Comparison Between FT-IR and XPS Characterization of Carbon Fiber Surfaces

T. Ohwaki[a]; H. Ishida[a]

[a] NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, U.S.A.

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NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

Fourier transform infrared internal reflection spectroscopy and X-ray photoelectron spectroscopy XPS have been applied to investigate the surface of polyacrylonitrile-based carbon fibers treated by chemical oxidation and electrochemical oxidation. We have found that infrared spectroscopy has comparable sensitivity to XPS and that the amount of the functionality introduced at the fiber surface depends on the oxidation time in the case of chemical oxidation and on the electrolyte used in the case of electrochemical oxidation.

KEY WORDS FT-IR; XPS; carbon fiber; surface treatment; electrochemical oxidation.

INTRODUCTION

It is now generally accepted that the interphase, the region near the matrix resin/ reinforcing fiber interface in a composite material, differs in composition and properties from the bulk material. In carbon fiber reinforced materials, the chemical and physical nature of carbon fiber surfaces influence the phenomena occurring in the interphase and play an important role in the resulting mechanical properties such as interlaminar shear strengths (ILSS). Thus, it is very important to understand the surface structure of carbon fibers.[1-3]

In order to improve the interactions between the surface of carbon fibers and the matrix resin, an oxidative treatment of carbon fibers has been used. There are mainly four kinds of treatment methods. One is chemical oxidation using nitric acid and other strongly oxidative acids and a second method is electrochemical oxidation with several types of electrolytes. The other methods are dry, gaseous oxidation and plasma treatment.[1] X-ray photoelectron spectroscopy (XPS) has been widely used to study carbon fiber surfaces after oxidative treatments. Ishitani[4] has pointed out that the usage of XPS in the surface study of carbon fiber is advantageous, since it is not disturbed by the strong absorption of the electromagnetic wave and is sensitive and selective to the surface structure. A pioneering work by Tuinstra and Koenig using laser Raman spectroscopy showed that new grain boundaries were created by

chemical treatment.[5] XPS studies have also confirmed that oxidative treatment will break the graphite structure of the fiber and increase the surface functionality by creating additional carbonyl groups, carboxyl/ester groups and/or hydroxyl/ether groups at the surface.[3,4,6−10]

The analysis of carbon fiber surfaces by Fourier trransform infrared (FT-IR) spectroscopy had been considered to be extremely difficult due to the aforementioned absorbing properties and severe scattering of the infrared radiation by the carbon fibers. However, Sellitti *et al.*[11] succeeded in obtaining the IR spectra of oxidized carbon fiber surfaces using the internal reflection technique, which is sensitive to the surface of a material. They also showed the possibility that FT-IR gives more detailed information about the chemistry of the carbon fiber surface than XPS.

The purpose of this work is to apply both FT-IR internal reflection spectroscopy and XPS to the characterization of the surfaces of carbon fibers which are treated by chemical oxidation or electrochemical oxidation.

EXPERIMENTAL

A cloth of carbon fibers (Mitsubishi Rayon "Pyrofile TR-30") was used in this study. The fibers are polyacrylonitrile-based, and of the high-tensile-strength-type. The chemicals were purchased from Aldrich Chemical Company and used as received. Prior to the oxidative treatments, the fibers were washed in a Soxhlet extractor for 5 days to remove impurities. Chloroform was used as the solvent. Samples were then dried at 140°C for 12 hours. These carbon fiber samples are referred to as the "as-received carbon fibers" in this paper. The oxidative treatment was performed by chemical oxidation or electrochemical oxidation. In chemical oxidation, samples were treated in boiling 70% nitric acid for desired time periods. Electrochemical oxidation was carried out in a custom-made cell. The carbon fibers acted as an anode and a wire of molybdenum coated with platinum (Johnston Matthey Electronics) as the counter electrode. A current of 1 ampere was applied to each sample. After the oxidative treatments, samples were washed repeatedly by de-ionized water and dried at 140°C for 12 hours.

The reduction was conducted by immersing the samples in a saturated solution of lithium aluminum hydride ($LiAlH_4$) in ethyl ether at room temperature for 1 hour. The samples were then washed in ethanol and dried at 140°C for 12 hours.

A germanium trapezoid, obtained from Harrick Scientific Corporation, with the dimension of $50 \times 20 \times 2$ mm and with the end-face angle of 45°, was used as the internal reflection element (IRE). This IRE was used in an internal reflection attachment from Wilks Scientific. The IR spectra were taken with a Bomem DA-3 FT-IR spectrometer. The spectra of the samples were taken under vacuum (0.5 torr) and a liquid-nitrogen-cooled, narrow bandpass mercury-cadmium-telluride (MCT) detector with a specific detectivity D^* of 2.1×10^{10} cmHz$^{1/2}$ W^{-1} was used. One thosuand scans were co-added at a resolution of 4 cm^{-1}. The aperture was set to 10 mm.

X-ray photoelectron spectroscopy was performed using a Perkin Elmer 5400 system equipped with Mg Kα source. The base pressure in the sample chamber was in the range 10^{-8} to 10^{-9} torr.

