

# ToF SIMS and XPS Studies of Carbon Fiber Surface during Electrolytic Oxidation in $^{17}\text{O}/^{18}\text{O}$ Enriched Aqueous Electrolytes

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Time-of-flight secondary ion mass spectrometry (ToF SIMS) has been applied in conjunction with isotope enrichment to investigate the chemical composition of the surface species of poly(acrylonitrile)-based carbon fibers, which were electrolytically oxidized in dilute hydrochloric acid solution in water with  $^{17}\text{O}/^{18}\text{O}$  enrichment. The technique provides a tool with greater specificity and sensitivity to elemental species than X-ray photoelectron spectroscopy (XPS), in which the effects of the presence of the heavier isotopes on the modification to surface chemistry cannot be detected. Peaks associated with oxygen-containing functionalities, for example,  $m/z = 16$  ( $\text{O}^-$ ),  $17$  ( $^{17}\text{O}^-$ ,  $\text{OH}^-$ ),  $18$  ( $^{18}\text{O}^-$ ,  $^{17}\text{OH}^-$ ), and  $19$  ( $^{18}\text{OH}^-$ ) were identified in negative ToF SIMS spectra of carbon fibers treated in isotope enriched solution. Only  $m/z = 16$  ( $\text{O}^-$ ),  $17$  ( $^{17}\text{O}^-$ ,  $\text{OH}^-$ ) were identified on carbon fiber surfaces treated in normal water. The concentrations of these surface species all showed an increasing trend with the level of treatment. The use of HCl solution as the electrolyte introduced  $\text{Cl}^-$  onto the fiber surfaces, and its concentration was determined using both XPS and SIMS, with SIMS showing a much improved sensitivity when the surface concentration is lower than 0.5 atom %.

## Introduction

Carbon fiber reinforced composite materials have found wide applications in many industries. The specific physical and mechanical properties of composite materials are governed not only by the properties of the individual components but also by the interface between them. Successful reinforcement of matrix materials requires a degree of stress transfer between the matrix and fibers, which can be achieved by physical and chemical adhesion between the two. Several surface treatment methods have been developed to improve the matrix/fiber interaction. These methods include wet chemical oxidation,<sup>1,2</sup> dry oxidation in hot air,<sup>3</sup> electrolytic oxidation in aqueous solution,<sup>4–6</sup> and cold plasma treatment.<sup>7,8</sup> Electrolytic oxidation proved the most useful for commercial applications as it is easily adapted for continuous treatment of fiber tows in an industrial environment.

The chemistry and physics of the interface are still subject to much debate. Some argue that these treatments remove weak links in interfacial bonding,<sup>9–12</sup> while others believe that the introduction of functionalities such as carboxyl ( $-\text{COOH}$ ) and hydroxyl ( $-\text{OH}$ ) enables good matrix/fiber bonding.<sup>13–15,19</sup> Presently, technical limitations prevent the in situ analysis of interfaces and interphases of the composites. Instead, the surface chemistry of the carbon fibers is investigated with a view to providing vital information regarding the complex nature of interfacial interactions.

X-ray photoelectron spectroscopy (XPS) has been used by many researchers to quantify carbon fiber surface

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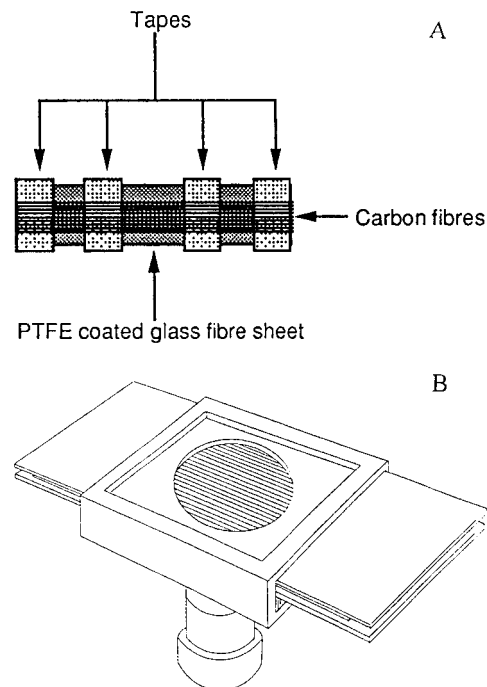
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chemistry.<sup>15–24</sup> Its main weakness is the difficulty in identifying the type and distribution of functional groups unambiguously, which could be partially solved by derivatization or metal ion labeling methods.<sup>17b,19b,21</sup> Time-of-flight secondary ion mass spectrometry (ToF SIMS) provides a tool with greater specificity and sensitivity to elemental species than XPS.<sup>19b,25,26</sup> SIMS also has a unique capability for isotope discrimination.<sup>27–30</sup> For example, oxygen isotopes have been used in studies of transport and reaction mechanisms, in both passivation and degradation of materials, and negative ions of <sup>16</sup>O and <sup>18</sup>O are often measured in SIMS when a metal oxide is analyzed with respect to its abundance of these isotopes.<sup>27</sup> Of course the use of nuclear magnetic resonance (NMR) sensitive isotopes, such as <sup>17</sup>O and <sup>13</sup>C, or radioactive isotopes such as <sup>3</sup>H or <sup>14</sup>C provide the possibilities of characterizing the surface chemistry using high-resolution NMR or autoradiography,<sup>31,32</sup> respectively.

