

the composite electrode in other electrolytes, such as H_2SO_4 , other promising metal fibers must be explored. Applications involving batteries and fuel cells also appear feasible using the flexibility offered by the composite electrode fabrication techniques described above.

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Electrochemical Bonding of Amines to Carbon Fiber Surfaces Toward Improved Carbon-Epoxy Composites

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ABSTRACT

Electrochemical oxidation of ω -diamines on carbon fibers allows the bonding of these molecules to the carbon fibers. The conditions leading to this surface modification are described, and the influence of the different parameters is discussed. The structure of the bonded layer is studied by voltammetry, XPS, and SIMS. A mechanism is proposed which involves the coupling of a radical cation to the fiber. Toughness of carbon-epoxy composites is improved when prepared from these modified fibers.

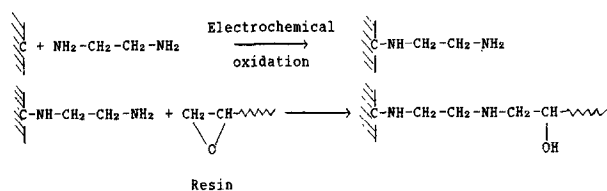
Among the numerous composite materials involving an organic matrix, those obtained from carbon fibers and epoxy resins are of particular interest; their use has undergone a large development in the aerospace industry. The mechanical properties of composite materials depend on that of the components, but also on that of the interface, therefore the treatment of carbon fibers is an important step in the fabrication process.

Industrial treatments involve the electrochemical oxidation in aqueous solution of the surface of carbon fibers at a potential positive to the decomposition of water; in this way oxygenated groups such as $-\text{C}-\text{OH}$, $-\text{C}=\text{O}$, $-\text{COOH}$ are formed on the carbon surface. This type of treatment leads to a high interfacial adhesion which is necessary to insure a good load transfer from the matrix to the fibers and to take advantage of the excellent tensile strength of the fibers (1). However, with this treatment the

choice of the surface groups is rather limited and as is also the means to improve the weak toughness of carbon-epoxy composites.

A possible way to improve the toughness of such composites would be the grafting of ω -diamines to establish a continuous succession of covalent bonds from the carbon fiber surface to the epoxy resin. For this purpose we decided to investigate the electrochemical oxidation of ω -diamines with the hope that one extremity would react upon oxidation with the carbon fibers and that the other one would remain free and therefore able to be reacted later on with the epoxy groups of the resin (2-5) (the chemical functions of epoxy resins hardeners are amino groups). This procedure is sketched in Scheme I. It should prove more versatile than the classical oxidation procedure quoted above, and it should permit the increase of the adhesion of the carbon fibers to the matrix by comparison with the untreated fibers (4, 5). Modification of the carbon fiber surface will be observed by cyclic voltammetry, specific chemical blocking, and surface analysis (XPS and SIMS).

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The detailed XPS and SIMS results and the mechanical measurements will be published elsewhere.

Experimental

Carbon fibers are high tensile strength Courtaulds XAU and in one case a high modulus Courtaulds HMU. The epoxy resin used to prepare the composite is Narmco 5208 (a mixed resin containing mainly tetraglycidylmethylenedianiline reticulated by diaminodimethylsulfone). Acetonitrile (ACN) was of analytical quality and was dried over 3Å molecular sieve before use, its water content measured by IR was 0.05% volume; this water content did not increase upon addition of the substrate (also dried on molecular sieve) and supporting electrolyte. The glassy carbon electrodes were prepared from 3 mm diam carbon rods (Tokai Corporation) embedded in epoxy resin and carefully polished before each use with diamond paste down to 1 μm and then rinsed in ethanol with an ultrasonic cleaner. Ethylene diamine **1** and triethylene tetramine **4** were of commercial origin and distilled before use. The other compounds were of commercial origin and used as received. N-(2-aminoethyl)-4-fluorobenzamide **3** was prepared (20) by refluxing for 8h a toluene solution containing stoichiometric amounts of ethyl-4-fluorobenzoate with ethylene diamine. On cooling a product precipitates, which is identified as the di(4-fluorobenzoyl) derivative of ethylene diamine. This compound is filtered, washed with ether, and the filtrate evaporated under vacuum and distilled. The pale yellow oil which is obtained crystallizes in methylene chloride to give a white solid, mp 50°C; NMR (CDCl₃, TMS); δ 2.6-3.1 (m, 2H); δ 3-5 (t, 2H); δ 7-9 (m, 7H, aromatics, NH, NH₂). Aminomethyl-9-anthracene **7**: 4g (0.02 mole) of 9-cyanoanthracene and 0.8g of LiAlH₄ (0.02 mole) are added to a benzene/ether (50/50) solution which is refluxed for 2h. After cooling, water is added and the dried organic layer is evaporated to give a yellow solid which is recrystallized in benzene: mp 106°C. Derivatization of bonded ethylene diamine molecules: the carbon fibers which have been treated by ethylene diamine are immersed in a solution of pyridine at 0°C containing an excess of 4-fluorobenzoyl chloride. After 15 min the fibers are washed with acetone and left for 12h in a vacuum oven at 50°C.

