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The Electrochemical Evaluation of the Surfaces of Carbon Fibres

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Electrochemical methods are used to follow the changes in wetted fibre area produced by surface treatment, to estimate the fraction of that area in pores and to detect surface chemical groupings. The changes in area wetted by electrolyte correlate with the changes in interlaminar shear strength of the corresponding epoxy resin composites.

1. Introduction

The surface properties of carbon fibres play an important part in their technological application. For example, the interlaminar shear strengths of composites are improved when the fibres are given treatments that increase surface roughness, as judged by electron microscopy. However, fibre areas measured by gas adsorption (Brunauer-Emmett-Teller method) and displacement methods with a variety of gases often do not change appreciably after treatment, and these methods are in any case too time-consuming to be used routinely to evaluate surface treatments. The area of an electrode wetted by an electrolyte can be determined electrochemically, and for a fibre electrode, should be a closer approximation to the significant area in a composite – that area wetted by the resin mixture. Electrochemical methods can give information concerning pores and surface groups too.

A metallic conductor in contact with an electrolyte bears a surface charge q^{M}, which depends on solvent, electrolyte, electrode material and the potential drop E across the interface, and which is proportional to the interfacial area [1]. Rather than determine q^{M} it is easier to measure changes in q^{M} following a change in E by integration of the resulting current and Δq^{M} can be used to compare wetted areas

$$\Delta q^{\mathrm{M}} = q^{\mathrm{M}}(E_2) - q^{\mathrm{M}}(E_1) = \int_0^t i dt \qquad (1)$$

The method was originated by Wagner [2] and used recently to measure the area of battery electrodes [3] (PbO_2, Ag, Zn).

Surface roughness or porosity slows the response of an electrode to a potential step. For a porous electrode the time constant corresponding to an observed charge transient has been related [4] to the parameter l^2/r for a model equivalent pore of length l and radius r. The range of fibre topography treatable in this way is limited, since the high resistance of these very thin electrodes, together with the capacity of the interface, introduce a further time constant which may be comparable with that predicted for significant pores.

The charge flow following a change in potential may also contain a contribution from charge transfer to a molecule or group. Such processes are best distinguished as peaks on current-voltage curves with cyclic linear voltage sweeps. Many dissolved organic molecules are known to undergo electron transfer in aprotic organic solvents to give fairly stable radical ions [5]. Adsorbed molecules give characteristic peaks on current-voltage curves too, and provided surface groupings on the fibres resemble adsorbed molecules they should be detectable. While many examples of electron transfer with adsorbed molecules are known, we know of only one of electron transfer involving a group forming part of the electrode structure [6].

2. Experimental Procedure

Electrodes were made from single fibres. The fibre and a length of copper wire were attached together on the inside wall of a 5 mm internal diameter glass tube with conducting cement. The length of fibre (~ 1 cm) to be immersed in the electrolyte was defined by sealing the end from which the fibre projected, with Araldite.

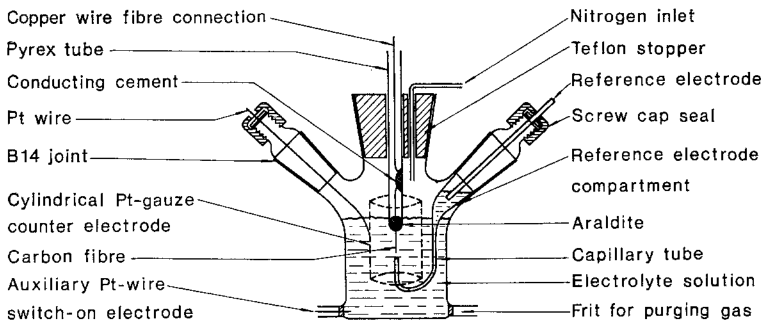

Figure 1 The electrochemical cell.

Water (triply distilled) and N,N-dimethylformamide (distilled *in vacuo*) (DMF) were used as solvents and sodium fluoride, potassium hexafluorophosphate (in water) and tetra-n-butylammonium perchlorate (in DMF) as electrolyte salts (0.1 M). Specific adsorption of ions on metallic electrodes from these solutions is thought to be unimportant.

