS. This may be due either to a polymer being formed on the surface, preventing fibre–resin bonding, or to the oxalate ions inhibiting the reaction responsible for good

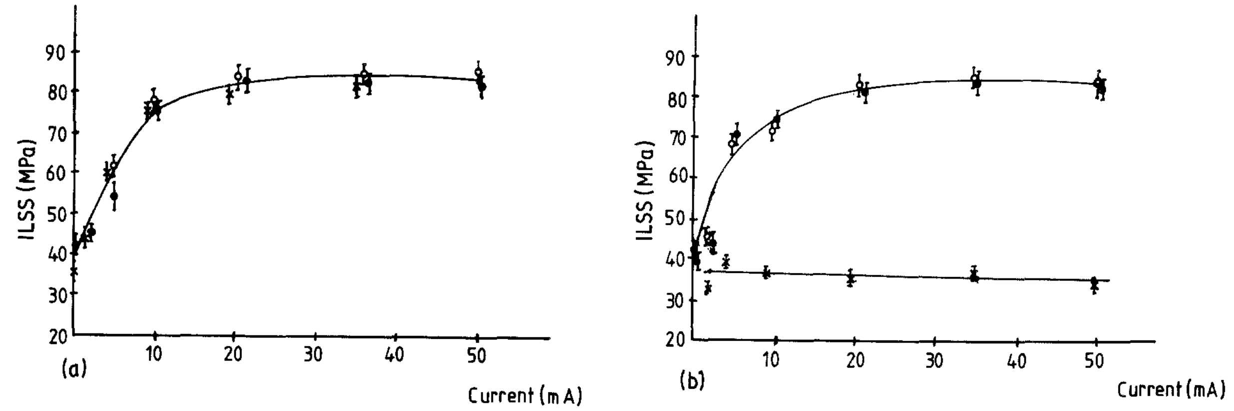


Figure 5 Graphs showing the variation of ILSS with cell current for galvanostatically treated fibres in (a) sodium hydroxide and potassium dichromate electrolytes (x) 0.5 M NaOH, (○) 6.7 × 10^{-3} M $K_2Cr_2O_7$, (●) 0.02 M $K_2Cr_2O_7$. (b) Sodium chloride and oxalic acid electrolytes. (○) 1.04 M NaCl, (●) 0.23 M NaCl, (×) 0.07 M oxalic acid.

adhesion. The latter seems to be the case because there is no evidence in the C–1s spectrum of a large amount of any chemically shifted species (e.g. C = 0) due to a polymer being formed on the surface. The O–1s : C–1s ratio is very low, 0.0257, suggesting that the oxidation of the fibre surface has been inhibited by the electrolyte.

A set of studies to estimate the effect of reaction time was also performed. The current used was 50 mA in potassium dichromate solution. The ILSS of the composites remained constant, even though the time that the fibres spent in solution was increased (see Fig. 6). It seems that 86 MPa is the maximum ILSS value that can be obtained for this type of treatment and composite production. For a cell current of 15 mA in 2 × 10^{-3} M NaOH, the time spent in solution was doubled. The ILSS of the resulting composite increased 10 MPa compared to the lesser reaction time (the maximum value of ILSS obtained for this solution). This suggests that the same reaction can occur at lower currents if the reaction time is increased.

3.3. The effect of potentiostatic treatment on carbon fibres

The only difference between this type of cell condition and those mentioned previously is that in this case the potential is kept constant using a potentiostat and a calomel reference electrode. It is not possible to maintain complete potential control in this experiment, as was possible in our experiments involving small number of fibres under laboratory conditions [1, 2, 4]. This lack of complete potential control arises because of the necessary cell design required to treat a large batch of fibres. Thus the potential (Fig. 2) will vary along the tow due to ohmic drop and other problems associated with scaling up the cell.

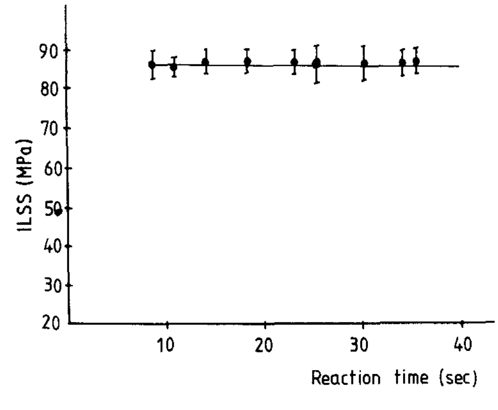


Figure 6 Graph showing the variation of ILSS with the time spent in the electrolyte as measured by the rate of the motor that drawns the fibres through the electrolyte.