The equipment of cyclic voltammetry is composed of a Tacussel GSTP4 signal generator, a home-built potentiostat provided with ohmic drop compensation (21) and a Itelec 2502 paper recorder or a 7313 Tektronix oscilloscope. The experimental setup for the oxidative bonding of ethylene diamine to carbon fibers included a 100 ml cylindrical cell, a cylindrical platinum grid used as the cathode, a saturated calomel electrode used as a reference and separated from the solution by a bridge containing ACN and the supporting electrolyte, and a 4 cm long bundle of 24,000 carbon fibers used as the anode (Fig. 1). The potential of the anode was controlled by a Tacussel PRT 100-1X potentiostat. The solution was maintained under argon. XPS data was obtained using a Riber LAS4000 apparatus with a magnesium anode ($h\nu = 1253.6$ eV). SIMS profiles were recorded on parts of bundles using a Riber LAS4000 apparatus, and on a single fiber using a Cameca IMS 3F.

Electrochemical Behavior of ω-Diamines

Ethylene diamine NH₂-CH₂-CH₂-NH₂ **1** presents by cyclic voltammetry (on a glassy carbon electrode in ACN) a single broad irreversible peak located at about +1.3 V/SCE (see Fig. 2).

This peak remains irreversible: no cathodic peak can be observed on the reverse scan when the scan rate is increased up to 20 Vs⁻¹, indicating that the species obtained

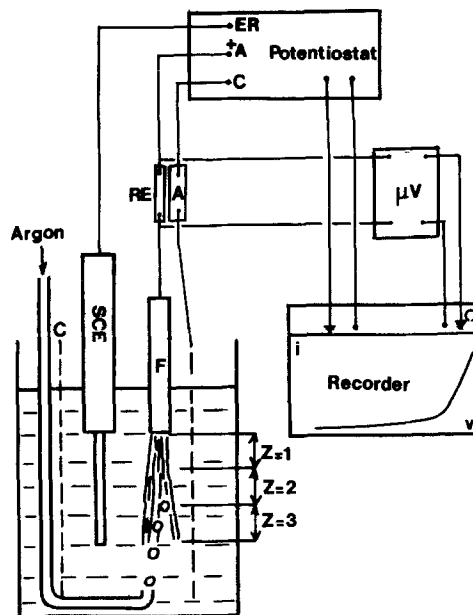
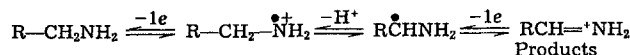


Fig. 1. Electrochemical cell for the treatment of carbon fiber bundles. R.E.: SCE; F: bundle of carbon fibers used as anode; C: platinum cathode; Z = 1, 2, 3, see text.

after the first electron transfer undergoes a chemical reaction. It disappears on a second scan due to the passivation of the electrode (6) (as we shall see later on, this passivation is related to the grafting of ethylene diamine on the electrode). The same phenomenon is evidenced by the sudden decrease in the current during the treatment of carbon fibers. It is therefore necessary to polish again the electrode before each scan. The transfer coefficient α was determined from the peak width: $\alpha = 0.23$. Once α is known it is possible to estimate from the peak current i_p the number of electrons per molecule, n , exchanged in the reaction (7)

$$i_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} ACD^{1/2} \nu^{1/2}$$

(A: electrode surface; D: diffusion coefficient; ν : scan rate; $n_a = 1$ is the number of electrons involved in the rate-determining step as always in aprotic solvents). Taking as an approximate value of D the value derived from the peak current of the reversible wave of ferrocene, one obtains a value of $n = 1.8 \pm 0.2$ electron per molecule. These numbers (α and n) should be used with some caution as they are obtained from Butler-Volmer kinetics and that adsorption is present in our case. They are, however, in agreement with the values obtained for other amines (see below). A similar behavior ($E_p = +1.45$ V/SCE) is observed in the case of hexamethylene diamine (NH₂-(CH₂)₆-NH₂) **2**. Two different behaviors can account for such a bielectronic transfer on ethylene diamine: (i) either a bielectronic transfer to a single amino group or (ii) two monoelectronic transfers on each of the amino functions. In the first case the observation of a single peak would imply that the second electron transfer be easier than the first one; the mechanism would be of the ECE type, the C step being a deprotonation as proposed by Mann (6) for primary amines

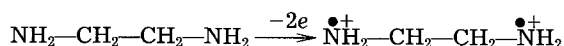


In the second case the observation of a single peak would result from two electronic transfers to two identical and electronically independent amino groups with closely spaced redox potentials as in the case of 4,4'-dinitrophenylethane ($\Delta E^\circ = 46.1$ mV) (8).

In order to distinguish between these two cases we investigated, under the same conditions, two related molecules: a primary amine isobutylamine and a derivative of ethylene diamine with one of the amino groups blocked by a 4-fluorobenzoyl group: NH₂-CH₂-CH₂-NH-CO-C₆H₄-F **3**. Isobutylamine presents a single monoelec-

tronic peak at $E_p = +1.50$ V/SCE. Compound **3** also shows a single monoelectronic peak at $E_p = +1.6$ V/SCE. [This peak is not that of the amide group; amides are oxidized at more positive potentials, i.e., benzamide $E_{1/2} \approx 2.15$ V/SCE (9). The shift of the peak from 1.3 to 1.6V may be due to intramolecular hydrogen bonding of the amino group with the carbonyl of the C_6H_5CO group.] For both compounds no corresponding cathodic peak can be observed on the reverse scan.