The authors have developed a complementary hydrogen–tritium exchange procedure to quantify the surface-exchangeable protons, which are available to form chemical bonds.<sup>33</sup> Molecular simulation<sup>34</sup> indicates that both functionalities and the change of geometry in graphitic structure play important roles in interfacial adhesion. In this paper we present our preliminary findings on the application of a technique which combines isotope enrichment with ToF SIMS to investigate the surface chemistry of carbon fibers during electrolytic oxidation in <sup>17</sup>O/<sup>18</sup>O enriched aqueous solutions.

### Experimental Section

**Materials.** Carbon fibers used in this investigation were poly(acrylonitrile) (PAN) based Courtaulds Grafil XAU (unsized, untreated) and XAS (unsized, commercially surface treated) fibers in the form of 6000 filament tow. The fiber diameter was  $\sim 7 \mu\text{m}$ . Nominal fiber surface area per mm of tow  $A_{\text{f}} = 1.32 \times 10^{-4} \text{ m}^2$ . <sup>17</sup>O/<sup>18</sup>O isotope enriched water (designated as water-<sup>17</sup>O, H<sub>2</sub><sup>17</sup>O, normalized, 20.2 atom % <sup>17</sup>O,



**Figure 1.** Schematic diagram of the carbon fiber specimen construction used in anodic surface treatment (A). Spring-loaded sample holder used in SIMS analysis (B).

28.6 atom % <sup>18</sup>O, Isotec Inc.), ammonium bicarbonate (99%, Aldrich), and hydrochloric acid (anal. 36% w/w, BDH) were used as received.

**Electrolytic Surface Treatment in Aqueous Hydrochloric Acid Solution.** XAU carbon fibers were treated with a hydrochloric acid (HCl) solution (0.2 M, 0.7 cm<sup>3</sup>) in a quartz cell (10 mm  $\times$  3 mm, at 30 mm depth). Carbon fiber tow (45 mm) was taped (Scotch Magic tape, 3M) on a strip of poly(tetrafluoroethylene) (PTFE) coated glass fiber cloth (45  $\times$  8 mm<sup>2</sup>). A schematic diagram of the specimen construction is shown in Figure 1A. The carbon fibers were connected to the anode through a “bull-dog” clip. The cathode was a strip of lead. The charge (coulomb) passing to the fibers in the electrolyte was used as a measure of the level of surface treatment. After treatment, the carbon fibers were kept in a 25 cm<sup>3</sup> glass vial and dried (120 °C overnight). The experiments were repeated using a 0.2 M HCl solution in water-<sup>17</sup>O. The isotope distributions in this solution are: 11.8 atom % <sup>17</sup>O and 16.7 atom % <sup>18</sup>O.