The three-electrode cell used is shown schematically in fig. 1. Care was taken that the fibre lay on the axis of the platinum gauze counter electrode, since lack of symmetry gives effects like those due to surface roughness. The input for the reference electrode (saturated calomel in water and Ag/Ag$^+$ in DMF) was via a voltage-follower stage to ensure the necessary high input impedance (fig. 2).

The potential of the fibre-electrolyte interface was controlled potentiostatically. An operational amplifier system maintains the desired potential difference between the fibre and a reference electrode of fixed potential irrespective of the cell current, which would otherwise introduce a voltage drop because of the finite cell resistance; a distorted charge-time transient would then be obtained. A potentiostat applies a compensating voltage equal to the drop across the cell by negative feed-back circuits. Occasionally the fibre was damaged by uncontrolled oscillations on first switching on the potentio-

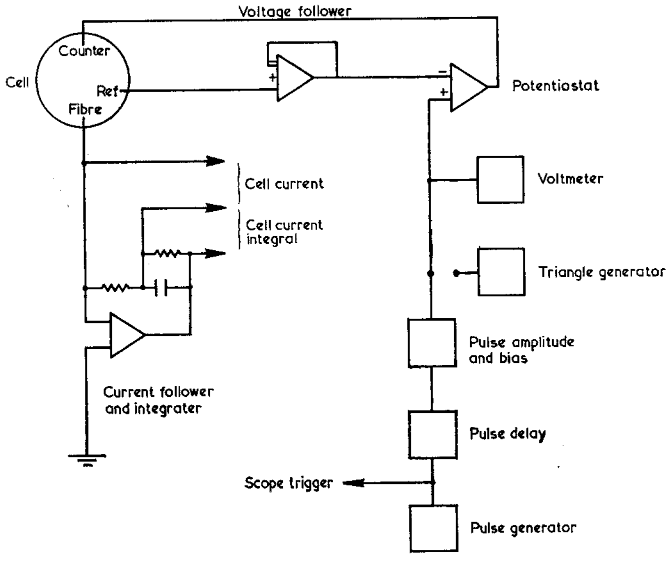

Figure 2 Schematic circuit.

stat; a fourth electrode, a platinum wire, was incorporated as the working electrode for switch-on.

Potential steps were applied by Aim Electronics units and potential sweeps by a Hewlett-Packard 3300A Function Generator with added bias and sweep controls. The fibre was held at virtual earth by a combined current-follower and integrator stage from which charge-time and current-voltage curves were displayed on a differential storage oscilloscope. A known rate of leakage from the measuring capacitor avoided complete charging at the sensitivity required. The schematic circuit is shown in fig. 2.

In each of the solvent/electrolyte combinations, current-voltage curves were recorded and a region of potential was chosen in which current was invariant so that the only apparent electrode process was charging of the interface. This was confirmed by recording the charge/time curves for the following potential steps (cf. equation 1),

E_1 to E_2 and then E_2 to E_1 after 70 mS.
E_2 to E_1 and then E_1 to E_2 after 70 mS.

For a simple charging process a symmetrical trace like those shown in fig. 3 results.

The potential regions for the charging experiments were chosen also to avoid electron transfer to dissolved oxygen. There was then no need to exclude air from the cell. In the potential sweep experiments, however, a nitrogen atmosphere was used. The values chosen for the potentials E_1 and E_2 were + 0.20 and + 0.60 V vs a saturated calomel reference electrode in aqueous solution and − 0.30 and − 0.50 V vs Ag/Ag^+ in dimethylformamide.

The fibres used were from two sources. Morganite fibres were of the standard commercial grades and the interlaminar shear strengths are those quoted in the Company's literature. The remaining fibres were kindly supplied by Mr W. Watt, RAE, Farnborough, from batches on which the effect of controlled surface treatment on the interlaminar shear strengths of Shell epikote resin composites had been measured. The resin used by Watt was a Shell epikote resin 828, MNA, BDMA. The proportions used were 100 parts of 828, 85 parts of MNA and 1 part of BDMA, all by weight. The composites of 0.62 volume fraction of fibre were set in the mould under pressure for 1 h at 100°C and cured while still under pressure for 24 h at 125°C giving beams 12.5 cm long, 12.5 × 2.5 mm cross section. A three point loading short-beam method was used for interlaminar shear strength determinations with a span of 1.5 mm between centres of 6 mm diameter rollers.