The most likely scheme for the oxidation of ethylene diamine in aprotic medium is thus



The following polyamines have also been investigated in cyclic voltammetry as we intended to appraise their effects on the mechanical properties of composites. Triethylene tetramine **4** shows two peaks, respectively, at +0.97 and +1.25 V/SCE. Diaminobenzidine **5** shows a more complicated voltammogram with four anodic peaks, but on repetitive scanning a single reversible peak remains at $E_{pc} = E_{pa} = +0.6$ V/SCE. On electrolysis at +1.1 V/SCE a thick flaky deposit is observed by scanning electronic microscopy on the carbon fibers. This behavior is indicative of the formation of a conducting polymer on the electrode as in the case of aniline (10). This deposit is responsible for the poor mechanical properties of the composite prepared from these modified fibers. In spite of its electrochemical interest, diaminobenzidine was not investigated any further.

Influence of Different Parameters on the Grafting of Ethylene Diamine on High Tensile Strength Carbon Fibers

These treatments have been carried out in the specially designed preparative cell shown on Fig. 1. In this cell the anode is composed by a 4 cm long bundle of 24,000 fibers. In order to control the homogeneity of grafting, after electrolysis this bundle was cut into three parts referenced by their abscissa Z as shown on Fig. 1. Each fragment is independently analyzed by XPS.

The different parameters are summarized in Table I along with the results of XPS analysis. XPS survey-scan spectra of untreated and treated fibers exhibit three major peaks: C_{1s} , O_{1s} , N_{1s} . We characterize our fiber treatments semi-quantitatively through atomic "pseudo" concentrations computed from the peak areas by taking into account analyzer transmission, photoelectron mean free path, and photoelectron production cross section and considering that the material surface is only made up of carbon, oxygen, and nitrogen (fluorine in some cases; hydrogen is not detected). The derived concentrations are indeed pseudo concentrations since they would correspond to an hypothetical situation where (i) concentrations are uniform over the analyzed depth and (ii) the sample is flat. Condi-

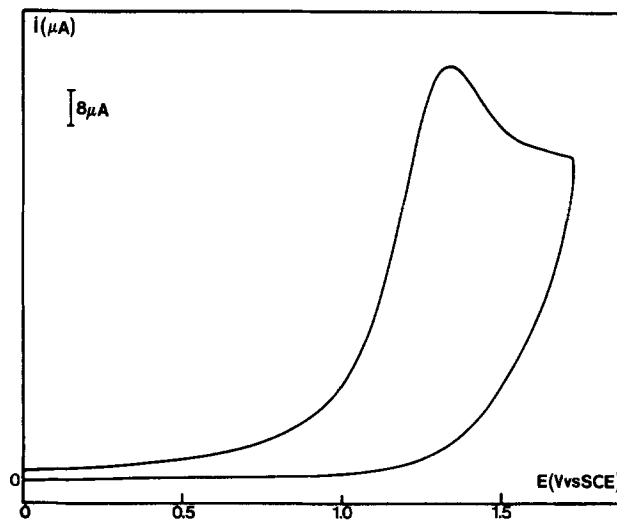


Fig. 2. Electrochemical oxidation of ethylene diamine ($7.4 \times 10^{-3}M$). Solvent: ACN. Electrode: glassy carbon. Supporting electrolyte: $10^{-1}M$ NBu_4BF_4 . Scan rate: $0.2 V s^{-1}$.

tion (i) is not satisfied as confirmed by SIMS profiles, neither is condition (ii) owing to the fibers geometry. Nevertheless, such pseudo concentrations are very useful for comparing surface treatments.

The percentage of nitrogen on untreated fibers measured by XPS is 2.2% and that of oxygen 9.8% (experiment 0, Table I). The treatment (experiment 1, Table I) increases the amount of nitrogen but this increase in nitrogen is uneven, being higher at the free extremity of the bundle ($Z = 3$, see Fig. 1) (N%: 20.6) than at the base of the bundle where fibers are tightened together ($Z = 1$) (N%: 7.3). This difference is due to the fact that convection is more important at the free end of the fibers which are agitated by the bubbles of argon; on the contrary the access to the other extremity where the fibers are tightened together is more difficult. Besides electrostatic screening of internal fibers certainly takes place at $Z = 1$. A small increase in the amount of oxygen is also observed, a mean value of 12% being observed after the treatment. This may be due to the oxidation of residual water contained in the solvent (although it is previously dried over a molecular sieve; see experimental part below) or to water which is adsorbed after the treatment. It may also come from some carbonation of the amino groups on carbon fibers surface. As the treatment is carried out for a longer and longer time (experiment 2) the percentage of nitrogen becomes more and more homogeneous along the carbon fibers varying only from 14.1 to 22.2% after 5 min. It should be noted that the maximum amount of nitrogen does not increase significantly. The amount of oxygen remains approximately con-