**XPS.** Carbon fiber samples (2 cm tow) were mounted on holders with sufficient fibers to cover the analysis area (ca. 10 mm<sup>2</sup>). XPS measurements were made using a VG Scientific ESCALAB Mk II spectrometer interfaced with a VG5000S data system based on a DECPDP 11/73 computer. The operating conditions were as follows: the X-ray source (Mg K $\alpha$  1253.6 eV radiation) was operated at a power of 450 W (i.e., 13 kV potential and 34 mA emission current). The spectrometer was operated in the fixed analyzer transmission mode at a pass energy of 50 eV (survey spectra) or 20 eV (high-resolution spectra). The base pressure in the sample chamber during analysis was approximately  $3 \times 10^{-8}$  mbar. Good-quality survey spectra were obtained with a single scan. Coreline high-resolution spectra of C 1s, N 1s, O 1s, Na 1s, and Cl 2p were integrated over 5–10 scans depending on the intensity of the spectral region of interest. Spectral analysis was carried out using the standard VGS5000S software for quantification and peak fitting.

**ToF SIMS.** Surface-treated carbon fiber ( $\sim 6$  mm tow) fixed on a PTFE-coated glass fiber strip was sandwiched between two aluminum plates (10  $\times$  25 mm<sup>2</sup>), with a circular aperture (6 mm). The specimen was then mounted on a spring loaded sample holder (see Figure 1B). High-resolution ToF SIMS

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**Table 1. X-ray Photoelectron Spectroscopy Surface Elemental Concentration (atom %) for Carbon Fibers Treated in HCl-H<sub>2</sub><sup>17</sup>O Solution**

no.	treatment level (coulomb)	surface elemental concentration (atom %)			
		C	O	N	Cl
1	0	95.0	2.0	3.0	0.1
2	0.1	95.2	2.2	2.5	0.1
3	0.3	92.7	4.1	2.8	0.4
4	0.6	88.4	7.9	3.1	0.6
5	2.2	83.4	13.6	1.7	1.3

analysis was performed using a VG Scientific Type 23 instrument (Fisons Instruments, East Grinstead, UK). This instrument is equipped with a single-stage reflectron analyzer with a MIG300PB pulsed liquid metal (Ga<sup>+</sup>) ion source. The Type 23 is also equipped with a pulsed electron source for charge compensation. Static SIMS conditions (i.e., a total ion dose of less than  $1 \times 10^{12}$  ions cm<sup>-2</sup> during analysis) were employed using a pulsed (20 kHz and 20 ns) 15 keV Ga<sup>+</sup> primary ion beam with pulsed charge compensation and 4 keV sample bias, rastered over a frame area of  $0.8 \times 0.8$  mm<sup>2</sup> at 50 frames/s. SIMS spectra were acquired over a mass range of  $m/z = 5-400$  in both the negative- and positive-ion modes for each specimen. Spectra were recorded from five fresh regions across each specimen. The intensity for a given peak was obtained as the average value of the five measurements.

## Results and Discussion

**Surface Treatment Using a Small Quantity of Electrolyte.** The cell configurations were chosen after a few trials. The size and shape must accommodate the use of a very small amount of electrolyte with isotope enrichment, at the same time providing sufficient amount of fiber samples for XPS and SIMS analysis. The quartz cell only requires a total of 0.7 cm<sup>3</sup> solution. In earlier experiments copper plates were used as cathode and copper (Cu<sup>+</sup>) contamination was found on the fiber surface as indicated by a Cu 2p peak at 934 eV in the XPS spectrum. Lead was used as a replacement, and no Pb 4f peak (at 138 eV) was observed in the XPS spectra. PTFE cloth served to separate the two electrodes and to provide a reasonably strong but flexible base to hold the fibers. Both PTFE and glass fiber are inert under the experimental conditions and so did not interfere with the electrolytic oxidation. The alignment of the fibers was maintained during the subsequent handling, and the surface was not disturbed. Spectra taken across the tow confirmed that the surface treatment was uniform. The choice of HCl solution as electrolyte was made because HCl as a volatile compound would be removed upon drying. Treated fibers could not undergo aqueous washing in order to avoid oxygen isotope exchange reaction on the surface.

**XPS Analysis.** The elemental surface composition of the carbon fibers treated in the aqueous hydrochloric acid solution in water-<sup>17</sup>O was determined by XPS, and the results are given in Table 1. Quantification was based on peak areas calculated from the high-resolution spectra, and the appropriate atomic sensitivity factors (ASF) defined by Wagner were used.<sup>35</sup> The quantification algorithm provided within the VGS5000S Datasystem corrects these ASFs to allow for the analyzer transmission function of the spectrometer and correction in electron attenuation length (resulting from the correction in electron kinetic energy). It must be noted,

however, that in common with all quantification carried out by XPS (unless sophisticated approaches such as angle-resolved XPS or multiphoton analysis are used) the analyst is provided with a surface composition that is an integral value and assumes the sample is homogeneous within the outer 3–5 nm. Thus, while providing particularly useful comparative analysis between specimens of a similar type, care must be taken in the treatment of such an analysis in isolation or in comparison with the results obtained from another quantitative technique. Generally speaking, electrolytic oxidation of the carbon fibers resulted in increases in oxygen, nitrogen, chlorine, and sodium peak intensities but a decrease in the carbon peak intensity in the XPS spectra.