When the XPS results of our previous surface studies carried out under laboratory conditions with small numbers of fibres are compared with those in this paper, it is clear that approximately the same surface chemistry corresponds to a higher potential in the cell in this paper. Thus after 10 sec polarization in nitric acid at 2.0 V the $C_{ox}:C_{graph}$ ratio was 0.48 for laboratory-treated fibres, while in the pilot plant the ratio is 0.18, illustrating the lower potential in the pilot plant. The XPS results show that the pilot-plant samples are always oxidized under the potentials discussed in this paper. The rest potentials of the fibres were measured in 0.5 M nitric acid and 1.3 M ammonium bicarbonate, and found to be 0.126 V and 0.208 V, respectively (with reference to the SCE). The cell was set up for steady state conditions and the potential measured on the DVM remained constant (±0.0001 V SCE).

While we recognize the reduced control over fibre treatment in the pilot-plant cell, we feel that the similarity of the surface chemistry to that in the controlled laboratory cell shows that fibres can be produced with controlled surface chemistry in the pilot plant by potentiostatic treatment. The pilot plant allows us to make sufficient amounts of treated fibre to examine composite properties.

3.3.1. Nitric acid results

Fig. 7 shows the C–1s spectra for fibres polarized to several potentials. It can be seen that at high potentials the amount of chemically shifted species increases significantly. At potentials +3.0 V and +4.0 V, the graphitic nature of the main peak is lost. We have previously discussed the exponential tail shape of the C–1s peak associated conduction band interaction due to the extended π system of graphitic carbon [4]. This tail is found to be lost from the C–1s peak associated with graphitic carbon at +3.0 V and +4.0 V. The loss of graphitic nature is most probably due to exfoliation

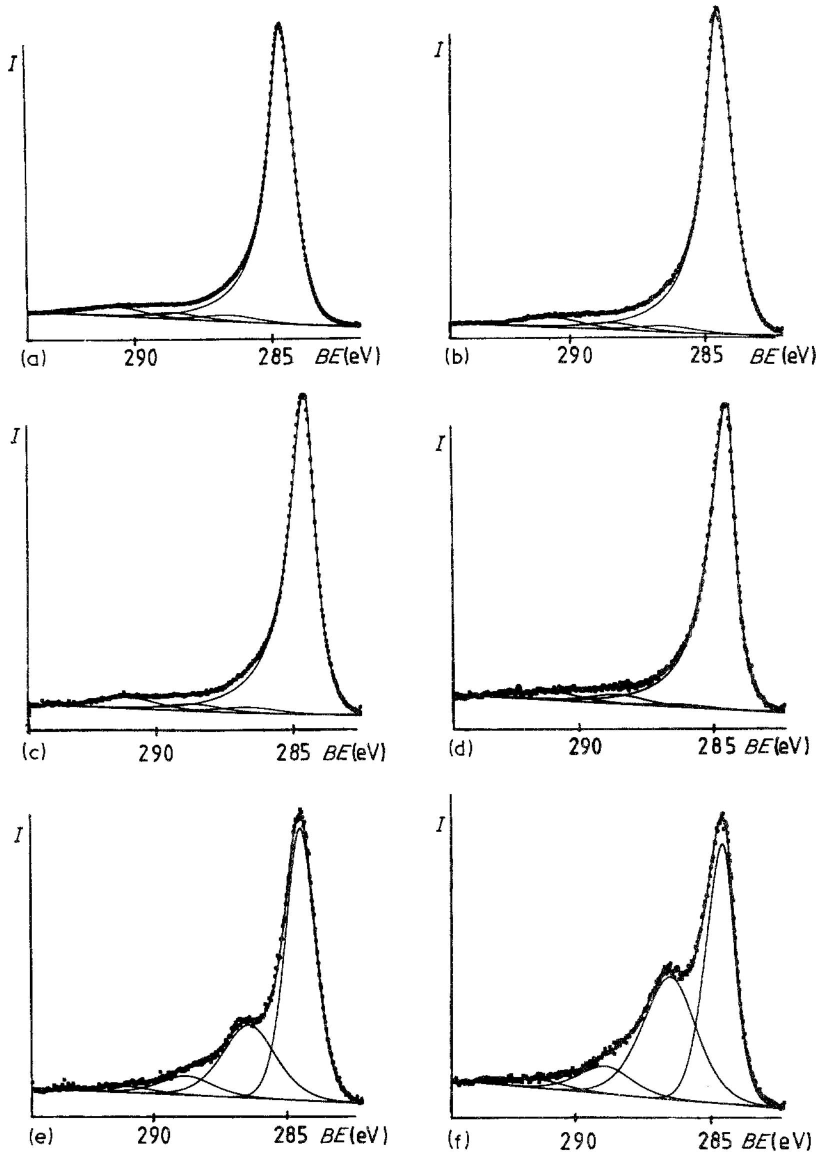


Figure 7 C–1s spectra of fibres polarized to various potentials (against SCE) in 0.5 M nitric acid solution. (a) 1.0 V, (b) 1.1 V, (c) 1.3 V, (d) 1.5 V, (e) 3.0 V, (f) 4.0 V.

of the fibre surface. In general as the graphite of the carbon fibres becomes more highly functionalized, so the extended π-system is eventually lost.