Table I. Electrochemical treatment of carbon fibers (Courtaulds XAU. Solvent ACN)

Experiment	C (M/l)	S Supporting electrolyte	E (V)	Time (s)	T (°C)	XPS nitrogen %
0	—	—	—	—	—	2.2
1	0.2	$LiClO_4$ 0.2M	+1.6	90	20	^a Z = 1 7.3 ^a Z = 2 15.7 ^a Z = 3 20.6
2	0.2	$LiClO_4$ 0.2M	+1.6	300	20	Z = 1 14.1 Z = 2 20.1 Z = 3 22.2
3	0.2	NBu_4BF_4 0.2M	+1.6	90	50	Z = 1 19.9 Z = 2 21.3 Z = 3 20.3
4	0.2	NBu_4BF_4 0.2M	+2.0	90	20	Z = 1 18.2 Z = 2 18.2 Z = 3 21.4
5	1	$LiClO_4$ 0.2M	+1.6	90	20	Z = 1 12.2

C: concentration of ethylene diamine

E: electrolysis potential, V/SCE

^a Fragment number, see Fig. 1.

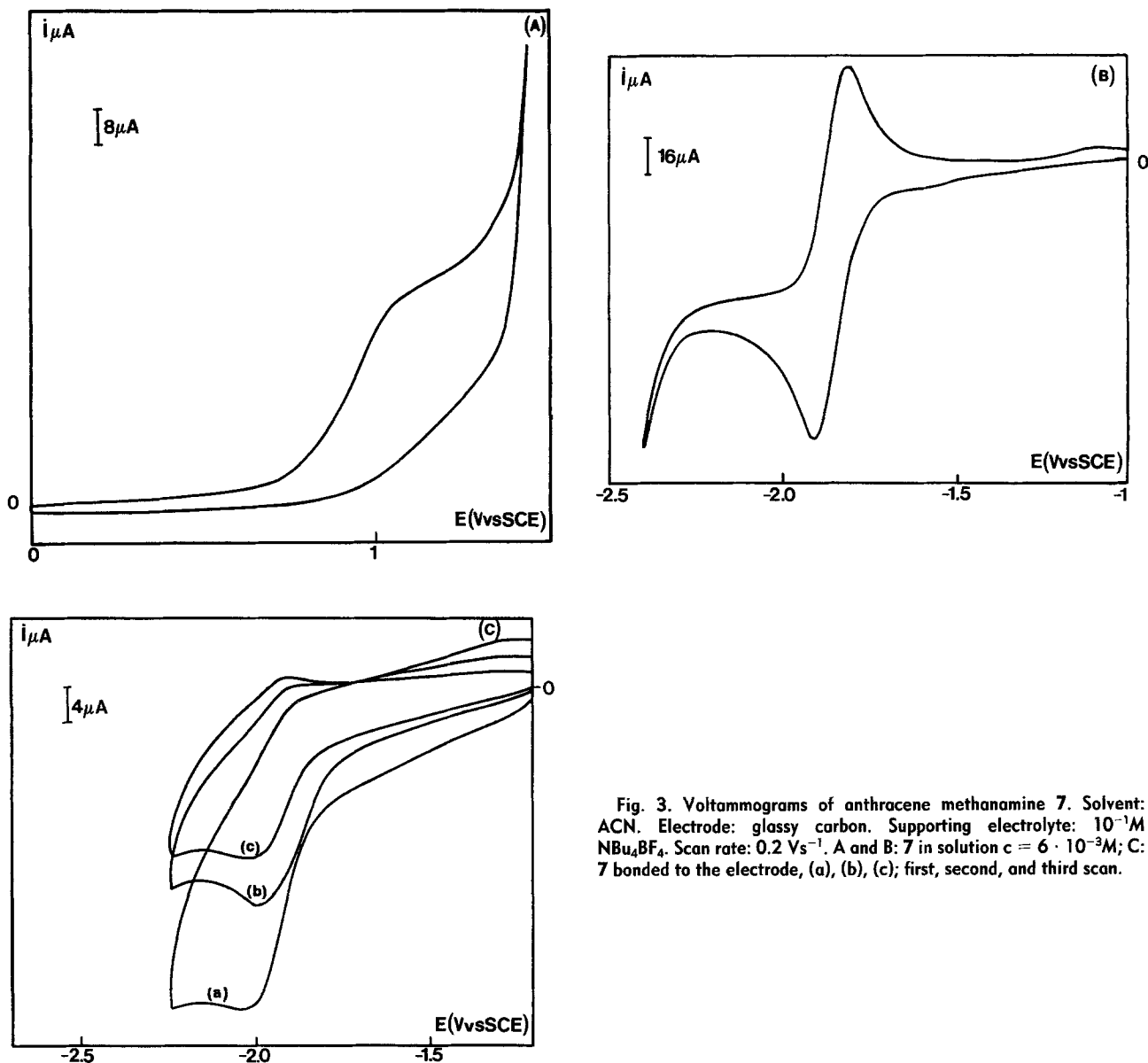


Fig. 3. Voltammograms of anthracene methanamine 7. Solvent: ACN. Electrode: glassy carbon. Supporting electrolyte: $10^{-1}M$ NBu_4BF_4 . Scan rate: $0.2 V s^{-1}$. A and B: 7 in solution $c = 6 \cdot 10^{-3}M$; C: 7 bonded to the electrode, (a), (b), (c); first, second, and third scan.