Further examinations of the C 1s spectrum, centered at 284 eV, showed a multicomponent peak which can be resolved into its five individual components by peak fitting, with each peak having a full width at half-maximum (fwhm) of ca. 1.70 eV. For example, four surface oxide peaks were identified in the XPS C 1s spectrum of electrolytically treated carbon fibers, corresponding to C–OH, carbonyl C=O, lactone C=O, and COOH. The high binding energy components of the C 1s peak increase with the level of surface treatment, indicating the introduction of more chemical functionalities. This is consistent with the spectrometer resolution employed and in keeping with our other experimental studies on carbon fibers. Ever since Sherwood and co-workers<sup>4,5</sup> carried out pioneering work on the application of XPS C 1s peak fitting to determine carbon fiber surface functionalities, it has been concluded that XPS is not routinely capable of resolving the individual contributions associated with different functionalities, as in a polymeric system, because of the conduction band interactions present in the partially graphitic carbon fibers.<sup>25,26</sup> This situation was further complicated by the low level of functionalities introduced as a result of surface treatment.

The N 1s peak, on the other hand, consisted of two components, one at 401 eV and the other at 398 eV, indicating that two distinct species exist on the surface, one was present on the untreated carbon fiber surface, and the other occurred through oxidation. The N 1s peak shape changed as a result of surface treatment, i.e., initially the nitrogen signal at 398 eV was weak but became of nearly equal strength to the peak 401 eV as the surface treatment level increased. Since there was no external nitrogen source in the electrolyte used, the N 1s peak at 398 eV emerged during the oxidation must be the result of exposing residue nitrogen retained during the carbonization of PAN precursor. The changes in N 1s peaks were also observed from samples treated in aqueous ammonium bicarbonate solution. It implies that NH<sub>4</sub><sup>+</sup> in the electrolyte is not involved in surface reactions during electrolytic oxidation. Our results are supported by those reported in Alexander and Jones' XPS study on electrolytic oxidized Hercules PAN-based carbon fibers.<sup>26</sup> They observed that the initially small nitrogen peak at 401.4 eV was obscured or replaced by a nitrogen signal at 400.3 eV introduced by the surface treatment. The nitrogen introduced was considered to be from an aromatic imide or urethane as opposed to the protonated amine on the untreated fiber. However, spectra obtained in our laboratory showed the coexist-

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**Table 2. XPS Analysis of Carbon Fibers before and after Washing Using HCl Solution**

no.	treatment	surface elemental concentration (atom %)			
		C	O	N	Na
1	before acid wash	79.0	10.4	4.1	6.5
2	after acid wash	87.4	6.4	5.5	0.7

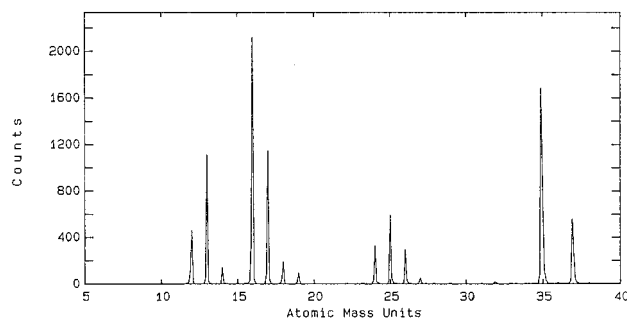
ence of the two peaks rather than one replacing the other.

No discernible change in O 1s peak shape was observed. Isotope enrichment of  $^{17}\text{O}$  and  $^{18}\text{O}$  in water- $^{17}\text{O}$  did not alter the XPS analysis, indicating that the modification to surface chemistry was not affected by the presence of the heavier isotopes. Na was detected from all samples at a level  $<1$  atom %. Sometimes highly treated carbon fibers contain a high level of sodium probably introduced as a result of absorption or by forming the sodium salt on the surface. Further treatment, e.g., washing with dilute acidic solution is required (discussed in next section).

