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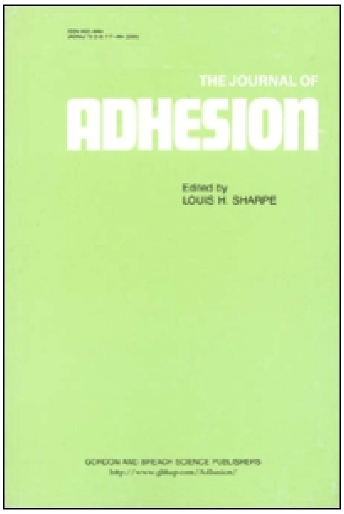

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Erich Fitzer[a]; Nadja Popovska[a]; Hans-Peter Rensch[a]
[a] Institut für Chemische Technik, Universität Karlsruhe, FRG

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Anodic Oxidation of Carbon Fibres in Diammonium Hydrogen Phosphate Solution

ERICH FITZER, NADJA POPOVSKA and HANS-PETER RENSCH

Institut für Chemische Technik, Universität Karlsruhe, FRG

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Anodic surface treatment of high tensile-carbon fibres under galvanostatic conditions has been performed in diammonium hydrogen phosphate solution, containing an addition of ammonium rhodanide.

The oxidized fibres have been characterized by monofilament tensile strength, XPS measurements and surface energetic analysis. Additionally, the acid-base interactions have been evaluated by wetting with aqueous solutions of different pH values.

An addition of ammonium rhodanide to the diammonium hydrogen phosphate anodization bath affects the oxidation of carbon fibres in terms of decreasing both the amounts of the surface oxides as well as that of degradation by-products. At the optimal treatment conditions ($I = 100$ mA) no changes in the tensile strength or BET-surface area of the fibre have been observed. The rise in ILSS values of amine cured epoxy composites is not dependent on O_{1s}/C_{1s} ratio or surface free energy of the reinforcing fibres, but on the acidic as well as nitrogen functional groups on their surface.

KEY WORDS carbon fibres; anodic oxidation; diammonium hydrogen phosphate solution; ammonium rhodanide addition; adhesion.

1 INTRODUCTION

The mechanical properties of carbon fibre reinforced plastics depend strongly on the level of adhesion between fibre and matrix.

Electrochemical treatment of carbon fibres is now widely accepted as a method for controlled surface oxidation and, hence, for controlled level of adhesion. Many patents and papers[1,2,3] as well as comprehensive reviews[4,5,17] on this field have been published.

One of the most important parameters in the electrochemical oxidation of carbon fibres is the electrolyte. Carbon fibres, anodically treated in neutral as well as in basic electrolytes, show better fibre-matrix adhesion than those oxidized in acidic solutions, due to different oxidation mechanism.[6,7,8] Several papers have been published, involving electrochemical treatment of carbon fibres in ammonium salt electrolytes.[2,3,16] The authors found that nitrogen functionality was produced on the fibre surface and that an increase in the interlaminar shear strength (ILSS) values of the corresponding composites was observed. Anodic oxidation of high tensile carbon fibres in basic electrolytes, such as aqueous solutions of sodium hydroxide and diammonium hydrogen phosphate, has been studied by us previously.[9,10] The effect on oxidation by various additions to the electrolytes has also been investigated. The best fibre-epoxy matrix adhesion with minimum loss in fibre tensile strength has been achieved in diammonium hydrogen phosphate solution, containing an addition of ammonium rhodanide.[10]

In the present paper a detailed study is performed on anodic surface oxidation of high tensile carbon fibres in diammonium hydrogen phosphate solution with an ammonium rhodanide addition, in order to investigate possible routes for improving and optimizing the interfacial interactions in epoxy composites.

2 EXPERIMENTAL

Commercially-available, high-tensile carbon fibres, TENAX HTA-6K (AKZO), without any surface treatment and sizing are oxidized anodically under galvanostatic conditions ($I = 50–1100$ mA) in a continuous, laboratory scale apparatus, discussed previously.[7]

As electrolyte 0.5 M aqueous solution of diammonium hydrogen phosphate ($pH = 8$) is used. As addition to the electrolyte, ammonium rhodanide (0.005 M) has been investigated.

The carbon fibre bundle as a working electrode (anode) contacts a graphite roller about 2 cm outside the electrolyte cell. Two graphite plates act as counter electrodes. After anodic treatment the carbon fibre tow is washed with tap water, followed by distilled water and dried.[7]

UV absorption spectra of the anodization baths are obtained on a Perkin Elmer 3300 UV/VIS spectrometer.