stant. Changing the temperature from 20° to $50^\circ C$ (experiment 3) allows one to obtain a homogeneous coverage of nitrogen all along the fibers. From one extremity of the fibers to the other the percentage of nitrogen remains at the highest level precendly observed, i.e., about 20%. This result is obtained after only 45s of treatment. The effect of temperature may be related to an increase of the kinetics of electron transfer and to an increase of the diffusion coefficient by a factor of 3 [$D = kT/6 \Pi \eta a$ (k : Boltzmann constant; a : radius of the molecule; η : viscosity of ACN which decreases with the temperature), Ref. (11).] When the oxidation potential is set at $+2.0 V/SCE$ (experiment 4) the percentage of nitrogen on the fibers is also increased along with a small increase of oxygen, as observed in the previous experiments. Changing the concentration of ethylene diamine from 0.2 to $1M$ (experiment 5) only produces a small increase of the percentage of nitrogen, as shown by XPS on the $Z = 1$ fragment. With a $0.2M$ concentration of ethylene diamine the electrolysis cell contains 0.02 mole of substrate while grafting of a monolayer on the 24,000 bundle of fibers would necessitate about $4 \cdot 10^{-7}$ mole. Two different supporting electrolytes $LiClO_4$ and NBu_4BF_4 were used without any change in the results and further experiments were performed with NBu_4BF_4 for safety and convenience reasons. Several experiments similar to experiment 2 were carried out to test the reproducibility and the percent N varied from 20 to 24% with NBu_4BF_4 . From the results of Table I it appears that a maximum value of 20-24% N is attained whatever the parameter and seems to

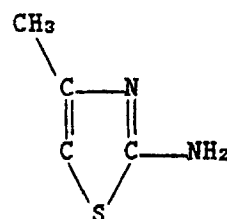
correspond to a saturation of the surface which is modified (but this maximum value is attained after different times).

Thus, it clearly appears that the electrochemical oxidation of ethylene diamine brings about a modification of the carbon fibers surface which can be evidenced by an increased amount of nitrogen as measured by XPS.

Structure of the Modifying Layer

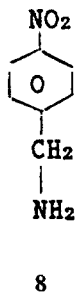
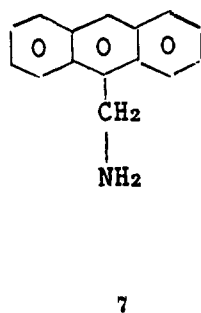
We first checked that a strong, most likely covalent bond is established and that ethylene diamine is not only physically adsorbed on the surface. A Courtaulds high tensile strength XAU bundle immersed in pure ethylene diamine, rinsed, and analyzed by XPS does not show any increase in nitrogen. Conversely, if carbon fibers treated according to experiment 2 are thermo-desorbed in high vacuum (10^{-9} torr) at $110^\circ C$ for 1h the percent N does not decrease.

To answer the question of a possible cleavage of the molecule during the treatment we oxidized a primary amine with a sulfur atom 2-amino-4-methyl thiazole 6



Sulfur can be easily recognized and quantified by XPS. **6** presents a voltammetric behavior ($E_p = +0.9$ V/SCE) similar to that of isobutylamine. After a treatment under the same conditions as experiment 2 at +1.4 V/SCE the negative SIMS spectrum shows a peak at $M/Z = 32$ indicating the presence of sulfur on the surface of the fibers. Besides, measurement of the area of N1s and S2p photoelectron peaks shows that the nitrogen over sulfur ratio equals two as could be expected if **6** was entirely bonded to the fibers without undergoing any cleavage at the level of the C—N bond of **6**.

The next question we addressed was the measurement of the surface density of amines on carbon fibers. For this purpose we used two molecules **7** and **8** with both an oxidizable amino group and a reducible function