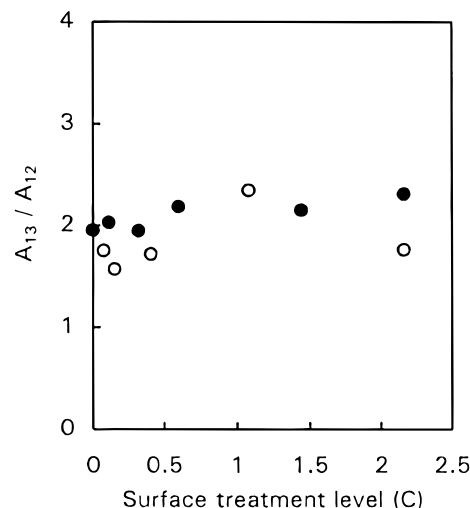
Chlorine (Cl 2p), centered at 199 eV, is a relatively symmetrical peak. Its intensity increases with the increase of surface treatment level. It is noted that the quantification of chlorine concentration becomes more difficult at lower levels, i.e.,  $<0.5$  atom %.

**Carbon Fibers Washed with Aqueous HCl Solution After Electrolytic Oxidation.** A high level of sodium residue was detected on the surface of XAU carbon fibers electrolyzed in ammonium bicarbonate solution. One sample was further treated with 0.3 M HCl aqueous solution ( $10\text{ cm}^3$ ) for 4 h at room temperature and then washed with distilled water ( $5 \times 10\text{ cm}^3$ ). The fibers were dried in an oven ( $170\text{ }^\circ\text{C}$ ) overnight and analyzed by XPS (see Table 2). The Na 1s peak intensity was significantly reduced, indicating that most of the sodium was removed from the surface. Sodium could be retained on the surface by either absorption (for example, as NaCl) or by forming sodium salts with surface acidic functional groups such as carboxyl, i.e.,  $-\text{COONa}$ , or phenolic, i.e.,  $\text{Ph}-\text{ONa}$ . Since it was difficult to remove sodium solely by washing with water, the possibility of sodium chloride salt depositing on the surface is minimized. On the other hand, a strong acid such as HCl could convert surface functionalities to their acidic form (i.e., carboxyl  $-\text{COOH}$  or phenolic  $\text{Ph}-\text{OH}$ ) and therefore replace sodium. No Cl 2p peak (at 199 eV) was observed, confirming that the washings after acidic treatment effectively removed all chlorine.

**Positive SIMS Analysis.** Positive ToF SIMS spectra were obtained for carbon fibers electrolytically oxidized in both aqueous solution in normal water and water- $^{17}\text{O}$ . Information provided by the positive SIMS spectra is limited. Peaks at  $m/z = 73, 133, 147, 207, 221,$  and  $281$  are an indication of poly(dimethylsiloxane) (PDMS) contamination, arising possibly from the release agent on the adhesive tape. However, at such low level the presence of PDMS does not attenuate peaks of interest in the negative SIMS analysis and hence does not obscure other useful chemical information. Lithium ( $\text{Li}^+$ ,  $m/z = 7$ ) and sodium ( $\text{Na}^+$ ,  $m/z = 23$ ) are present in all samples. The intense peaks in the lower part of the mass range are mainly due to hydrocarbon fragments ( $\text{C}_n\text{H}_m^+$ ,  $m/z = 15, 27, 29, 39, 41, 43, 55, 57$ ). There are also peaks associated with aromatic species ( $m/z = 91, 105, 115, 128, 141, 152, 165, 178$ ). All the



**Figure 2.** Typical example of negative ToF SIMS spectrum for carbon fibers treated in 0.2 M hydrochloric acid solution in water- $^{17}\text{O}$ .