The possible effect of fibre damage is assessed by monofilament tensile strength measurements (gauge length 25 mm, 40–60 test samples).

XPS measurements of the fibre surface are performed by Perkin Elmer Surface GmbH, using an electron spectrometer model 5500 with an aluminum Kα x-ray source. The pressure in the sample chamber is $<10^{-9}$ Torr.

The surface free energy of the carbon fibres is determined by measuring the contact angle (micro-Wilhelmy technique) of a variety of liquids, having known polar and dispersive components of their total surface energy and analyzing the results, according to the method described by Hammer and Drzal.[11] Ten single filament samples were measured for each wetting liquid and surface treatment. The liquids used included water, ethylene glycol, formamide, glycerol and bromonaphthalene.

The wetting of carbon fibres by aqueous solutions of different pH values for evaluation the acid-base interactions, according to idea of Hüttinger,[12] is determined by the Wilhelmy-technique, using a microbalance.[11]

Unidirectional (UD) composites are prepared by a dry winding technique and subsequent resin impregnation. A liquid epoxy resin LY 556 and a powdered aromatic diamine hardener component HT 976 (both CIBA-GEIGY) are used as precursors for the polymer matrix (100:30). The composites with a fibre volume fraction of 60% are cured under pressure for 8h at 110°C, 2h at 135°C, 6h at 160°C and 6h at 180°C.

The adhesion between fibre and matrix is estimated by ILSS measurements with the short beam test, according to ASTM-D-2344-76T.

3 RESULTS AND DISCUSSION

3.1 Anodic Oxidation of Carbon Fibres

Figure 1 presents both the tensile strength of the carbon fibres, oxidized at different currents, as well as the ILSS values of the corresponding unidirectional (UD) epoxy composites. Obviously, the anodic treatment in both electrolytes reduces the tensile strength of the monofilaments, mostly because of the handling procedure of the non-sized carbon fibres, but additionally by the oxidation itself.

The oxidation current of 100 mA causes maximum improvement of adhesion with minimum fibre damage. The best effect, however, is achieved in diammonium hydrogen phosphate solution with ammonium rhodanide addition. As can be seen in Figure 1, the properties of the carbon fibres oxidized under such conditions approach those for commercially oxidized samples.

Carbon fibres, treated at higher currents than 500 mA, are strongly damaged and hence, unsuitable as reinforcing material.

It is well known that the electrochemical oxidation of carbon in alkaline solutions occurs with formation of CO, CO_2, surface oxides and water soluble organic products.[6] Evolution of solid carbon particles in the electrolyte has also been observed. All of these reactions, except surface oxide formation, lead to corrosion of the carbon, decreasing its mechanical properties. As shown previously,[10] intensive brown coloration appears in the diammonium hydrogen phosphate anodization bath, due to water soluble organic degradation products. An addition of ammonium rhodanide to the electrolyte reduces the brown coloration significantly.

In order to get more information about both the intensity of the brown coloration, as well as the nature of the water soluble organic products, UV spectra of the anodization baths, after centrifugation to remove the solid carbon particles, are measured (Fig. 2). The $(NH_4)_2HPO_4$ bath shows a very intense absorption maximum at 205 nm, due probably to unsaturated aliphatic acids.[13,14] An addition of NH_4SCN to the main electrolyte causes significant change in the UV spectrum, as seen in Figure 2. The original UV adsorption is about ten times lower and three new maxima at higher wavelength appear, indicating the presence of substituted aromatic substances.[13,14] From these results, it appears that an addition of ammonium rhodanide to the diammonium hydrogen phosphate solution decreases the rate of the degradation reactions which cause corrosion of the carbon fibre.

Carbon fibres, anodically oxidized in both electrolytes at the optimal conditions (Fig. 1), were selected for further study of their surface properties, in order to investigate the reasons for the improved fibre-matrix adhesion. A commercially oxidized carbon fibre from the same producer was also investigated for comparison.