RESULTS AND DISCUSSION

XPS and Internal Reflection Infrared Spectra of Treated and As-received Carbon Fibers

Figure 1 shows the XPS spectrum (C_{1s}) of as-received carbon fiber. This spectrum indicates that the fibers we used in this study have been surface treated but unsized as discussed by the following authors.

Santantiago et al.[12] studied pitch-based carbon fiber sized by poly(vinylalcohol) using XPS. They stated "the characteristic carbon peak of the sized fiber is broader than that of the unsized fiber" and that "The XPS spectrum after treatment in the water bath is almost identical to that before treatment."

Their results suggest that the full width at half maximum (FWHM) of the C_{1s} spectrum of sized carbon fiber is much broader than that of the unsized fiber, yet it is not affected by the washing procedure of the fiber. Their results also suggest that the fiber is unsized if the FWHM of any PAN-based high-tensile-strength-type carbon fiber is close to that of unsized similar type carbon fiber.

Takahagi et al.[7] reported the XPS spectrum of unsized, PAN-based, high-tensile-strength-type carbon fiber (TORAYCA T-300) and the FWHM of the C_{1s} spectrum of the sample is 1.8 eV before surface oxidation and is in the range of 1.8 to 2.1 eV after the oxidation procedure. Kim et al.[13] reported the XPS spectrum of sized PAN-based carbon fiber (TORAYCA T-300) and found the FWHM of the C_{1s} spectrum of the sample to be about 3.3 eV. The FWHM of our sample is around 1.8 eV.

While Santantiago et al.[12] stated "the sized fiber surface contains a much larger amount of oxygen than the unsized fiber" and that "Removal of the sizing should therefore restore the fiber to its unsized condition with a very low level of surface oxygen" Kim et al.[13] studied the difference in the XPS spectra of sized carbon fibers with and without a poly(vinylalcohol) coating and claimed that "Quantification identifies the actual surface compositions of the two fibers with and without the coating to be essentially the same." Therefore, the oxygen-to-carbon ratio cannot
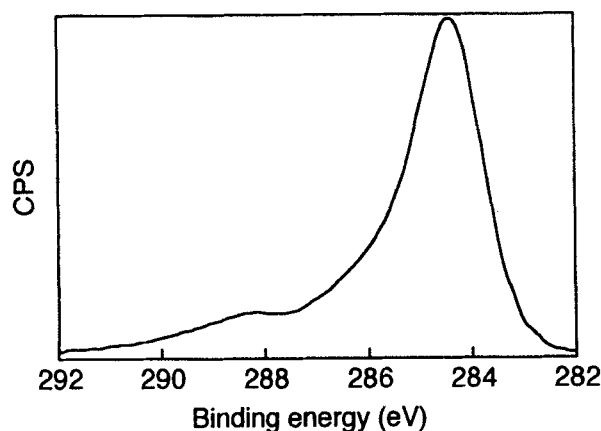

FIGURE 1   The XPS spectrum of as-received carbon fibers.

show the existence of the sizing agent on the PAN-based carbon fiber, while it can in the case of pitch-based fibers.

Kim et al.[13] also stated that "Cazeneuve et al.[14] observed a small amount (normally less than 4%) of nitrogen and sodium in the unsized fibers." "These elements were completely absent in the sized fiber surface." "Sizing almost completely covers the fiber surface so that the small amount of impurities existing underneath the size can not be detected by XPS analysis." Cazeneuve et al.[14] used the sized carbon fiber (T-300) as their sample and stated "both sized and unsized fibers were analyzed. To obtain unsized fibers, the size was removed by chemical dissolution, with "The main difference between sized and unsized fiber being the quantity of nitrogen." "The nitrogen is therefore characteristic of the unsized carbon fibers and, more generally, of the carbon fiber without polymer." According to the XPS spectrum of our sample, the fiber surface consists of 79.8% carbon, 17.6% oxygen, and 2.6% nitrogen.

The O_{1S} spectrum is not available to judge the existence of the sizing agent since, as Cazeneuve et al.[14] stated, "the oxygen peak is nearly the same for both fibers."

It has been found that the XPS C_{1S} spectrum of the surface-treated carbon fibers shows the presence of two different carbon species other than graphitic carbon. The graphitic carbon peak appears around 284.5 eV and two other peaks appear at 286.0 eV and 286.0 eV which have been assigned to C—O (ether/hydroxyl groups) and to C=O (ester/carboxyl groups), respectively.[4,6-10]

The shoulder in Figure 1 clearly suggests the presence of several different carbon species other than graphitic carbon, and this spectrum is the exact image of the XPS spectrum of moderately-oxidized PAN-based carbon fiber reported by Takahagi et al.[7]

As a result, it can be stated that the carbon fiber which we used for this study has been moderately surface treated but unsized, or the amount of the sizing residue was small enough to treat the sample as unsized.

Figure 2 is a schematic representation of the internal reflection phenomenon. When an electromagnetic wave reflects at the interface between a transparent medium 1 with the refractive index of n_1 and a transparent medium 2 with n_2, total reflection occurs if n_1 is greater than n_2 and the angle of incidence, θ_1, is higher than the critical angle, θ_c, which is given as;

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$

However, total reflection never occurs if medium 2 absorbs the electromagnetic wave. The internal reflection technique measures the reduction of reflectivity due to the absorption by medium 2 or the sample.