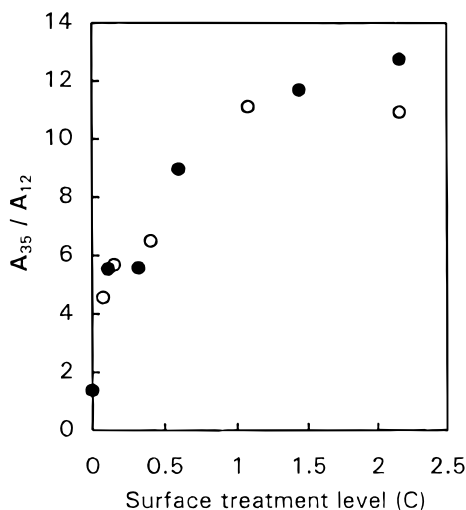


**Figure 3.**  $A_{13}/A_{12}$  vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (●) and in water- $^{16}\text{O}$  (○).

unsized and untreated XAU fiber and unsized, but commercially treated, XAS fibers have the above-described characteristic peaks in their positive SIMS spectra. These spectra are in good agreement with SIMS results obtained on similarly PAN-based carbon fibers treated using ammonium bicarbonate solution.<sup>25</sup>

**Negative SIMS Analysis.** Detailed SIMS analyses were carried out on samples treated in HCl solution with water- $^{17}\text{O}$  and HCl solution in ordinary water. A typical negative ToF SIMS spectrum of the low mass region is shown in Figure 2. Peaks associated with oxygen-containing functionalities, i.e.,  $m/z = 16$  ( $\text{O}^-$ ),  $17$  ( $^{17}\text{O}^-$ ,  $\text{OH}^-$ ),  $18$  ( $^{18}\text{O}^-$ ,  $^{17}\text{OH}^-$ ), and  $19$  ( $^{18}\text{OH}^-$ ) were observed in ToF SIMS spectra of carbon fibers treated in isotope-enriched solution. Only  $m/z = 16$  ( $\text{O}^-$ ),  $17$  ( $^{17}\text{O}^-$ ,  $\text{OH}^-$ ) were identified on carbon fiber surfaces treated in normal water. Other species, such as  $\text{C}^-$  ( $m/z = 12$ ),  $\text{CH}^-$  ( $m/z = 13$ ),  $\text{C}_2^-$  ( $m/z = 24$ ),  $\text{C}_2\text{H}^-$  ( $m/z = 25$ ),  $\text{CN}^-$  ( $m/z = 26$ ), and  $\text{Cl}^-$  ( $m/z = 35, 37$ ) were present in all spectra.

The ratio of an individual peak intensity  $A_x$  to the peak intensity of carbon ( $m/z = 12$ )  $A_{12}$  is used as a measure of the concentration of each species during surface treatment. Although this value sometimes reflects more the stability of the species, it also serves as a good indicator of the concentration of related surface functional groups.  $A_x/A_{12}$  values are plotted against the level of treatment.  $A_{13}/A_{12}$  are constant in both cases (Figure 3). This can be observed on most PAN-based carbon fibers as the majority of the surface consists of carbons ( $\text{C}^-$  or  $\text{CH}^-$ ). The increase in



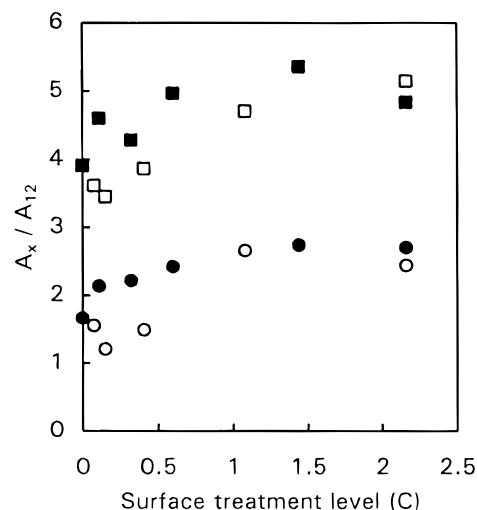
**Figure 4.** Surface concentration of chlorine ( $A_{35}/A_{12}$ ) vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (●) and in water- $^{16}\text{O}$  (○).

oxidation level was also reflected in the change in nitrogen-containing species ( $\text{CN}^-$ ,  $m/z = 26$ ).