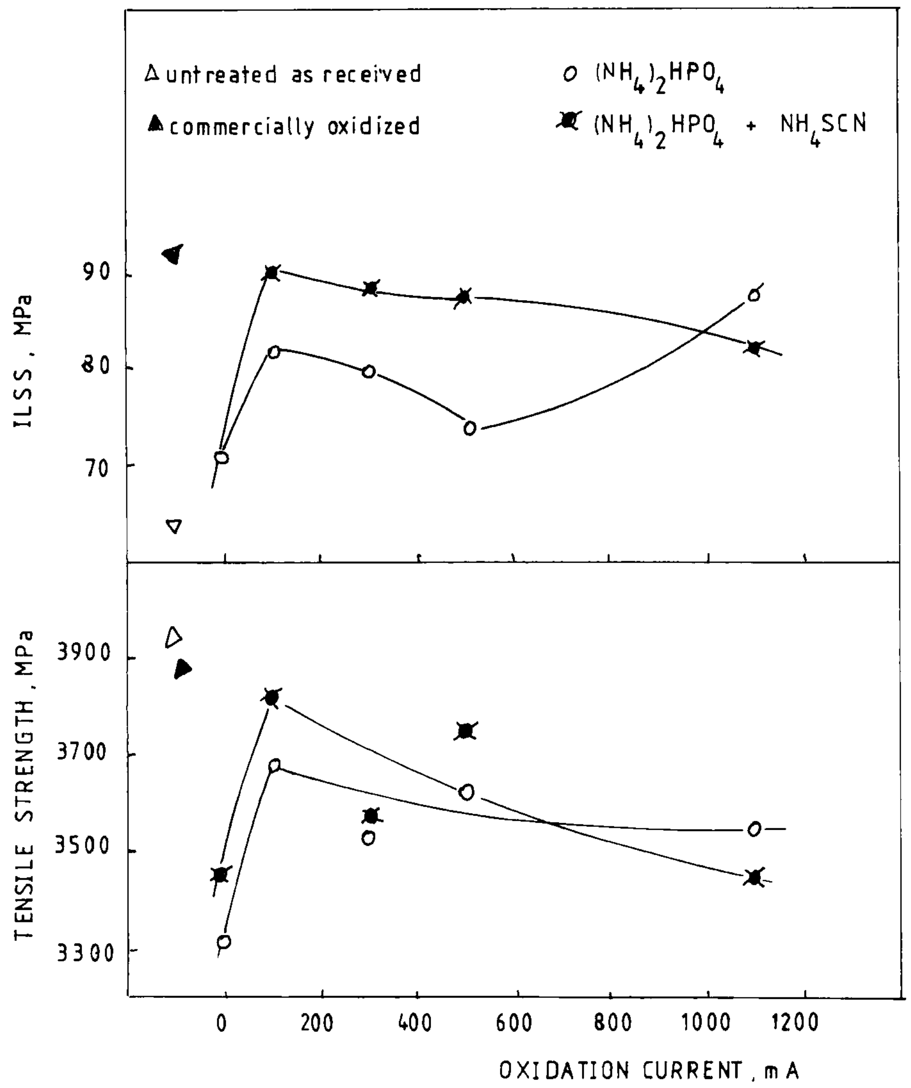

FIGURE 1 Tensile strength of carbon monofilaments, oxidized at different currents, and ILSS of UD epoxy composites.

3.2 XPS Measurements

XPS is an effective method for determining the chemical composition of the fibre surfaces, using the parameters O_{1s}/C_{1s} and N_{1s}/C_{1s}, which are atomic ratios estimated from the corresponding peak area ratio.

As seen in Table I, anodic treatment increases both the amount of surface oxides and the amount of nitrogen groups. The highest surface oxygen content is measured for carbon fibres anodically treated in diammonium hydrogen phosphate solution. An addition of ammonium rhodanide to the electrolyte seems to delay the fibre