Since the IR source is polychromatic, some of the electromagnetic waves are totally reflected while others are not for the usual organic materials meausred by the internal reflection technique. The reflected beam is a mixture of totally-reflected and partially-reflected waves, thus the name attenuated total reflection (ATR) technique. However, it is known that graphite-like materials such as carbon fiber absorb the electromagnetic radiation in the entire infrared region. Therefore, total reflection never occurs at any frequency with any angle of incidence, which means that the

critical angle does not exist in this system. Figure 3 shows the internal reflection IR spectrum of as-received carbon fibers. It can be seen that the baseline always has a value (it never drops to zero), showing the lack of total reflection at any wavenumber.

The additional feature seen in Figure 3 is the slope of the baseline. This sloping baseline is caused by the dispersions of the optical constants, which are the refractive index, n, and the extinction coefficient, k. Both n and k of the graphite-like materials in
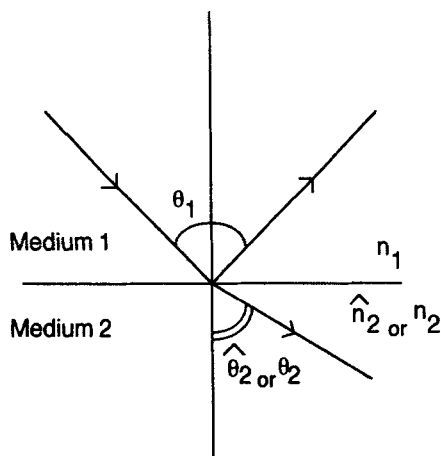

FIGURE 2   A schematic representation of internal reflection spectroscopy. Medium 1 acts as the IRE and medium 2 is the sample to be measured.
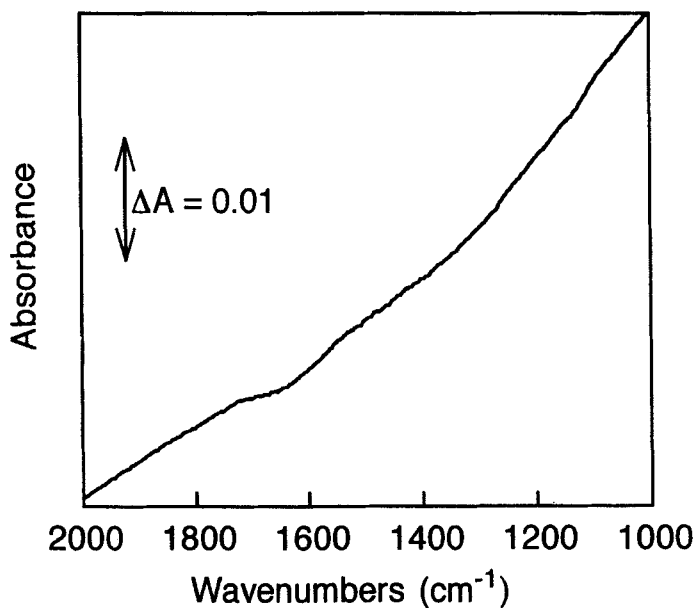

FIGURE 3   The internal reflection IR spectrum of the as-received carbon fibers.

the infrared region change with the wavelength,[15,16] causing the absorbance in the internal reflection IR spectrum of carbon fibers to increase at smaller wavenumbers.

Figure 4 is a typical spectrum of carbon fibers treated by chemical oxidation. Several features can be recognized in this spectrum. First, three regions around $1720\,cm^{-1}$, $1580\,cm^{-1}$, and $1200\,cm^{-1}$ are of interest. The band at $1720\,cm^{-1}$ has been assigned to the C=O stretching mode of carboxyl/ester groups and the band at $1200\,cm^{-1}$ to C—O stretching and O—H bending modes.[11] This broad band might contain more than one structure and will be discussed in a later section. The band at $1580\,cm^{-1}$ is not well understood yet. This band can be assigned to the aromatic ring mode and its intensity increases as the oxidative treatment breaks the symmetric structure of graphite. Another possible assignment is the conjugated C=O mode, making the assignment of the band at $1580\,cm^{-1}$ still uncertain.[17] However, it is obvious that the presence and intensity of this band is strongly related to the oxidative treatment of the carbon fibers.