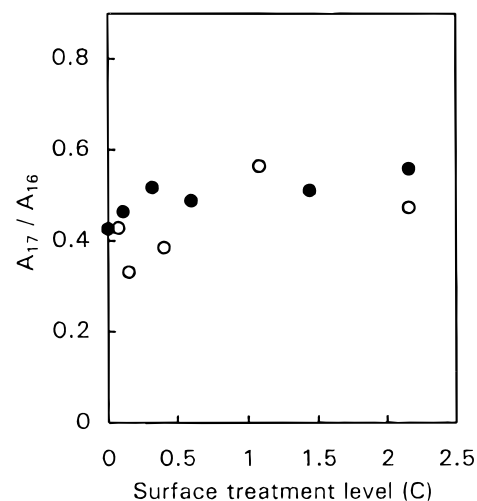
The surface concentration of chlorine ( $\text{Cl}^-$ ) increases significantly with the degree of surface treatment (Figure 4). This increase was also observed in XPS analysis of the same samples, albeit with less sensitivity. Hearn and Briggs<sup>25</sup> found evidence of sodium salt deposits, but with distinct chloride particles in SEM and SIMS images of PAN-based carbon fibers, which had been treated with 10% ammonium bicarbonate solution. XPS results obtained in our laboratory for HCl-washed carbon fibers indicated that sodium can be removed by acidification without introducing  $\text{Cl}^-$  on the surfaces (see Table 2). The increase in the  $\text{Cl}^-$  concentration during oxidation far exceeds the increase in  $\text{Na}^+$  concentration. Sodium chloride salt deposition is therefore unlikely the main source of chlorine. It is noted that when an electrode surface is polarized anodically anionic species, sometimes at extremely low level in the electrolyte, are absorbed on the electrode surface. In the present case,  $\text{Cl}^-$  ions are absorbed from the electrolyte onto the carbon fiber surface during the anodic treatment. The overall concentration is low (<1 atom %), but the amount does increase with the degree of fiber treatment.

The oxygen related peaks are mainly  $m/z = 16$  and  $m/z = 17$ . They all display an upward trend, as surface treatment increases the number of carboxylic and phenolic groups on the surface. Peak intensities of both peaks  $A_{16}/A_{12}$  and  $A_{17}/A_{12}$  are similar in both water- $^{17}\text{O}$  or in water- $^{16}\text{O}$  (Figure 5). Plots of  $A_{17}/A_{16}$  for both solutions against treatment level are shown in Figure 6. A small increase of  $A_{17}/A_{16}$  for fiber treated in water- $^{17}\text{O}$  can be seen, possibly due to the fact that the peak intensity at  $m/z = 17$  is from the combination of two species  $^{17}\text{O}^-$  and  $^{16}\text{OH}^-$ , while in water- $^{16}\text{O}$  peak intensity at the same position could only be from the contribution of  $^{16}\text{OH}^-$ .

The two peaks at  $m/z = 18$  and  $m/z = 19$  are due to the  $^{17}\text{O}$  and  $^{18}\text{O}$  label in the water- $^{17}\text{O}$ . These peaks did not appear in the SIMS spectra of XAU and commercially treated XAS fibers. Therefore,  $\text{F}^-$  ( $m/z = 19$ ) contamination was unlikely.  $A_{19}/A_{12}$  and  $A_{18}/A_{12}$  levels are very close to the baseline for fibers treated in water- $^{16}\text{O}$  (Figure 7). Peak intensities of both peaks for

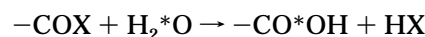


**Figure 5.** Surface concentration of oxygen-containing functionalities ( $m/z = 16$  and  $m/z = 17$ ).  $A_{16}/A_{12}$  vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (●) and in water- $^{16}\text{O}$  (○).  $A_{17}/A_{12}$  vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (■) and in water- $^{16}\text{O}$  (□).



**Figure 6.**  $A_{17}/A_{16}$  vs treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (●) and in water- $^{16}\text{O}$  (○).

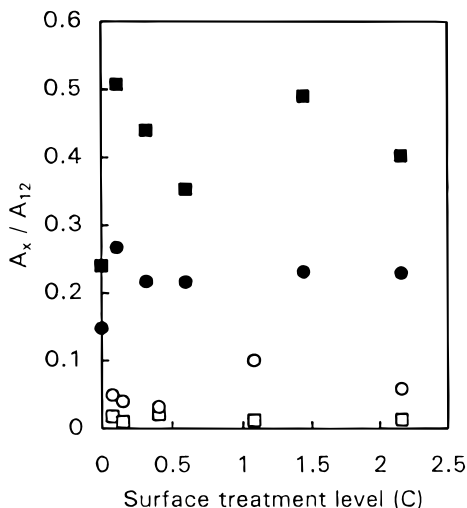
fibers treated in water- $^{17}\text{O}$  are much higher (also see Figure 7). The  $m/z = 19$  and  $m/z = 18$  species were also detected on the XAU carbon fiber surfaces, which were only immersed in the electrolyte without applying an electric current. SIMS analysis clearly demonstrated there was isotope labeling via a nucleophilic substitution with the surface functional groups. Carboxylic acid and derivatives, but neither alcohols nor ketones undergo this reaction:<sup>36</sup>