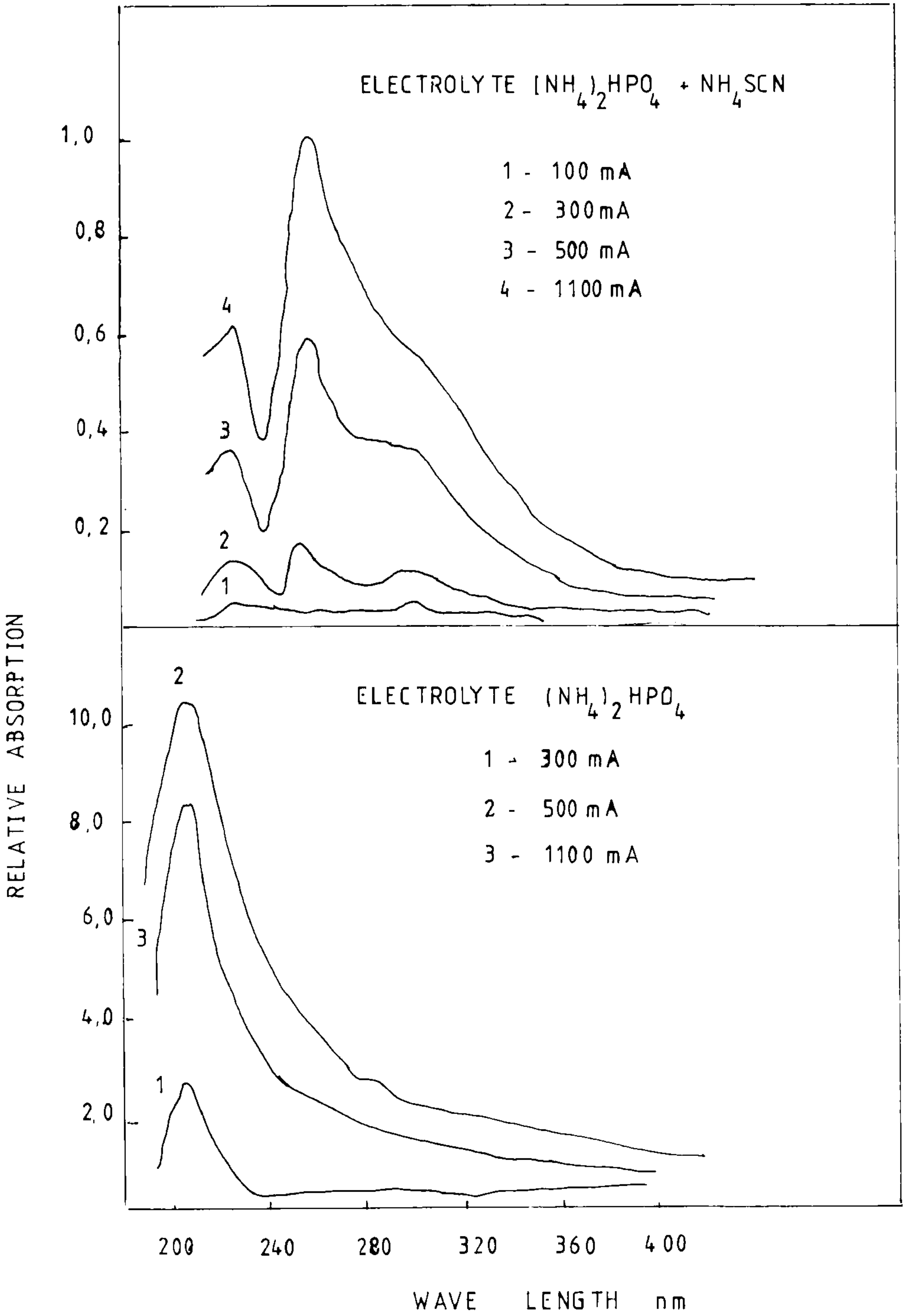

FIGURE 2 UV spectra of anodization baths.

TABLE I
Chemical composition of carbon fibres surfaces from ESCA measurements

Sample	Surface composition, at%				$\frac{O_{1s}}{C_{1s}}$	$\frac{N_{1s}}{C_{1s}}$
	C_{1s}	O_{1s}	N_{1s}	Others		
untreated as received	92.8	4.9	2.0	Na (traces)	0.053	0.021
commercially oxidized	88.8	8.9	2.3	—	0.100	0.026
lab. anodically oxidized in: 0.5 M $(NH_4)_2HPO_4$ I = 100 mA	81.6	11.7	5.8	Na, Ca (traces)	0.143	0.071
0.5 M $(NH_4)_2HPO_4$ + 0.005 M NH_4SCN I = 100 mA	85.5	9.2	5.3	—	0.108	0.062

oxidation, decreasing the amount of surface oxides which are formed. The increased nitrogen functionality on the fibre surface after anodic treatment is probably due to secondary reactions of the ammonium ions with the surface oxides, as reported in other publications.[2,3]

No traces of phosphorus, meaning no residuals from the electrolyte, are detected on the surface of the anodically treated carbon fibres.