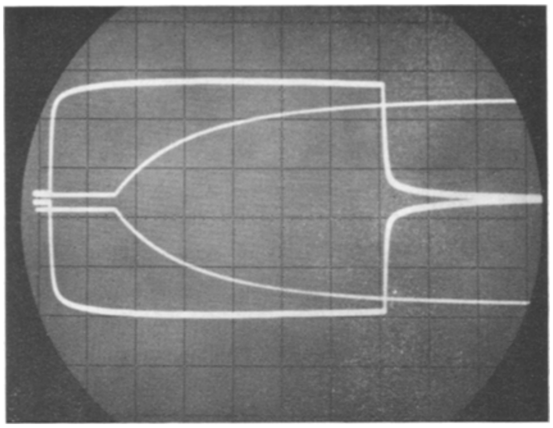

Figure 3 Charge-time curves following potential steps between + 0.20 and + 0.60 V vs SCE applied to a Rolls-Royce fibre in 0.1 M NaF. Charge scale (vertical) 10^{-2} μC per large division. Time scales 5 and 0.2 mS per large division.

3. Results

3.1. The Total Charge and the Wetted Area

Table I lists values Δq^M of the charge 70 mS after application of the potential step, expressed as charge on unit length of fibre. These measurements were made shortly (~ 1 min) after immersion of the fibre in the electrolyte. Longer immersion at a potential controlled at either end of the step used gave smaller Δq^M values. Such effects are common at solid electrodes and are thought to result from adsorption of trace organic impurities which block the surface.

If variations in fibre diameter can be neglected, differences in Δq^M (table I) may be attributed to different wetted areas, interfacial capacities and any space charge capacities. We have no way of separating these contributions. Scanning electron micrographs of surface replicas [7] show, however, that pitting of a particular fibre batch is increased by surface treatment in a way roughly parallel to the increases of Δq^M. There is thus some support for the simplest hypothesis – that differences in Δq^M produced by treatment of a given fibre batch reflect changes in area wetted by electrolyte. If the fibre area wetted by a resin mixture and by electrolyte change in a parallel way the Δq^M values should correlate with the

TABLE I Comparison of total charge and charge transients from carbon fibres in water–0.1 M NaF and dimethylformamide–0.1 M $NBu_4{}^nClO_4$ with ILSS of Shell epikote resin composites [7,8]. Results from 5 to 10 samples of each fibre batch.

Fibre source	ILSS $lb\,f/in^2$	Charge $\pm$ 10%, $\mu C/cm \times 10^{-3}$, Water	DMF	$\frac{q_{70}\,mS}{q_5\,mS} - 1$ Water	DMF
Harwell	5200*	3.1	6	0.10	0.15
	6416	3.7			
	8770	7.0			
	10620	27			
	11865	30	7	0.10	0.15
Rolls-Royce	10020*	10	8	0.35	0.10
	12800	19			
	12640	22			
	12150	22			
	12490	43	12	0.15	0.15
Courtaulds	—	2.5	3	0.05	0.00
	increased	19	9	0.10	0.20
Morganite I	3000*	6.2		0.10	
	8000	13		0.05	
Morganite II	6000*	10.8			
	11000	20			

*Untreated fibre.