An additional feature of the spectrum of the oxidized carbon fibers is the distortion seen around $1800\,cm^{-1}$. Sellitti et al.[18] performed spectral simulations using optical theories to understand this distortion. They assumed that the oxidized layer had optical constants similar to the usual organic compounds and used Fresnel's equations for a three-layered system to model the *IRE/oxidized layer/bulk of carbon fiber* system. They found that the distortion or inversion of the spectrum can occur if the oxidized layer thickness is around several tens of nanometers. Nakayama et al.[6] used XPS for characterization of oxidized carbon fibers and suggested that the oxidative treatment may completely destroy the graphite-like structure of carbon fiber and convert it into an aliphatic structure. Hophgarten[19] also used XPS with an
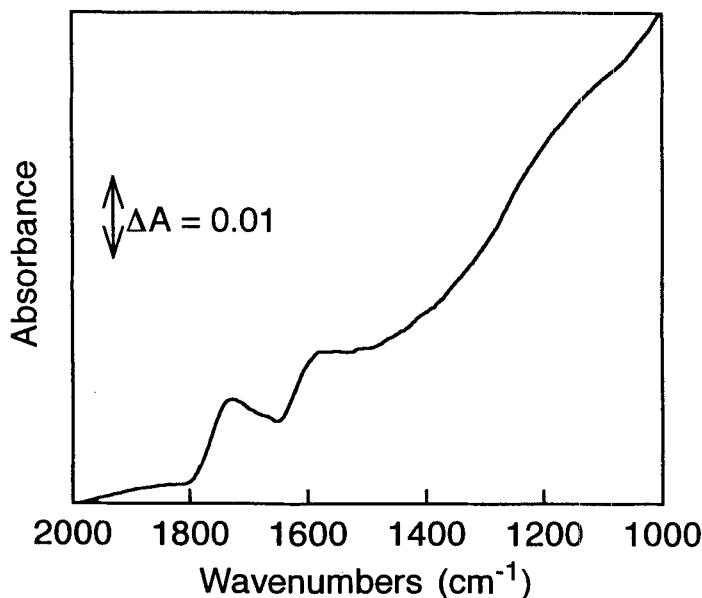

FIGURE 4   A typical internal reflection IR spectrum of the treated carbon fibers.

ion-etching facility and found that the thickness of the oxidized layer is around 50 nm. Therefore, the assumption made by Sellitti et al. to model this system agrees well with those results of XPS.

The penetration depth of the electric field, d_p, in internal reflection spectroscopy is an important parameter and is defined as the depth at which the field strength (amplitude of the electromagnetic wave) decreases to $1/e$ of the value at the interface. d_p is expressed as;[20]

$$d_p = \frac{1}{2\pi\bar{v}\,\text{Im}[\hat{n}_2\cos\hat{\theta}_2]}$$

where $\bar{v}$ is the wavenumber of the incident radiation in vacuum, $\text{Im}[\hat{z}]$ is the imaginary part of $\hat{z}$ which is a complex number, $\hat{n}_2$ is the complex refractive index of medium 2 (Fig. 2) which is expressed as $\hat{n}_2 = n_2 + ik_2$, and $\hat{\theta}_2$ is the complex angle of refraction. If medium 1 is an infrared transparent material, $\hat{\theta}_2$ follows the Snell's equation as;

$$n_1\sin\theta_1 = \hat{n}_2\sin\hat{\theta}_2$$

Since the usual organic materials have a refractive index around 1.5 in the transparent region, the d_p for the case that $n_1 = 4, \theta_1 = 45°$, and $n_2 = 1.5$ represents the penetration depth into the oxidized layer of carbon fiber when germanium is used as the IRE. The calculated d_p at $1720\,\text{cm}^{-1}$ is about $0.39\,\mu\text{m}$. This d_p is large enough for the electric field to reach the bulk of the carbon fiber. The dispersions of the optical constants of the oxidized layer are ignored here for simplicity. If there is no oxidized layer and the complex refractive index of the carbon fiber is assumed to be $3.5 + 1.5i$ at $1720\,\text{cm}^{-1}$,[15,18] the calculated value of d_p is about $0.44\,\mu\text{m}$. As we discussed before, the system which is measured by the internal reflection spectroscopy can be assumed to be a three-layered system, which consists of the *IRE/ oxidized layer/bulk of carbon fiber* system (Fig. 5). Therefore, the actual d_p of the electric field is probably in the middle.

Chemical Oxidation of Carbon Fibers

Figure 6 shows the spectra of carbon fibers treated by chemical oxidation for different time periods. All spectra have been normalized to give the same absorbance values at $2000\,\text{cm}^{-1}$ and another fixed absorbance value at $1000\,\text{cm}^{-1}$. The spectra have been shifted vertically to show a better visual comparison.

To obtain the exact difference of peak areas between two spectra taken by the transmission technique, the spectral subtraction procedure has been widely used since an overlapping peak can sometimes be assumed to be a simple sum of individual peaks.[21] However, such a procedure does not seem to be feasible for quantitative purposes in this study for the following reasons. The system is a three-layered system when treated fibers are measured by the internal reflection technique and is a two-layered system when untreated fiber is measured. Such a difference in systems and the variation of the thickness of the oxidized layer can affect the baselines and the peak shapes of the spectra. To correct these effects, the optical constants of
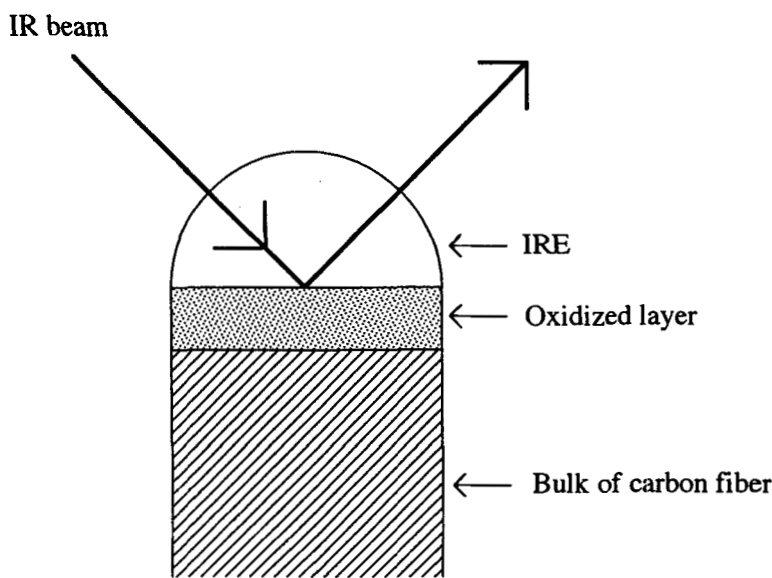
IR beam