3.3 Surface Free Energy Analysis

In order to obtain more information about the physical properties of carbon fibre surface after anodic treatment, an analysis of the surface free energy is performed. Both dispersive and polar terms of the surface free energy of the carbon fibre are determined by measuring the contact angle of a variety of liquids having known polar and dispersive components of their total surface energy, and analyzing the results according to the method proposed by Kaelble.[11]

$$[\gamma_L(1+\cos\theta)]/(2\gamma_L^{d\,1/2}) = \gamma_S^{d\,1/2} + \gamma_S^{p\,1/2}(\gamma_L^p/\gamma_L^d)^{1/2} \qquad (1)$$

A plot of $\gamma_L(1+\cos\theta)/2\gamma_L^{d\,1/2}$ *versus* $(\gamma_L^p/\gamma_L^d)^{1/2}$ yields a straight line (Fig. 3), with the slope and intercept providing a solution to polar and dispersive terms of surface free energy of the carbon fibres.

As can be seen from Table II, no change in the dispersive component of the carbon fibre surface energy is observed either for anodically or commercially oxidized fibres.

According to Donnet[15] γ_S^d, being the result of long range dispersive interactions, may be sensitive to the density and mass of the underlying material, which have not been affected significantly as a result of the electrochemical treatment. On the contrary, the polar term, being the result of short range polar interactions, is only sensitive to the density of polar atoms per unit area. Therefore, it increases in proportion to the superficial oxygen content as shown in Figure 4.

As can clearly be recognized from Figure 5, there exists no correlation between ILSS values of the composites and total surface oxygen content, or the polar term of the surface free energy of the corresponding carbon fibres.

A possible explanation of this fact, also observed by other authors,[16] may be found by comparing the surface properties of fibres and matrix.

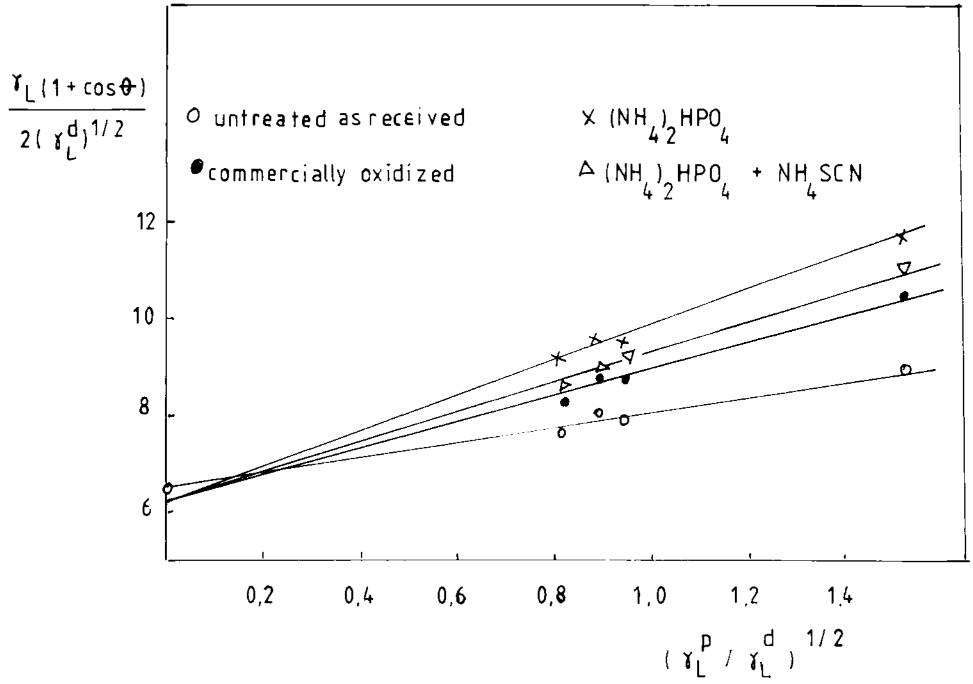

FIGURE 3 Plot according Kaelble[11] for determination of the components of surface free energy of the carbon fibres.

The surface free energy of an amine cured epoxy resin as well as its polar term ($\gamma_L^t = 44$ mJ/m^2, $\gamma_L^p = 4$ mJ/m^2)[11] are slightly lower than the corresponding values for all surface oxidized carbon fibres (Table II). Therefore, the thermodynamic criterion for spreading ($\gamma_s \geq \gamma_L$) is met and does not appear to be a limiting factor for the fibre-matrix adhesion.