where X = hal, OCOR, OH, OR, and  $\text{NR}_2$ . The order of reactivity is acyl halides > anhydrides > acids, esters > amides. The acyl halides are the most active groups, and the amides are the least reactive groups.

The labeled water was diluted, and the final isotope distribution in the electrolyte was  $^{17}\text{O}$  11.8%,  $^{18}\text{O}$  16.7%, which gives an initial isotope ratio  $(^{17}\text{O}/^{16}\text{O})_0 = 0.165$  and  $(^{18}\text{O}/^{16}\text{O})_0 = 0.233$  in the solution. The average

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**Figure 7.** Surface concentration of oxygen containing functionalities ( $m/z = 18$  and  $m/z = 19$ ).  $A_{19}/A_{12}$  vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (●) and in water- $^{16}\text{O}$  (○).  $A_{18}/A_{12}$  vs surface treatment level on the surfaces of carbon fiber treated in water- $^{17}\text{O}$  (■) and in water- $^{16}\text{O}$  (□).

ratios on the carbon fiber surface are  $A_{18}/A_{16} = 0.03$  and  $A_{19}/A_{16} = 0.05$ . Of all the possible functionalities on the carbon fiber surface, only carboxylic acid undergoes the isotope exchange reaction. The ratio  $[A_{19}/A_{16}]:[(^{18}\text{O}/^{16}\text{O})_0]$  can give an estimation that the acid concentration was only  $\sim 20\%$  in all oxygen-containing chemical surface groups, since  $^{18}\text{OH}^-$  ( $m/z = 19$ ) represents 1 equiv of  $-\text{COOH}$ . The ratios  $[A_{18}/A_{16}]_{\text{XAU}}$  and  $[A_{19}/A_{16}]_{\text{XAU}}$  were only half those of surface-treated carbon fiber samples, indicating that acid and/or derivatives already exist on unsized and untreated carbon fiber surfaces. Electrolytic surface treatment increases the number of acidic groups by as much as twice that number. Obviously, more accurate results can be obtained using higher isotope enrichment. Alexander and Jones estimated that the acid group concentration, expressed as a proportion of the total oxygen concentration, remained approximately constant at 30–40%, determined by derivatization with aqueous barium salts.<sup>19</sup> Their carbon fibers were electrolytically oxidized in aqueous ammonium bicarbonate solution. Another study pro-

duced a much lower figure (ca. 20%) although the fibers were oxidized in 65%  $\text{HNO}_3$ .<sup>24</sup>

Matrix resins used in carbon fiber reinforced composites function differently within the interphase region. It is recognized that the formation of covalent bonds in sufficient number should improve the interfacial adhesion between matrix and carbon fibers.<sup>37</sup> Furthermore it is postulated that the increase in interlaminar shear strength (ILSS) observed upon surface treatment is the result of interaction of surface oxygen containing functionalities with the epoxy resin or amine hardener functionalities. In model reactions end groups of the epoxy resin are known to react with  $-\text{COOH}$  or  $-\text{OH}$  but not with  $-\text{COOR}$  or  $-\text{CONR}_2$ .<sup>38</sup> It has been reasoned that acid–base interactions between acidic groups at the fiber surface and basic functional groups of the polymer strengthen interfaces between carbon fiber and high-temperature thermoplastics, such as polycarbonate.<sup>39</sup> The importance of such results from quantitative analysis is that the amount of the active groups among all oxygen-containing moieties on carbon fiber surfaces could be potentially related to the composite interfacial mechanical properties. The use of SIMS, assisted by isotopic labeling, and XPS or several combined analytical methods are part of the efforts to establish such quantitative information. With such information available it may be possible to ascertain whether the improvement in ILSS depends on the matrix–fiber links by means of chemical bonding or another mechanism.

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