← IRE

← Oxidized layer

← Bulk of carbon fiber

FIGURE 5   A schematic representation of the *IRE/oxidized layer/bulk of carbon fiber* system.

carbon fibers and the influence of the cylindrical shape of the fiber must be known. Unfortunately, these parameters have not been measured yet. However, these unknown parameters do not affect the reproducibility of the spectra or peak area as long as the same procedure is consistently used. Therefore, the peak areas around $1720 \, cm^{-1}$ and $1580 \, cm^{-1}$ were obtained by simply connecting the minimum values of absorbance spectra and calculating the peak areas above the connecting lines (from $1800 \, cm^{-1}$ to $1650 \, cm^{-1}$ for the peak at $1720 \, cm^{-1}$, and from $1650 \, cm^{-1}$ to $1530 \, cm^{-1}$ for the peak at $1580 \, cm^{-1}$). In Table I, the obtained peak areas are listed. The minus value is due to the sloping baseline of the spectrum. The results are summarized in Figure 7. It should be noted that the integrated intensities are not relative but absolute values, due to the lack of an internal reference band. In Figure 7, linear relationship between the oxidation time and peak intensities is seen with R (correlation coefficient) $= 0.982$ for the peak at $1720 \, cm^{-1}$, and $R = 0.988$ for $1580 \, cm^{-1}$. The general trends seen in Figure 7 are consistent with those obtained by volumetric analysis (NaOH-titration)[22] including the time scale.

Since XPS has been widely used for this kind of study, the XPS spectrum of the same specimen was taken for comparison. In Figure 8, the XPS spectra (C_{1S}) of fibers treated by chemical oxidation for 2 hours are shown. The XPS spectrum (C_{1S}) of as-received carbon fibers is also shown for comparison (dotted line). The shoulder in the (C_{1S}) spectrum suggests that the main difference after treatment is an increase of the C=O (ester/carboxyl groups) peak at around $288.4 \, eV$. The C—O (ether/hydroxyl groups) peak around $286.0 \, eV$ has not changed very much probably because the as-received carbon fibers had been surface treated. The O_{1S}/C_{1S} ratios of the samples are listed in Table II. The O_{1S}/C_{1S} ratio increased due to this oxidation process. Our XPS results agree generally with those reported by others.[4,6–10]
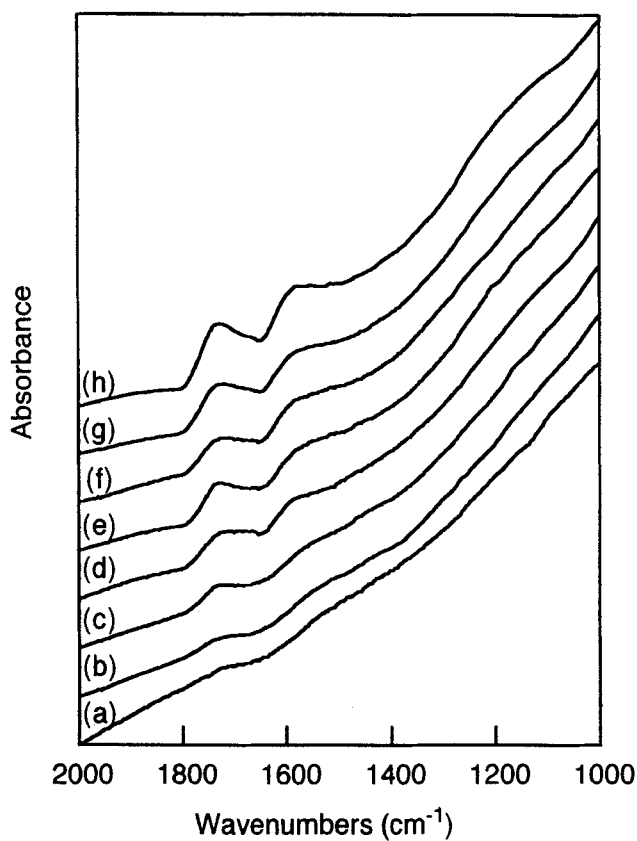
FIGURE 6   The internal reflection IR spectra of (a) as-received carbon fibers, and carbon fibers treated by chemical oxidation for (b) 30 min., (c) 1 hour, (d) 2 hours, (e) 3 hours, (f) 4 hours, (g) 5 hours, and (h) 6 hours.