In order to investigate, indirectly, the character of the surface oxides by means of acid-base (electron donor-electron acceptor) interactions, the wetting of carbon fibres by aqueous solutions of different pH values, according to idea of Hüttinger,[12] has been measured. The results are presented in Figure 6.

No significant dependence of the acidity or basicity of the test liquids on the contact angle is found with untreated carbon fibres. Commercially oxidized fibers, as well as those anodically oxidized in electrolyte with rhodanide added, are much better wetted by basic aqueous solution, than by acidic solution, indicating the dominant presence of acidic surface oxides.

TABLE II
Components of surface free energy (γ_s) of carbon fibres (mJ/m^2)

Carbon fibre	γ_s^d	γ_s^p	γ_s^t
untreated as received	42.0	2.5	44.5
commercially oxidized	40.0	7.4	47.4
lab. oxidized in:			
0.5 M $(NH_4)_2HPO_4$	40.0	12.5	52.5
0.5 M $(NH_4)_2HPO_4$ + 0.005 M NH_4SCN	40.0	9.0	49.0

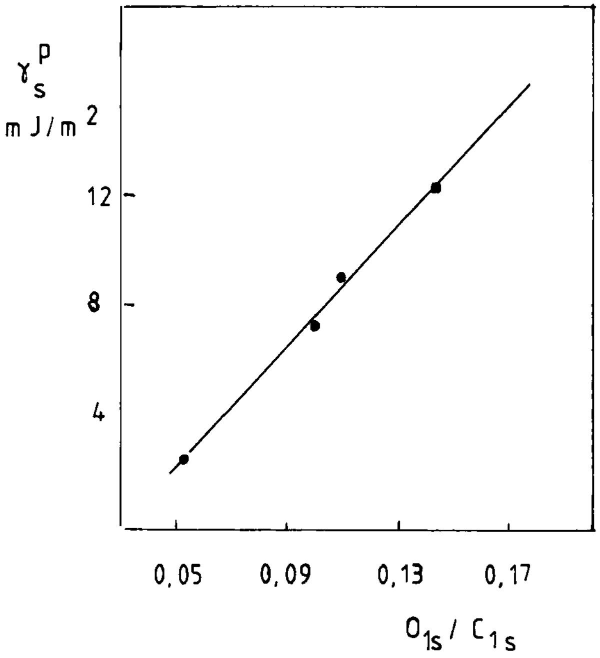

FIGURE 4 O_{1s}/C_{1s} ratio of carbon fibres from XPS measurements, correlated with their polar component of surface free energy.

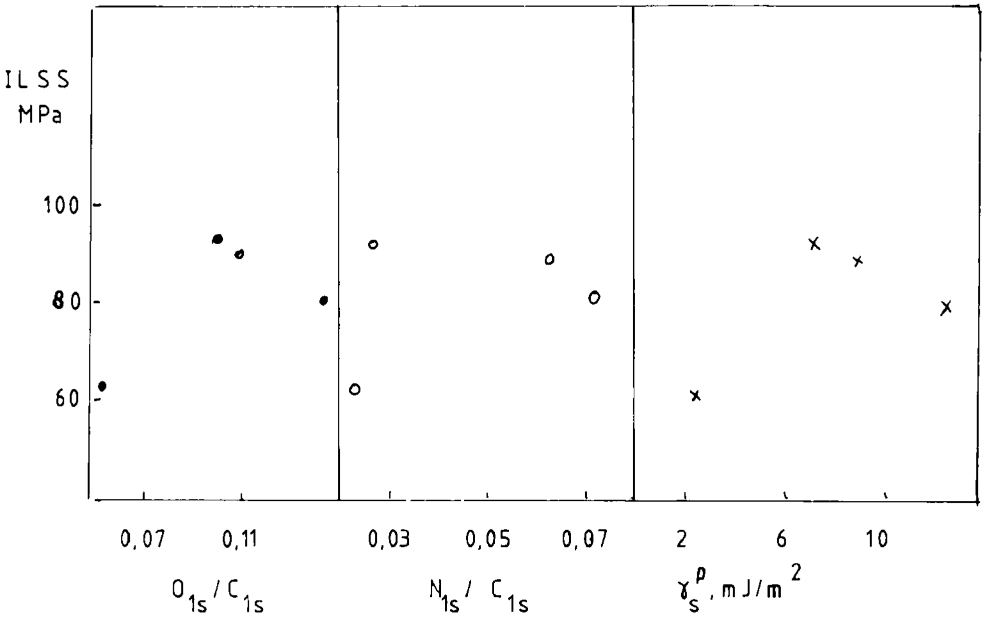

FIGURE 5 ILSS *versus* O_{1s}/C_{1s} ratio, N_{1s}/C_{1s} ratio and polar component of surface free energy of carbon fibres.