The spectra have been fitted to four peaks (as in studies of laboratory-treated samples [1]), a main carbon peak, and three chemically shifted species at 2.1, 4.2 and > 6.0 eV. The peak above 6.0 eV may have plasmon and satellite contributions, but using two separate peaks to describe this region did not allow the curve-fitting program to converge. The variation in area ratio for the chemically shifted species (with respect to the main carbon peak) against potential is shown in Fig. 8. The total intensity of chemically shifted species is also shown. It can be seen that a rise in oxidation starts to occur at 2.0 V. The intensity of both oxide 1 and oxide 2 increases with potential, but as in the laboratory case the peak at 2.0 V increases to a much greater extent. The signal intensity above 6.0 eV remains constant.

Unlike the laboratory-treated fibres (in HNO_3), the O–1s spectra consist of two resolvable components at low potentials and three at higher potentials (3.0 V and 4.0 V). The binding energies for the two main components are 533.5 eV (± 0.2 eV) and 532.1 eV (± 0.1 eV). For higher potentials, e.g. 3.0 V and 4.0 V, these peak positions alter to 532.96 eV (± 0.02 eV) and 531.95 eV (± 0.02 eV) for fibres polarized at 3.0 V and 532.85 eV and 531.17 eV for fibres polarized at 4.0 V. At 4.0 V the fibres seem to have individual C=O and –O– character. The area ratios are given in Table VI, which shows the general trend for the O–1s : C–1s ratio to increase with increasing potential.

3.3.2. Ammonium bicarbonate results

The details of the fitted C–1s spectra are given in Table VII. There is very little change in the main profile of the spectra (just as in the laboratory case [2, 6]. The spectra were fitted to four peaks, with all the peak positions being allowed to float. The total area ratio of the chemically shifted species with respect to the graphitic peak is constant falling within the range 0.14 to 0.16 (see Table VII). This total ratio is only very slightly lower than that obtained for laboratory-treated fibres [6] in the same electrolyte over the same range of potentials. The chemical shifts are also much larger than those obtained with nitric acid, the oxide

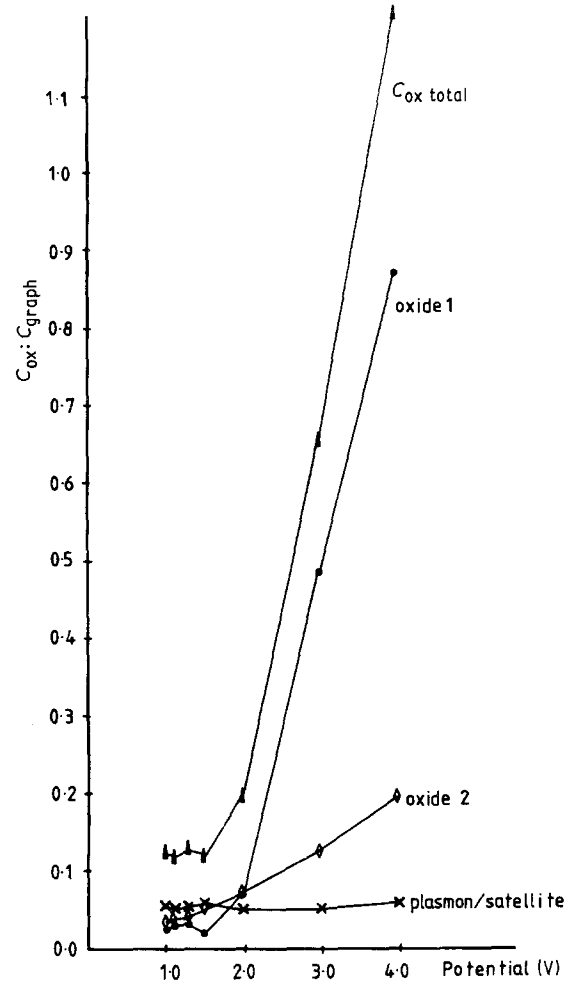


Figure 8 Variation of chemically shifted species in the C–1s spectra with potential in 0.5 M nitric acid solution.

chemical shifts being 2.64 eV (±0.2 eV) and 4.98 eV (±0.1 eV). These are also slightly higher than the laboratory fibres treated in ammonium bicarbonate. It has already been shown [e.g. 3, 4] that the binding energy of a particular functional group can vary significantly depending on neighbouring functionalities. This is probably the reason for the observed changes in chemical shifts.