TABLE I
Peak areas in IR spectra

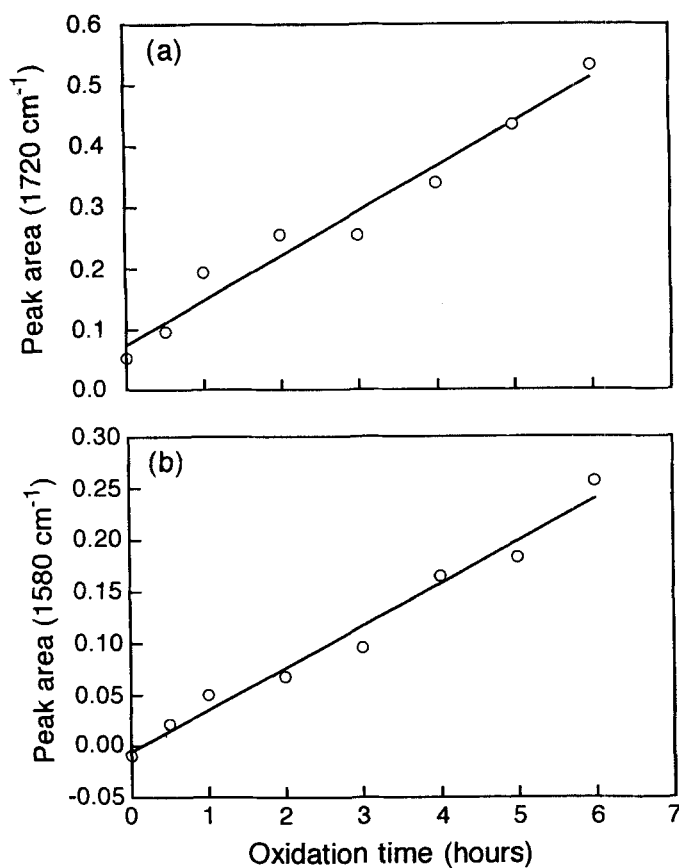| Treatment time (hours)	Peak position	
	$1720 \, (cm^{-1})$	$1580 \, (cm^{-1})$
As-received	0.0531	− 0.0096
0.5	0.0967	0.0215
1	0.194	0.0500
2	0.256	0.0679
3	0.255	0.0958
4	0.340	0.165
5	0.435	0.183
6	0.533	0.257

FIGURE 7   Plots of peak areas *versus* oxidation time.

As a first consequence, FT-IR internal reflection spectroscopy has been found to have a comparable signal-to-noise (S/N) ratio to XPS within a similar time frame for the study of carbon fiber surfaces. Since the S/N ratio is a strong function of the instrument, it should further improve with advances in instrumentation.

Electrochemical Oxidation

In the commercial production of carbon fibers, fibers are treated by electrochemical oxidation because it is fast and uniform, and therefore suitable for production lines.[1] Thus, the characterization of carbon fiber surface treated by electrochemical oxidation is the most important for commercial purposes. While XPS spectra of carbon fibers treated by electrochemical oxidation have been obtained,[8-10] no IR spectrum has been reported yet.

Figure 9(a) is the FT-IR internal reflection spectrum of the carbon fibers treated by electrochemical oxidation. Nitric acid was used as the electrolyte. All the features
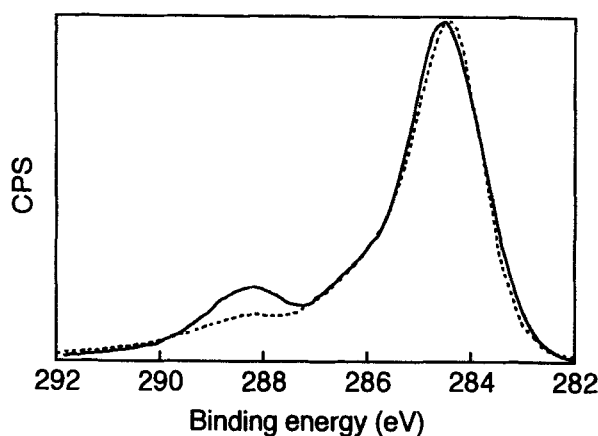
FIGURE 8 The XPS spectrum of fibers treated by chemical oxidation for 2 hours, solid line and as-received fibers (dotted line).

TABLE II
O_{1s}/C_{1s} ratios in XPS spectra

Oxidation method	O_{1s}/C_{1s}
As-received	0.221
Chemical (2 hours)	0.342
Electrochemical (in HNO_3 for 40 min)	0.353
Electrochemical (in NH_4NO_3 for 40 min)	0.314
Electrochemical (in NH_4HCO_3 for 40 min)	0.163
Reduction by $LiAlH_4$	0.972
Re-oxidation (electrochemical NH_4NO_3 for 40 min)	0.190

that have been seen in the spectra of carbon fibers treated by chemical oxidation can be recognized. Figure 9(b) is the XPS spectrum of the same specimen. This XPS spectrum is consistent with the spectrum reported by Kozlowski and Sherwood.[8]