Total different wetting behaviour has been observed for carbon fibres treated in $(NH_4)_2HPO_4$ solution without addition of rhodanide. Such fibres show much better wettability by acidic aqueous solution than do the other oxidized fibres, but the value of cos θ does not change significantly if neutral or basic aqueous solutions are used as test liquids. Therefore, it appears that the carbon fibre surface, in this case, may be predominantly basic. The surface properties of the oxidized carbon fibres, as well as the ILSS values of the corresponding epoxy composites, are summarized in Table III.

A rough correlation could be found between the relative amount of acidic oxides on the fibre surface, expressed as the ratio cos θ_2/cos θ_1, and the adhesion in the composites, which can be explained by the basic character of the epoxy resin system used as the matrix. The nitrogen functionality also contributes to improving the fibre-matrix adhesion. This can be seen by comparing the properties of carbon fibres oxidized in diammonium hydrogen phosphate solution containing ammonium rhodanide with those for commercially treated samples (Table III).

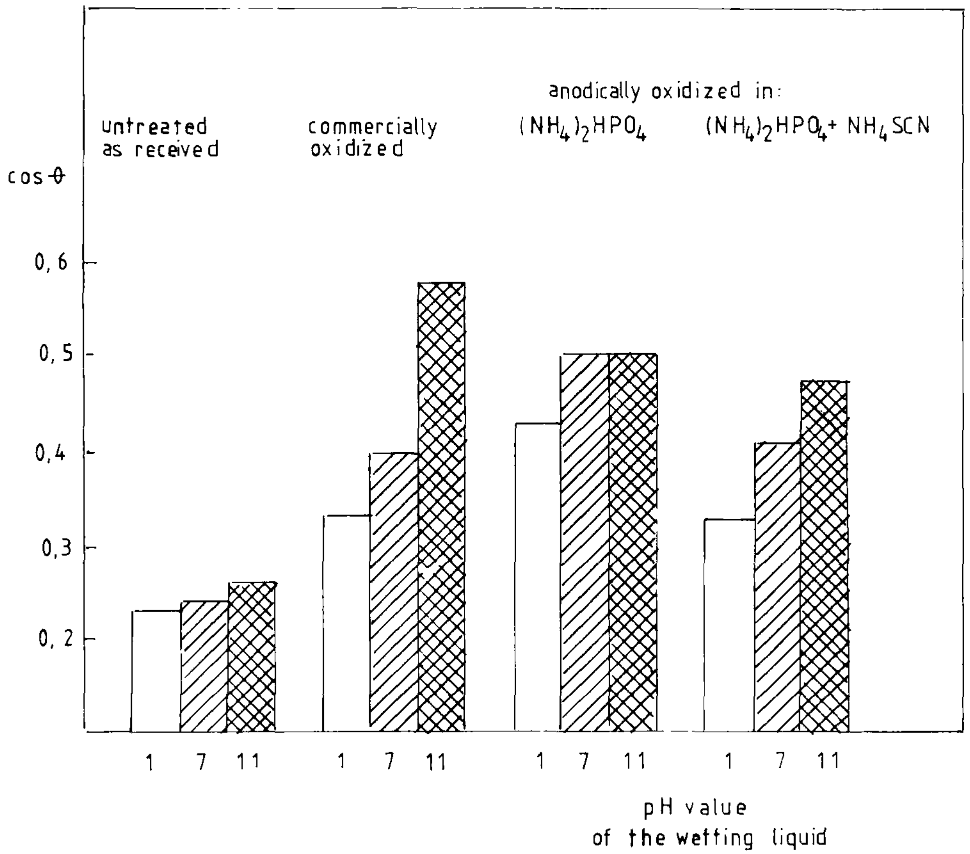

FIGURE 6 Wetting of carbon fibres by aqueous solutions of different pH values.