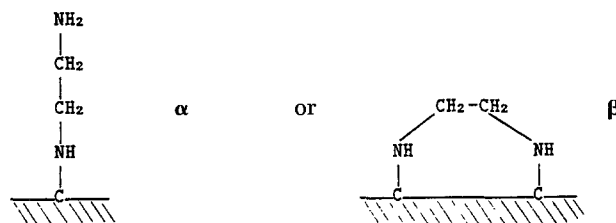


Oxidation of the amino group with a carbon electrode should allow the molecule to be bonded to the carbon. Once the molecule is bonded it should be possible to observe its reduction. From the area of the reduction peak of the voltammogram one can deduce the number of molecules which are bonded. The oxidation and reduction voltammograms of **7** are shown on Fig. 3A and B on a glassy carbon electrode. The oxidation of **7** is monoelectronic and irreversible (as in the case of **1**) while the reduction is monoelectronic, reversible, and involves a fast electronic transfer ($\Delta E_p = 100$ mV). **7** is bonded to glassy carbon by treatment similar to those already described ($E = +1.1$ V/SCE during 5 min). The electrode is then carefully rinsed in an ultrasonic cleaner and transferred to a new solution containing only the solvent (ACN) and supporting electrolyte (NBu_4BF_4 10^{-1}M). The reduction voltammogram of Fig. 3C is then observed. Most of the reversibility has been lost and upon successive scans the voltammogram slowly disappears, increasing the scan rate from 0.2 to 2 Vs^{-1} , slows down the decrease of voltammogram. The loss of reversibility and the disappearance of the voltammogram can be ascribed to the protonation of the radical anion by residual water; in the case of Fig. 3C and at the difference of what is observed in Fig. 3B, no diffusion occurs which can bring new molecules of substrate to the electrode. From the area of the first voltammogram (corrected for the background current) the number of molecules which have undergone a monoelectronic reduction can be deduced. Knowing the apparent area of the electrode (which is probably somewhat smaller than the real one) a concentration of 1.2×10^{-9} mol/cm² can be calculated which corresponds to a surface of 14\AA^2 occupied by each molecule. This number is in fair agreement with the surface of 17\AA^2 which can be obtained from molecular models for molecules standing up on the surface. The surface density is also in good agreement with the values of about 10^{-9} mol/cm² generally given by Murray (12) for monolayers. These results show that on glassy carbon an approximately monolayer of **7** is bonded to the carbon surface, and it is likely the same occurs for **1**.

The same experiment was performed with **8**. Its reduction and oxidation voltammograms are shown on Fig. 4A and B. A single 5 mm long carbon fiber was treated under the conditions of experiment 2 with NBu_4BF_4 at +1.7 V/SCE and transferred to a new (ACN, NBu_4BF_4) solution. The voltammogram of Fig. 4C was obtained, from which a surface coverage of 7.3×10^{-10} mol/cm² could be calculated which corresponds to a value of 23\AA^2 per molecule. The approximate area occupied by a molecule of **8** standing up on the surface is 24\AA^2 as measured from mo-

lecular models and 52\AA^2 for a molecule lying on the surface. These results point to a monolayer of molecules standing up on the carbon (both on glassy carbon and on the fiber). These measurements are in good agreement with the results of SIMS experiments performed on a single fiber. The secondary ion profiles display the presence of nitrogen and show that the thickness of the grafted layer is compatible with the voltammetric measurements, taking into account that an ionic profile depends on the surface topography (height of asperities, micropores) and on the atomic stirring up produced by the primary ion beam. (As noted heretofore the detailed XPS and SIMS results and the mechanical measurements will be published elsewhere.)

The next problem related to the structure of the bonded layer is the stereochemistry of bonded ethylene diamine. Does it bind by one end, the other one being free in the solution (situation α) or does it bind by both ends to the carbon surface in a bridge configuration (situation β) (13, 14)



To determine the relative amount of each configuration a bundle of fibers was treated as in experiment 2 with NBu_4BF_4 and then reacted with 4-fluoro-benzoyl chloride

($\text{F}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$ **9**), a protecting reagent for amino groups which can be identified by XPS through its fluorine atom (15). The fluorine to nitrogen ratio F/N of treated fibers is defined as

$$\text{F/N} = \frac{\% \text{F in treated fibers}}{\% \text{N in treated fibers} - \% \text{N in untreated fibers}}$$

(Untreated fibers contain about 2.2% nitrogen and no fluorine.)

The results are given in Table II. Similar results are obtained if the reaction with **9** is carried out under sonication to improve the penetration of the reagent between the fibers. If one assumes, which is likely, that it is mainly the NH_2 groups of unbridged ethylene diamine molecules (α

Table II. XPS measurements on Courtaulds XAU fibers

Fiber	Atomic %	ESCA			
		C	N	O	F/N
a		64.7	22.4	12.9	—
b		68.2	16.0	14	0.138 ^c

a. Treated as in experiment 2 (0.2 M/liter of ethylene diamine, in ACN with NBu_4BF_4 0.2 M/liter, $E = +1.6$ V/ECS, $t = 300$ s at 20°C)

b. Treated as above and further reacted with $\text{F}-\text{C}_6\text{H}_4\text{COCl}$.

^c $\text{F/N} = \% \text{F in fibers b} / \% \text{N in fibers b} - \% \text{N in untreated fibers}$

Table III. Mechanical data for carbon-epoxy composites

Fibers	Epoxy resin	G_{IC} (J/m ²)	τ_d (MPa)
XAU, untreated	NARMCO 5208	400	88.5 ± 5
XAS, commercial oxidized	NARMCO 5208	315	≈ 125
XAU (1)	NARMCO 5208	385	117 ± 5
XAU (2)	NARMCO 5208	640	107 ± 3.5

G_{IC} : fracture energy release rate; a : length of the crack: 120 mm.

τ_d : debonding stress as measured by a pull-out test (18).

(1), Treated with ethylene diamine as in experiment 2 with NBu_4BF_4 0.2M.

(2), Treated with triethylene tetramine as in experiment 2 with NBu_4BF_4 0.2M.