The O–1s spectra for the above samples are shown in Fig. 9. They consist of two resolvable species with binding energies 533.4 eV (±0.2 eV) and 532.1 eV (±0.1 eV). The area ratios vary with potential but show no trend, the lower binding energy component, corresponding to =O type groups, usually being of greater intensity. Such groups correspond to the chemically shifted species at 2.64 eV in the C–1s spectra.

There is also a general trend for the O–1s : C–1s ratio to increase with potential. No nitrogen was present on the fibres. This is most likely to be due to the short reaction times. It has been suggested [6] that the bicarbonate ion inhibits the oxidation of the surface. The O–1s : C–1s ratios for commercially and laboratory-treated fibres using ammonium bicarbonate have similar values, even though the reaction times are vastly different.

3.4. The effect of potentiostatic surface treatment on the ILSS of the composites

Fig. 10 is a plot of ILSS against polarizing potential for both electrolytes. The lowest ILSS values were obtained by polarizing the fibre to 0.0 V (SCE) in both electrolytes. Polarizing to negative potentials causes only a very slight increase in ILSS, if at all, but polarizing the fibres to positive potentials causes significant changes in the ILSS. This rise in the ILSS occurs at different potentials in the two electrolytes. For ammonium bicarbonate a rise from 40 to 84 MPa occurs between 0.5 V and 1.0 V (SCE), whereas with nitric acid a similar rise in ILSS occurs between 1.0 V and 1.3 V. These voltages, if the ohmic drop is taken into account, are slightly lower than the oxygen potentials in both electrolytes.

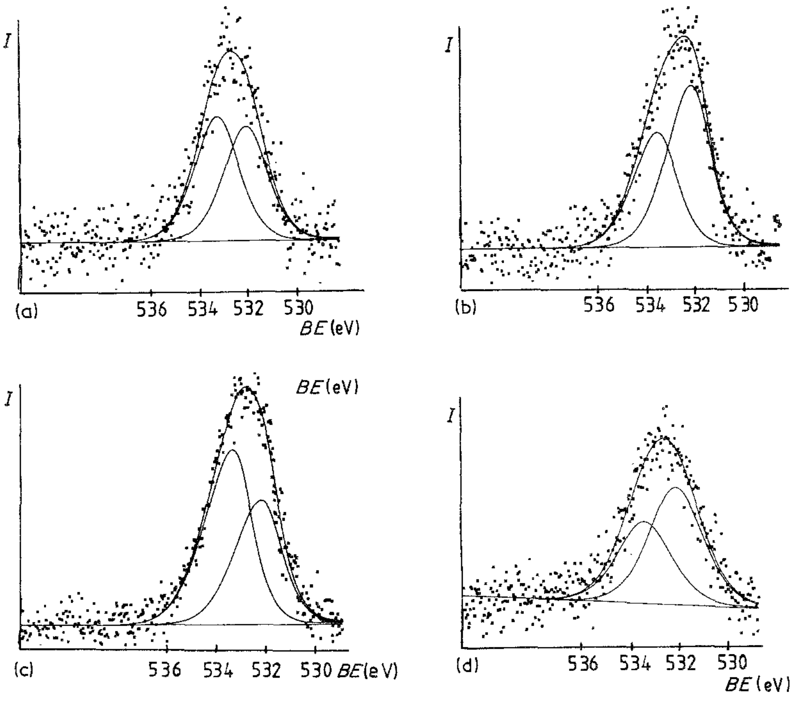
Although the greatest ILSS is almost the same using both electrolytes, the O–1s : C–1s ratio is, in some cases, far greater for nitric acid than for ammonium bicarbonate.

TABLE VI Curve-fitting results and relative areas for O–1s spectra of fibres potentiostatically treated in nitric acid (0.5 M)

Potential (against SCE) (V)	Binding energies (eV)			Fraction of total O–1s area		
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
1.0	532.2	533.6	–	0.715	0.285	–
1.1	532.0	533.4	–	0.479	0.521	–
1.3	532.2	533.5	–	0.519	0.481	–
1.5	532.1	533.5	–	0.577	0.423	–
2.0	532.3	533.7	–	0.542	0.458	–
3.0	531.9	532.9	535.9	0.448	0.505	0.047
4.0	531.1	532.8	535.9	0.191	0.764	0.045

TABLE VII Curve-fitting results and relative areas for C–1s spectra of fibres potentiostatically treated in ammonium bicarbonate (1.3 M)

Potential (against SCE) (V)	Chemical shifts (eV)			Fraction of total C–1s area		
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
0.1	2.74	5.01	6.73	0.039	0.050	0.052
0.4	2.65	5.03	6.61	0.049	0.050	0.051
0.6	2.37	4.80	6.60	0.057	0.049	0.053
0.7	2.64	5.07	6.93	0.050	0.052	0.057
1.0	2.64	5.05	6.82	0.036	0.055	0.052
1.5	2.73	4.99	6.81	0.041	0.050	0.052