TABLE III
Surface properties of carbon fibres (CF) and ILSS values of the corresponding epoxy composites

Properties	CF anodically oxidized in		
	0.5M $(NH_4)_2HPO_4$	0.5M $(NH_4)_2HPO_4$ 0.005M NH_4SCN	Commercially oxidized CF
O_{1s}/C_{1s}	0.143	0.108	0.100
N_{1s}/C_{1s}	0.71	0.62	0.26
Polar component of the surface free energy γ_s^p, mJ/m^2	12.5	9.0	7.4
Wettability			
—by water pH = 1, cos θ_1	0.4236	0.3240	0.3302
—by water pH = 11, cos θ_2	0.5015	0.4673	0.5747
—cos θ_2/cos θ_1	1.18	1.44	1.74
BET-surface area, m^2/g	0.51	0.50	0.50
ILSS, MPa	83	91	93

4 CONCLUSIONS

An addition of ammonium rhodanide to the diammonium hydrogen phosphate anodization bath for oxidizing carbon fibres may be used as a means for regulating the oxidation process of the carbon fibres. It delays the oxidation reactions, reducing both the amounts of surface oxides formed (Tables I and III) and of water-soluble, organic degradation products (Fig. 2). At mild treatment conditions (I = 100 mA) no appreciable change in the tensile strength (Fig. 1) or in the BET-surface area (Table III) of the fibre has been observed. There is indirect information, from the wetting measurements (Fig. 6), that rhodanide addition to the main electrolyte changes the character of the oxides formed on the fibre surface from basic to predominantly acidic. Therefore, in spite of the lower surface oxygen content, a rise in the ILSS value of the corresponding epoxy composite is achieved, which approaches the value obtained with commercially-treated carbon fibres (Table III).

From the data, summarised in Table III, it appears that the rise in ILSS in the case of amine cured epoxy resin is not dependent on the O_{1s}/C_{1s} ratio or surface free energy, but on the acidic as well as nitrogen functional groups on the fibre surface. No change in BET-surface area has been observed at such mild oxidation conditions, so that mechanical interactions in the binding of the fibre to the resin may be neglected. The results of the present study confirm the model proposed by Matsui.[17] Adhesion between fibre surface and epoxy resin seems to be due to van der Waal forces, hydrogen bonds and sometimes covalent bonds, and to a lesser extent, mechanical interlocking.

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References

1. J. B. Donnet and G. Guilpain, *Carbon* **27,** 749 (1989).
2. C. Kozlowski and P. M. A. Sherwood, *Carbon* **24,** 357 (1986).
3. A. Proctor and P. M. A. Sherwood, *Carbon* **21,** 53 (1983).
4. E. Fitzer, *Carbon Fibres and Their Composites* (Springer-Verlag, New York, 1985).
5. J. B. Donnet and R. C. Bansal, *Carbon Fibres* (Marcel Dekker, New York, 1984).
6. K. Kinoshita, *Carbon-Electrochemical and Physicochemical Properties* (John Wiley & Sons, New York, 1988).
7. E. Fitzer and H.-P. Rensch, *Proc. 3th Int. Conf. on Composite Interfaces*, Cleveland, USA (1990), p. 241.
8. E. Fitzer, H. Jäger, N. Popovska and F. V. Sturm, *J. Appl. Electrochem.* **18,** 178 (1988).
9. H.-P. Rensch, Ph.D. Thesis, University of Karlsruhe, Institut für Chemische Technik (1990).
10. E. Fitzer, N. Popovska and H.-P. Rensch, *Carbon '90*, Paris, Extended Abstracts (1990), p. 50.
11. G. E. Hammer and L. T. Drzal, *Appl. Surf. Sci.* **4,** 340 (1980).
12. K. J. Hüttinger, *High Temp. High Press.* **22,** 317 (1990).
13. M. Hesse, H. Meier and B. Zeech, *Spektroskopische Methoden in der Organischen Chemie*, Stuttgart (1987).
14. J. B. Lambert, *Organic Structural Analysis* (Macmillian, New York, 1976).
15. J. B. Donnet, M. Brendle, T. L. Dhami and O. P. Bahl, *Carbon* **24,** 757 (1986).
16. J. Harvey, C. Kozlowski and P. M. A. Sherwood, *J. Mater. Sci.* **22,** 1585 (1987).
17. J. Matsui, in *Critical Reviews in Surface Chemistry*, **vol. 1,** Issue 2 (CRC Press, Inc., Boca Raton, Florida, 1990), pp. 71–130.