In order to compare the effect of different electrolytes, carbon fibers were oxidized in ammonium nitrate and ammonium bicarbonate. Figure 10(a) shows the IR spectra of carbon fibers treated by electrochemical oxidation for 10 minutes and 40 minutes using ammonium nitrate as the electrolyte. Figure 10(b) is the XPS spectrum of the sample oxidized for 40 min. The O_{1s}/C_{1s} ratios and peak areas of the IR spectra are listed in Table II and III, respectively. These values show the same trends seen in chemical oxidation. However, if the fibers are treated using ammonium bicarbonate as the electrolyte, this trend is no longer seen (Fig. 11). The O_{1s}/C_{1s} ratio (Table II) and IR band intensities (Table III) decrease after the treatment in ammonium bicarbonate for 40 min. The disappearance of the C=O peak at 288.4 eV is recognized, although it is minor. It is known that the O_{1s}/C_{1s} ratio decreases toward the center of the fiber.[18] Therefore, these results suggest that the treatment using ammonium bicarbonate as an electrolyte does not oxidize the fiber surface but only etches the fiber surface if it is performed on the treated fibers.
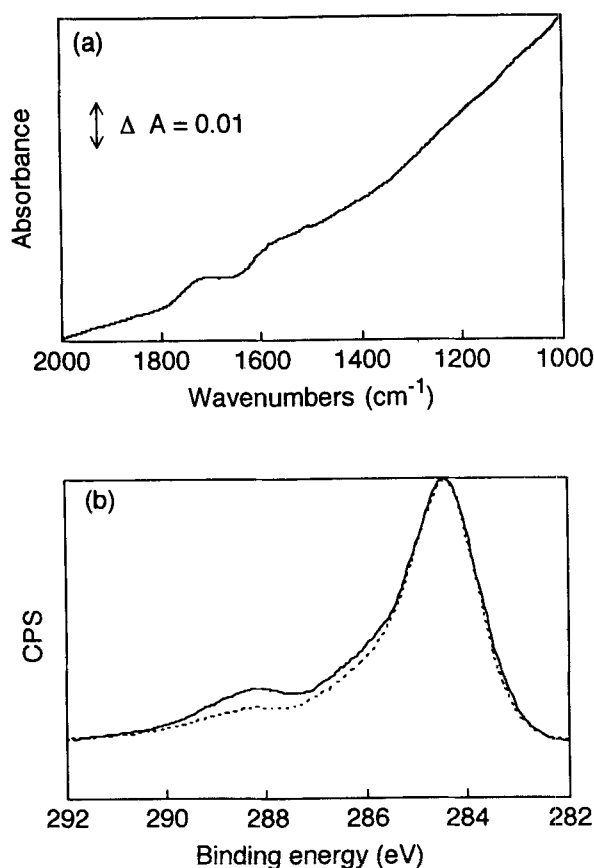
FIGURE 9   Spectra of carbon fibers treated for 40 minutes by electrochemical oxidation using HNO_3 as the electrolyte: (a) the internal reflection IR spectrum; (b) the XPS spectrum (C_{1s}) of the treated fibers (solid line) and of the as-received fibers (dotted line).

This fiber surface etching by ammonium bicarbonate is not necessarily a disadvantage of this electrolyte since an increase in surface oxygen on the carbon fibers is not always advantageous for the final properties of carbon fiber reinforced materials. For example, while oxidative treatment usually improves the mechanical properties of the composites such as ILSS and fatigue life,[23] there exists a maximum value of the ILSS with increasing surface treatment,[24] while tensile strength slightly decreases on the treatment.[25] Besides, surface functional groups may reduce the thermal stability of the matrix resin in the interphase if cyanate polymer is used as the matrix resin.[26] On the other hand, it was proposed that the oxidative treatment etches the fiber surface and the removal of native flaws can also improve the adhesion between fibers and the matrix resin.[27] Therefore, the difference in surface properties caused by the different electrolytes allows us to produce the required properties of the carbon fiber reinforced materials by varying the treatment method.
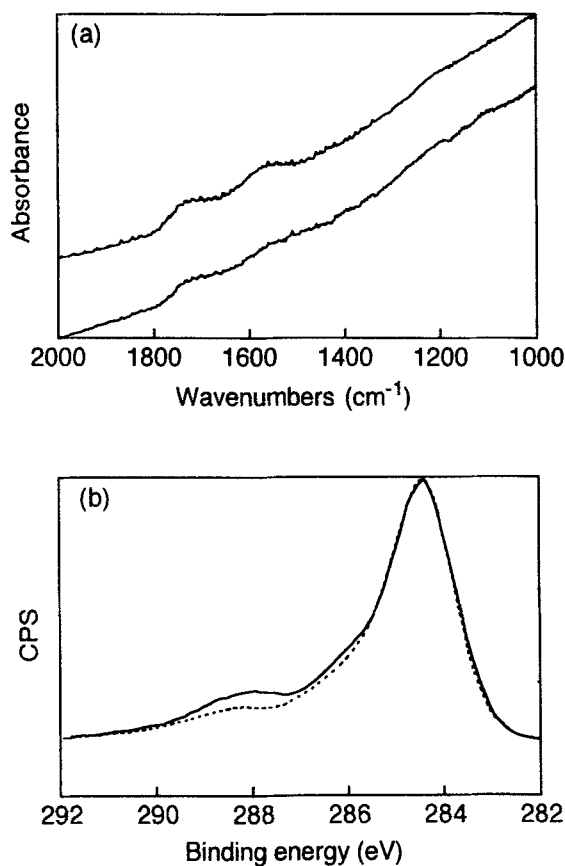
FIGURE 10   Spectra of carbon fibers treated by electrochemical oxidation using NH_4NO_3 as the electrolyte: (a) the internal reflection IR spectra for 10-minute treatment (bottom spectrum), 40-minute treatment (top spectrum); (b) the XPS spectra (C_{1s}) of the fibers treated for 40 minutes (solid line) and of the as-received fibers (dotted line).