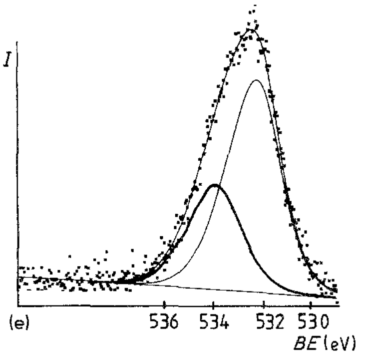


Figure 9 O–1s spectra of fibres polarized to various potentials (against SCE) in 1.3 M ammonium bicarbonate solution. (a) 0.4 V, (b) 0.6 V, (c) 0.7 V, (d) 1.0 V, (e) 3.0 V.

3.5. The variation of ILSS with surface functionality

Fig. 11 shows a plot of the ILSS of the composites made from galvanostatically and potentiostatically treated fibres against the O–1s:C–1s of their component fibres. Fig. 12 shows a plot of ILSS against the relative amount of oxide 2 on the fibre surface. It can be concluded that the ILSS of a composite does not directly depend upon the amount of surface oxygen, nor upon the total amount of acid/ester type groups.

The nitric acid results (Fig. 13) do show a correlation between the ILSS and the amount of surface oxygen. The ILSS increases with surface concentration until an optimum value is reached (O–1s:C–1s = 0.25, ILSS = 83 MPa). Further increase in the surface oxygen concentration leads to a decrease in ILSS. An extensive study of fibres treated with nitric acid has been carried out by Fitzer and co-workers [10, 11]. These workers suggest that the rise in ILSS is related

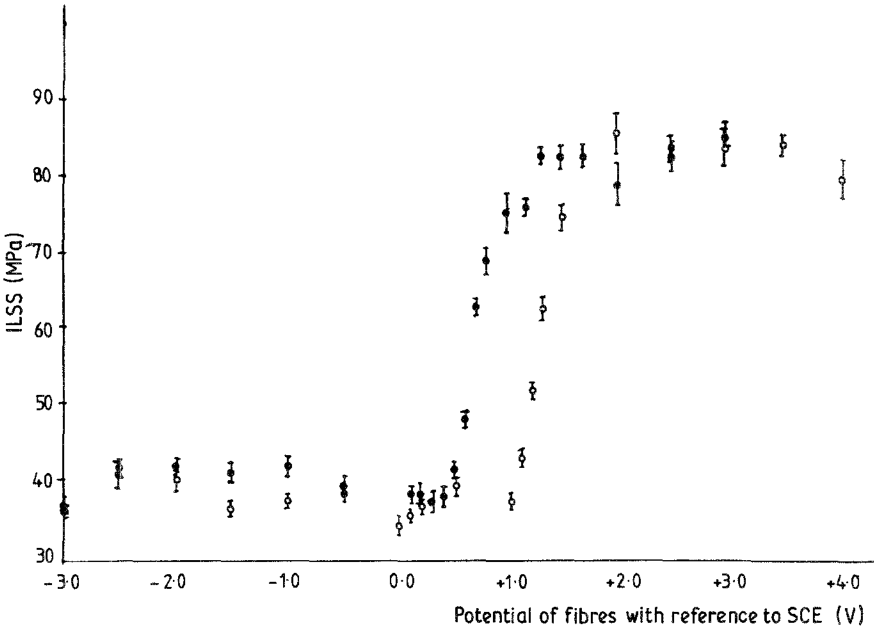


Figure 10 Graph showing the variation of ILSS with cell potential for potentiostatically treated fibres in ammonium bicarbonate and nitric acid electrolytes. (●) Ammonium bicarbonate, (○) nitric acid.