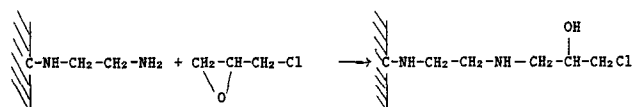
two and four electrons in excess of what we have measured.

2. This oxidation would lead to an imine or to an iminium ion (9b, c) which would be readily hydrolyzed by residual water (which even in dried acetonitrile is far in excess to the surface concentration of amino groups). This hydrolysis would lead to the cleavage of the grafted molecule, a reaction that we have shown not to occur both by XPS and by cyclic voltammetry. However, it should be remarked that on nickel, silver, cobalt . . . electrodes secondary amines are more difficult to oxidize than primary amines (9c).

In the case where the potential is set at +2.0 V/SCE (experiment 4) there is also the possibility that some carbon atoms in the fiber be oxidized to positively charged species (carbocation or radical cation) (16). If this is the case it should be possible to bind ethylene diamine molecules to high modulus fibers by operating at +2.0 V/SCE. This is indeed what is observed on Courtaulds HMU fibers when treated as in experiment 4. The following XPS analysis is obtained: C: 62.2%, N: 27.3%, and O: 10.5%.

Reaction of Ethylene Diamine Modified Carbon Fibers with Epoxy Resins

The amino groups bonded to the surface should be able to react with the epoxy groups of the resins as do the amino functions of hardeners. This is indeed the case as checked by XPS (4) by reacting previously treated fibers with epichlorohydrine



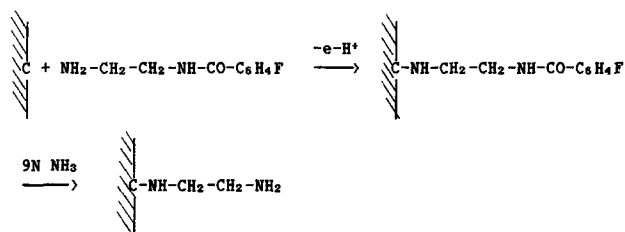
When untreated carbon fibers are reacted with epichlorohydrine at 120°C for 22h in a sealed tube and then carefully rinsed and dried, they evidence the following XPS analysis: C: 94%, O: 5.3% Cl: 0.7%, and no N detected. There is no change in the C1s peak shape. If the same reaction is carried out with fibers previously oxidized in the presence of hexamethylene tetramine the following analysis results: C: 73.7%, O: 20.8%, N: 4.3%, and Cl: 1.2%. Besides, XPS analysis shows a two-fold C1s peak; the second component is due to contributions of various types of chemical bondings in the epichlorohydrine molecules grafted on the fiber surface (4).

In the case of ethylene diamine the reaction with the epoxy resin can take place both with primary and secondary amines but, as stated before, secondary amines are probably less reactive due to steric hindrance. A possible way to increase the ratio of primary amino groups would be to oxidize 3 and to deprotect the primary amino group once the molecule is bonded to the fibers (17) (Scheme 3)

Mechanical Properties of Composites Prepared from Fibers Treated with Diamines

Industrial preparation of composites requires high lengths of treated bundles (≈ 1 km). A pilot cell has been constructed which permits a continuous electrochemical grafting of carbon fibers (5, and our other work). XPS analyses have shown that the grafting is homogeneous in the whole section of the bundle.

Toughness of unidirectional composites has been appraised by following the opening of a double cantilever



Scheme 3

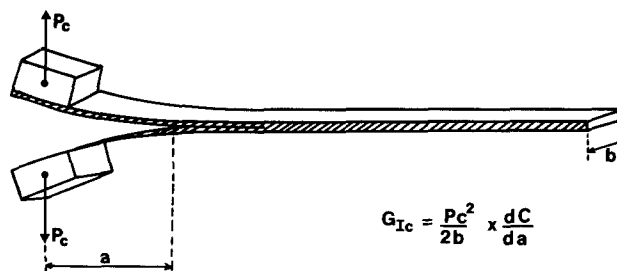


Fig. 5. Double cantilever beam test measurement of strain energy release rate G_{IC} for unidirectional composite materials P_c : critical load for fracture propagation. C : double beam compliance.

beam induced by the crack growth in a parallel direction to the fibers (Fig. 5). This experiment allows one to measure the strain energy release rate in mode I, G_{IC} (or fracture toughness) (to be published, 18, 19), i.e., the energy necessary to create the unit area in delamination. A micromechanical test ("pull-out test") was used to measure the debonding shear stress τ_d between fiber and matrix, as shown on Fig. 6. A single filament ($\phi \approx 7 \mu\text{m}$) is embedded in a layer of resin. When the force F_o applied on its free end reaches the debonding force F_d then the fiber is pulled out. The mean value of τ_d is given by F_d/pl (p : fiber perimeter, l : embedded length). Using Greszczuk theory (22) one can calculate τ_d .

Three amines have been used for the modification of carbon fiber surfaces: ethylene diamine 1, triethylene tetramine 4, and diaminobenzidine 5. Two bundles of untreated XAU fibers and of industrially oxidized XAS fibers were taken as references. As stated before, diaminobenzidine 5 electropolymerizes on carbon fibers and forms a thick, incoherent deposit. This deposit does not improve the toughness of the composite. As shown on Table III ethylene diamine 1 and triethylene tetramine 4 lead to a higher toughness of the carbon-epoxy composite by comparison with industrially treated fibers.