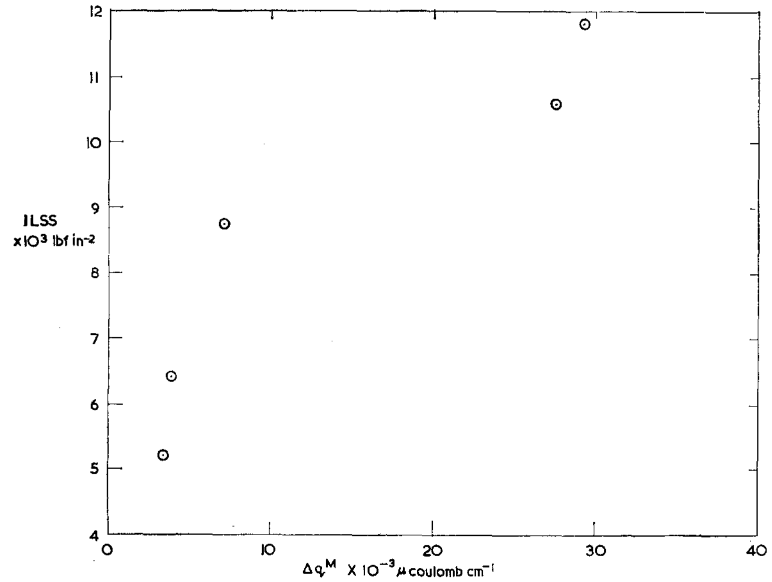

Figure 4 Relation between Δq^M and interlaminar shear strengths of Shell epikote resin composites for Harwell fibres.

changes in interlaminar shear strength on surface treatment. In fig. 4 we plot the measured total charge in water/NaF of the treated Harwell fibres against the ILSS of the resulting composite [7]. Results for the Rolls-Royce fibres are less satisfactory, but the change in interlaminar shear strengths is smaller and there is more scatter (table I). Precise shear strengths for the composites from the Courtaulds fibres are not available. Note that the apparent increase in area on surface treatment as deduced from the Δq^M values in water is larger than that from those in dimethylformamide; the case of the Harwell fibres is particularly striking. The surface exposed by treatment must be more accessible to aqueous electrolyte, and water is clearly the more useful solvent for following these changes. There was little difference between results for the two electrolyte salts (NaF, KPF_6,) used in water.

3.2. Charging Transients and Fibre Porosity

Table I compares the lengths of the charging transients as the fractional increase of charge between 5 and 70 mS $[(q_{70}\,\mathrm{mS})/(q_5\,\mathrm{mS}) - 1]$. The information derivable about real fibre surfaces is limited by the charging behaviour of an ideally smooth, non-porous fibre. Experiments with a model fibre, a transmission line circuit with resistors and capacitors chosen to reproduce the measured impedance of a real fibre, showed that charge-time curves were sensitive to electrode construction and cell geometry at times shorter than 5 mS. Porous electrode theory [4] links the shape of an observed transient to specific resistances and capacitances and to a parameter l^2/r, which characterises an equivalent pore of length l and radius r. Transients longer than 5 mS are predicted to contain contributions from pores with $l^2/r > 3.7$ cm for aqueous solution (0.1 M NaF) and > 1.9 cm for dimethylformamide. Most of the real fibres had transients longer than this. Two observations show that these transients are a function of the electrolyte side of the interface. Firstly, increasing the electrolyte resistance by using a smaller concentration of sodium fluoride lengthens the transient. And, secondly, there are fibre batches (e.g. Rolls-Royce untreated) that gave longer transients in NaF/water than in $\mathrm{NBu_4^nClO_4}$/DMF. Pores shown to the right of the dotted line in table II are those predicted to contribute to transients beyond 5 mS after the potential step in the solutions used. The $[(q_{70}\,\mathrm{mS})/(q_5\,\mathrm{mS}) - 1]$ values given in table I measure the fraction of the total wetted area of the fibre in these relatively long, narrow pores.

TABLE II Dependence of the parameter l^2/r (cm) which characterises pores on the length l and radius r of cylindrical pores

r	l = 1 μm	10 μm	100 μm
10 Å	0.1	10	1000
50 Å	0.05	5	500
100 Å	0.01	1	100
0.1 μm		0.1	10
1 μm		0.01	1

The fraction is largest for untreated Rolls-Royce fibres in aqueous electrolyte (table I). The smaller fraction of long, narrow pores seen on those fibres by dimethylformamide may mean that those apparent in water are not accessible to the organic solvent. Treatment of these fibres decreases the fraction of the area in long, narrow pores seen by aqueous electrolyte, and there is no longer a differentiation between pore sizes in the two solvents. In most of the remaining cases listed in table I no significant change in the fraction of area in long, narrow pores is produced by the surface treatments employed, although the total charge increases. Treatment must increase the total area and the number of long, narrow pores proportionately.