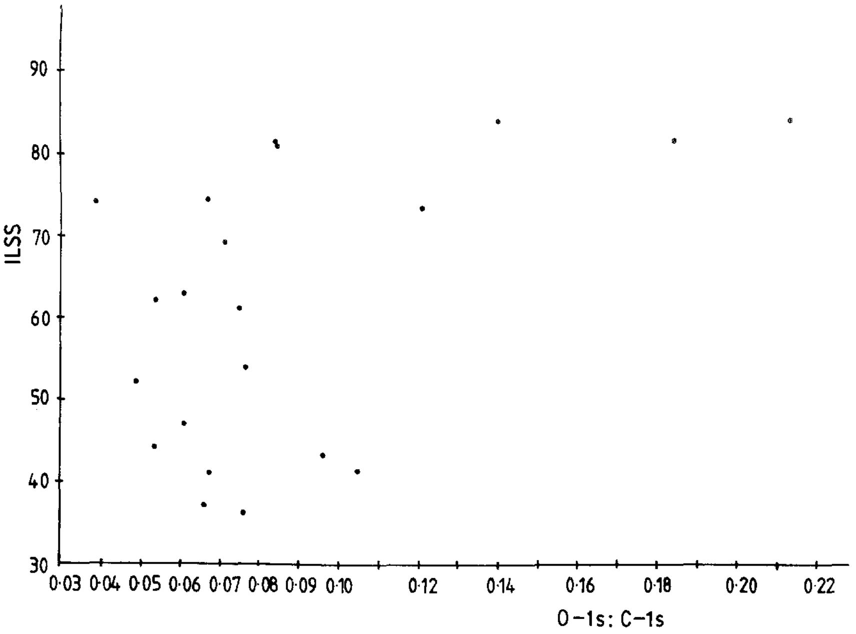


Figure 11 Graph showing the variation of ILSS with O–1s : C–1s XPS area ratio for treated fibres in various electrolytes.

to the amount of carboxyl surface functionality. We find the number of surface carboxyl groups (oxide 2) to increase with potential for nitric acid studies (see above). However, although a different hardener was used by Fitzer and co-workers [10, 11], their conclusions may only be applicable to treatment in nitric acid and not to other types of surface treatment, since our studies using a range of electrolytes show no overall correlation with carboxyl group intensity (Fig. 12).

Epoxy resins contain highly polar functional groups and consequently readily absorb water. As these structures absorb water the resin becomes plasticized, with a resultant loss of strength. This strength is largely regained on drying. However, if the composite is subjected to moist conditions at high temperatures irreversible damage occurs. It is therefore necessary to produce composites with low hydrophilicity. This can be achieved by altering the resin to make it more moisture resistant and/or by decreasing the number of polar functional groups on the fibre surface. For the treatments carried out in this study, polarization in ammonium bicarbonate solution results in the lowest O–1 s : C–1 s ratio (0.06) for a satisfactory ILSS (85 MPa).

3.6. The effect of reaction time and heat treatment

Fibres were polarized to 3.0 V in nitric acid using the pilot-plant cell. The time the fibres spent in solution was varied using a dc motor to pull the fibres through the system at different rates. The reaction times used were 36, 45, 60 and 120 sec. Enough fibre was treated for two composite bars to be made for each reaction time. One set of composite bars (one for each reaction time) was made in the usual way, while the other set of fibre samples was heated in a vacuum to 1000° C prior to incorporation into the resin.

3.6.1. Reaction time

As the reaction time was increased, the amount of chemically shifted species increased. The O–1s : C–1s ratio also increased with reaction time. The carbon 1s

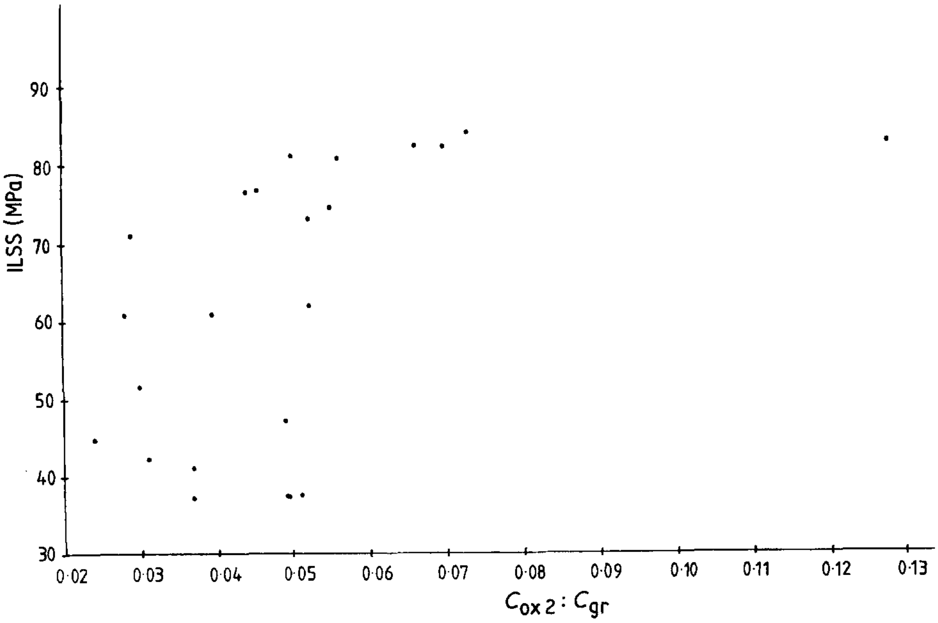


Figure 12 Graph showing the variation of ILSS with carboxyl group C–1 s XPS area (represented by the ratio of the area of the C–1 s peak due to carboxyl and that due to graphitic carbon).