Adhesion between fibers and epoxy resin is strongly increased by industrial oxidizing treatments. Grafting of ω -diamines 1 and 4 leads to a good adhesion smaller, however, than that obtained with industrial treatments (Table III).

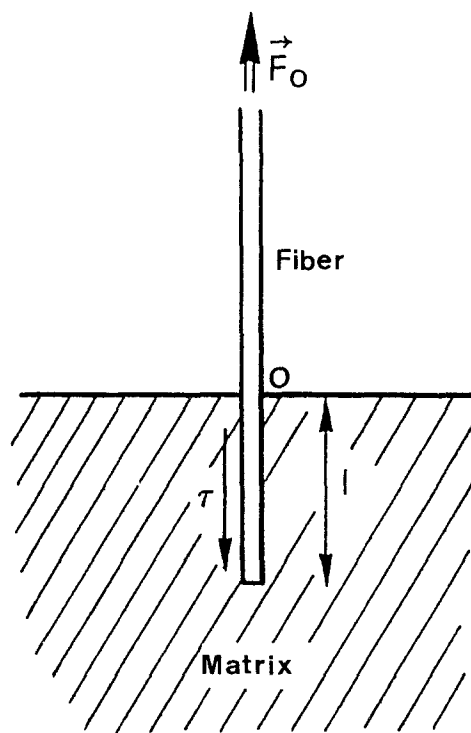


Fig. 6. Geometry of pull-out test; F_o : applied force, l : embedded length, τ : interfacial shear stress. Debonding occurs when $\tau = \tau_d$ at $l = 0$.

Contrary to ethylene diamine **1**, triethylene tetramine **4** can give rise to multiple bridges on the surface, thus favoring an interpenetration with the epoxy polymer. It is possible that the structure of the grafted layer of **4** promotes an increased interfacial toughness due to electrostatic interactions between the modified surface and the resin. This better interfacial toughness is responsible for the improved toughness of the composite.

Conclusion

Oxidation of ω -diamines leads to radical cations which form covalent C—N bonds with the carbon fiber surface without any cleavage of the starting molecule. The deposit obtained by this method constitutes approximately a monolayer. The variety of molecules which can be bonded in this way offers a wide scope of possible surface modification. Among the molecules which have been tested triethylene tetramine **4** leads to the highest toughness of the composite.

Such treatments are not limited to carbon fibers, but may be applied to any carbon surface (massive carbon pieces, carbon blacks, graphites . . .). This grafting process may be of interest not only for composite materials in the aerospace industry, but also for selective deionization and detoxication, for the concentration of very dilute substances, for catalysis or for biotechnologies.

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On-Line Mass Spectrometric Insights Into Electrochemical Reactions: Oxidation of Thiopurines

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ABSTRACT

Electrochemistry was used on-line with high-performance liquid chromatography with mass spectrometric and UV-vis spectrophotometric detection to characterize the electrochemical oxidation pathways of 6-thiopurine and 6-thioxanthine. At low potentials, the electrochemical oxidation of 6-thiopurine proceeds via one electron resulting in disulfide formation. It is proposed that purine-6-sulfenic acid is formed at potentials $> +0.50$ V. Further oxidation of this unstable sulfenic acid presumably results in the formation of purine-6-sulfinate and purine-6-sulfonate. At potentials $> +0.50$ V purine-6-sulfinate, purine-6-sulfonamide, and purine-6-sulfonate have been identified as the final products of 6-thiopurine oxidation. On-line electrochemical studies indicate that at potentials less than $+0.30$ V, oxidation of 6-thioxanthine results in disulfide formation. The disulfide readily disproportionates to regenerate the original thiol plus small amounts of a sulfenic acid. At potentials $> +0.30$ V, it is proposed that the thiol group of 6-thioxanthine is further oxidized to a sulfenic acid. Xanthine and 2-hydroxypurine presumably form as a result of nucleophilic and electrophilic attack, respectively, on the sulfenic acid. At potentials greater than $+0.40$ V, both the thiol group and the purine ring of 6-thioxanthine undergo oxidation. Subsequent hydrolysis reactions produce an imine alcohol, the same intermediate which forms during uric acid oxidation, providing proof that oxidation of the purine ring occurs at potentials $> +0.40$ V.

When electrochemical methods are used in combination with mass spectrometry (1-8), high-performance liquid chromatography (2, 7, 9), or molecular spectroscopy (1, 10), important information about the structures of electrochemical intermediates, products, and the chemical reactions which may occur following electro-oxidation can be obtained. Electrochemistry on-line with mass spectrometry

(EC/MS) has become a powerful tool which allows fast identification of electrochemically generated species as a function of electrode potential where hydrodynamic EC/MS results can be obtained and compared with off-line cyclic voltammetry (4-8). While chemical information, in addition to that obtained by electrochemistry, may be obtained by other spectroscopic techniques such as on-line UV-vis absorption spectrophotometry (spectroelectrochemistry) (10), the inherent selectivity and sensitivity of

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