Transients for most of the fibres extend to 100 to 200 mS, corresponding to values of l^2/r of 90 and 180 cm respectively. Table II shows that the pores responsible must have lengths greater than the fibre diameter (~ 10 μm) and hence probably lie along the fibre axis.

There is clearly no correlation between the shape of the charging transients and the interlaminar shear strengths of composites formed from the fibre.

3.3. Surface Groupings

Surface groups were detected by linear voltage sweeps in $\mathrm{NBu_4^nClO_4}$/DMF on Courtauld fibres but not on those from Rolls-Royce and Harwell, irrespective of surface treatment (cf. figs. 5a and b).

The area beneath the peak in fig. 5b gives the charge consumed in the reduction of the surface groups. The corresponding concentration ($\sim 10^{-9}$ moles cm^{-2} for the addition of one electron) ranged over an order of magnitude on different fibres. Treated Courtauld fibres showed similar values and a similar scatter. The reduction (at $-$ 2.1 V vs SCE) appeared to be a simple electron transfer, and produced fibres with an enhanced electron spin-resonance signal. The product of reduction was stable enough to be reoxidised by reversal of the voltage sweep. This stability and the potential at which reduction occurred suggest that carbonyl groups or aromatic heterocycles are responsible. There was no correlation between their surface concentration and surface treatment or interlaminar shear strength.

4. Conclusions

The changes in Δq^{M} value in aqueous sodium fluoride following surface treatment of a given fibre batch correlate with the resulting interlaminar shear strengths of composites formed. Some limited information on fibre porosity is deducible from the rate of change of charge following a potential step, but there is no cor-

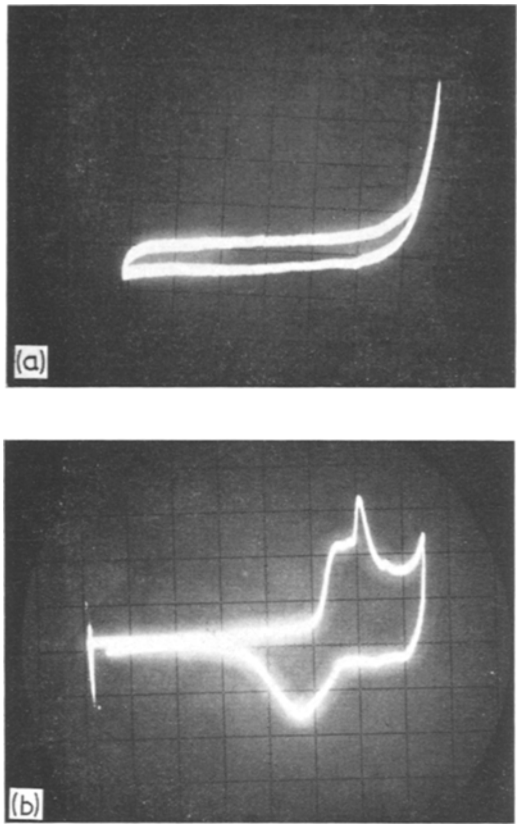

Figure 5 Current-voltage curves in N,N-dimethylformamide (0.1 M $NBu_4{}^nClO_4$). Potential sweep + 0.60 to − 2.82 V vs SCE at 0.2 Hz. Current scale (vertical) 0.2 μA per large division (a) Harwell fibre, (b) Courtauld fibre.

relation with shear strengths. Surface groups are detectable on Courtauld fibres only, but their concentrations are not related to shear strengths.

Scanning electron micrographs of surface replicas of sample fibres [7] from the Harwell and Rolls-Royce batches show that many orifices some 0.1 μm wide are produced by surface treatment and that these link up to form longitudinal channels (~ 1.5 μm) in the surface. The untreated Harwell fibres have few pits; those from Rolls-Royce are heavily pitted. Surface replicas, then, agree qualitatively with our results.

Areas of some of the fibre batches used have been measured by adsorption and displacement methods, and there are cases in which surface treatment has no effect on the area estimated [7]. This surprising result has been explained by supposing the pits formed to be smoother than the surface they replace. Our results suggest that the pits formed are in fact present with restricted orifices in the original fibre, being accessible to gas molecules before and after treatment, but to electrolyte and resin mixture only after treatment.

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