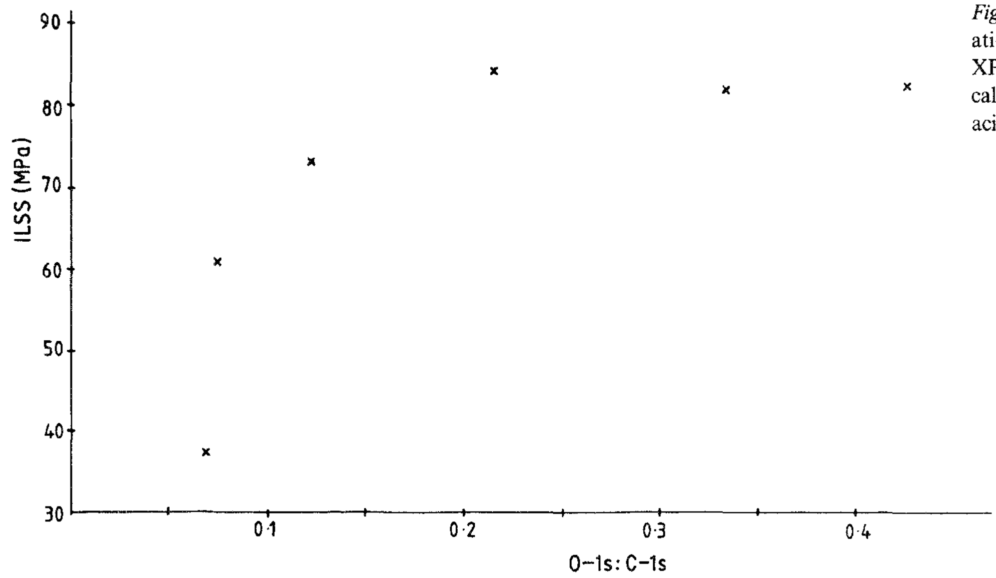


Figure 13 Graph showing the variation of ILSS with O–1 s : C–1 s XPS area ratio for potentiostatically treated fibres in 0.5 M nitric acid.

spectra of fibres polarized to 3.0 V (with reference to SCE) in 0.5 M nitric acid solution for reaction times of 45 and 120 sec are shown in Fig. 14a. These spectra consist of chemically shifted signals at 2.1, 4.0 and > 6.0 eV from the main peak as discussed above (see section 3.3.1). As previously explained, the main graphitic peak has lost its exponential tail, implying a loss of conduction band interaction and thus true graphitic character.

A plot of ILSS against reaction time is shown in Fig. 15. The solid line represents fibres which have not been heated prior to composite production. It shows that as the reaction time increases the ILSS of composites decreases significantly. This means that as the O–1s : C–1s ratio increases, the ILSS decreases. This may be due to the oxide layer causing the failure of the fibre–resin bond. The maximum O–1s : C–1s ratio before the ILSS of the composite decreases is 0.337. The same ILSS value can be achieved at an O–1s : C–1s ratio of 0.076 for the same electrolytic treatment (the latter level of oxidation being far more desirable because of the lower level of surface polarity).

3.6.2. Heating in a vacuum at 1000° C

It has been shown in an earlier paper [4] that nitric acid produces an oxide layer resembling graphitic oxide. On heating, graphitic oxide decomposes at temperatures above 120° C. The carbon 1 s spectra of fibres after heating are shown in Fig. 14b. It can be seen that heating causes a marked decrease in the amount of carbon–oxygen complexes present on the fibre surfaces. Some basic oxides may also have been produced

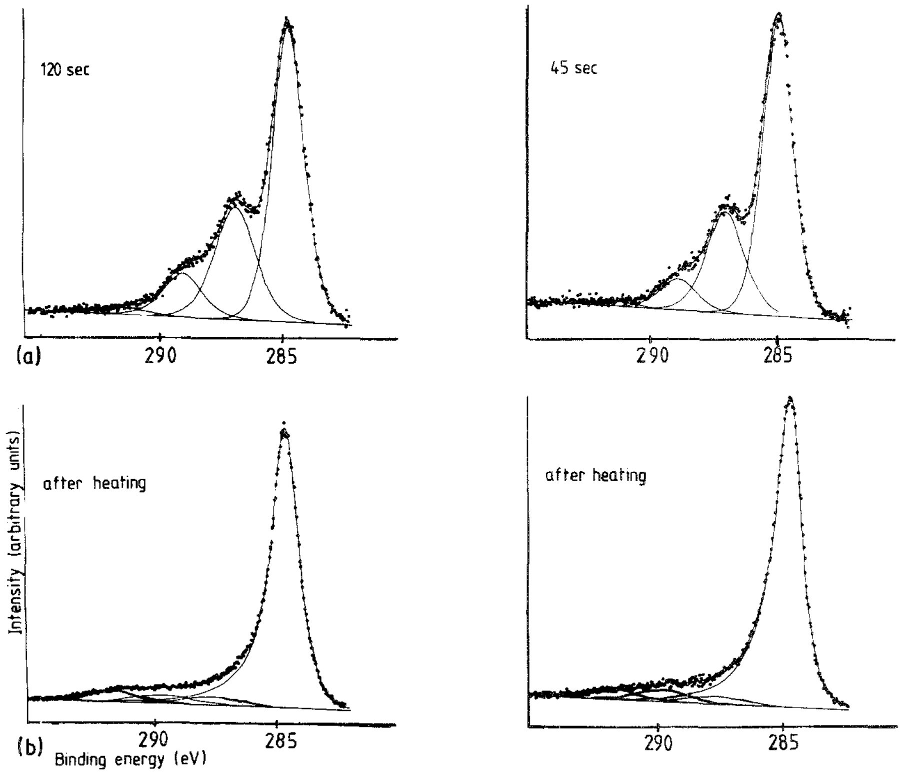


Figure 14 C–1s spectra of fibres polarized to 3.0 V (against SCE) in 0.5 M nitric acid solution, for reaction times of (a) 45 sec and 120 sec (b) after heating to 1000° C the spectra appears as shown.

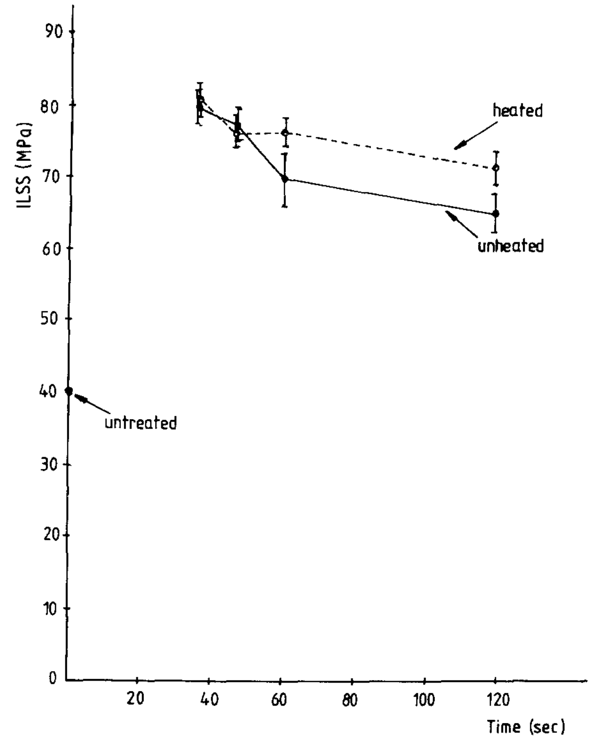


Figure 15 Graph showing the variation of ILSS with reaction times for fibres potentiostatically treated in 0.5 M nitric acid.

after heating fibres in a vacuum; cooling, and exposing them to air. Fig. 15 shows the ILSS of composites made from heated fibre samples plotted against reaction time (represented by the broken line). For fibres treated to short reaction times (36 and 45 sec) the ILSS remains roughly at the same level, but for longer reaction times heating causes an increase in the ILSS. This is probably due to the decomposition of the oxide layer into gaseous products on heating. The evolution of gas was detected by monitoring pressure fluctuations during the heating process.

4. Conclusions

Both galvanostatic and potentiostatic control of cell conditions proved satisfactory in the treatment of fibres to produce composites with a high ILSS (80 to 90 MPa). (Slightly higher values of ILSS may be achieved by altering the volume fraction of fibres in the resin, which is usually 60%.)

Changing the electrolyte in which the fibres were treated results in a change in the amount and relative proportions of functional groups produced. For the treatments carried out in this study polarization in ammonium bicarbonate solution results in the lowest O–1s : C–1s ratio (0.06) for a satisfactory ILSS (85 MPa). As in earlier studies [3, 5] we found that an industrial treatment gave less control over fibre surface oxidation than in the laboratory-treated fibres. Short reaction times (9 sec) gave a composite with a high ILSS, while longer reaction times led to more surface functionality, but usually lower ILSS values.

With galvanostatic conditions, the cell current needed to produce fibres that give high ILSS of the composite is the same for a wide range of electrolytes. With potentiostatic conditions high ILSS composites resulted when the potential applied between a reference electrode and the fibres is close to the oxygen potential for the chosen electrolyte (which varies with electrolyte).

The rise in ILSS is not dependent on the O–1s : C–1s ratios or the amount of carboxyl functionality present on the surface. Whilst it cannot be concluded, therefore, that the nature of the fibre–resin bond is purely physical, mechanical keying of the resin to the fibre surface is likely to play a more important role in the fibre–resin bond than is appreciated by many research workers.

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