TABLE III
Peak areas in IR spectra

Treating method	Peak Position	
	1720 (cm^{-1})	1580 (cm^{-1})
Electrochemical (in HNO_3 for 40 min)	0.227	0.105
Electrochemical (in NH_4NO_3 for 40 min)	0.157	0.0959
Electrochemical (in NH_4NO_3 for 10 min)	0.136	0.0372
Electrochemical (in NH_4HCO_3 for 40 min)	0.0505	− 0.0228
Reduction by $LiAlH_4$	− 0.0054	− 0.0390
Re-treatment (electrochemical, in NH_4HCO_3 for 40 min)	0.0464	− 0.0116

Reduction of Carbon Fibers by LiAlH$_4$

Since the as-received carbon fibers are the products of the commercial process, they have already been oxidatively treated. Hence, these as-received carbon fibers were reduced using LiAlH$_4$ which is known to cause the disappearance of the functional groups introduced by the oxidative treatment of carbon fibers.[11] Figure 12(a) shows the internal reflection IR spectrum of the carbon fibers reduced by LiAlH$_4$. The disappearance of the broad peak around $1720 \, cm^{-1}$ can be recognized. The peak areas listed in Table III also suggest the disappearance of both peaks at 1720 and $1580 \, cm^{-1}$. The disappearance of the band at $1580 \, cm^{-1}$ is interesting. If the band at 1580 is the C=C stretching mode and it appears by the symmetry consideration, it should not disappear, since there is no symmetry change of the molecules by this reduction process. The band probably originates from a conjugated quinone-like structure. The XPS spectrum of the same sample (Fig. 12(b)) indicates the disappearance of the C=O peak at 288.4 eV and the increase of the C—O (286.0 eV).
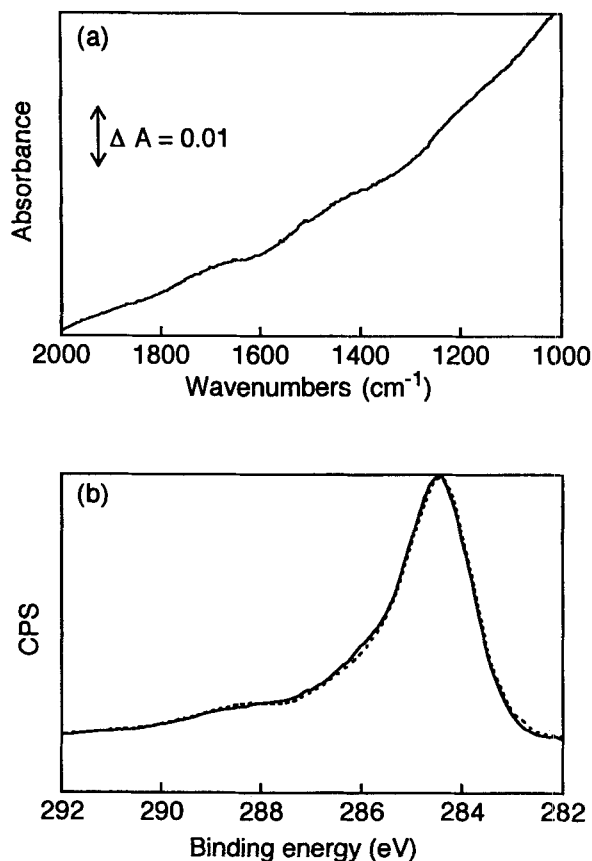

FIGURE 11 Spectra of carbon fibers treated for 40 minutes by electrochemical oxidation using NH$_4$HCO$_3$ as the electrolyte: (a) the internal reflection IR spectrum; (b) the XPS spectra (C$_{1s}$) of the treated fibers (solid line) and of the as-received fibers (dotted line).

In order to look closely at the change caused by the reduction process, spectral subtraction was performed. For carbon fibers studied by the internal reflection technique, this procedure is valid only when it is used for semi-quantitative purposes. Therefore, the IR spectrum of as-received fibers was subtracted from that of reduced fibers. This subtraction is especially valid since we can assume that the oxidized layer thickness does not change after this chemical treatment, expecting that no densification occurs during this process. The result is shown in Figure 13(a). Figure 13(b) is the baseline-corrected IR spectrum of the oxidized carbon fibers from which the spectrum of the as-received carbon fibers is subtracted. While oxidative treatment causes the appearance of the C—O band at $1200 \, cm^{-1}$ (Fig. 13(a)), the C—O band in Figure 13(b) arises at $113 \, cm^{-1}$. Because the oxidized fibers have both carboxyl and alcohol related C—O groups that give rise to bands at 1200 and $1130 \, cm^{-1}$, the reduced sample has only C—O groups of alcohol.

The reduced carbon fibers were oxidized again by electrochemical oxidation for 40 minutes using the ammonium bicarbonate as the electrolyte. Figure 14 shows the
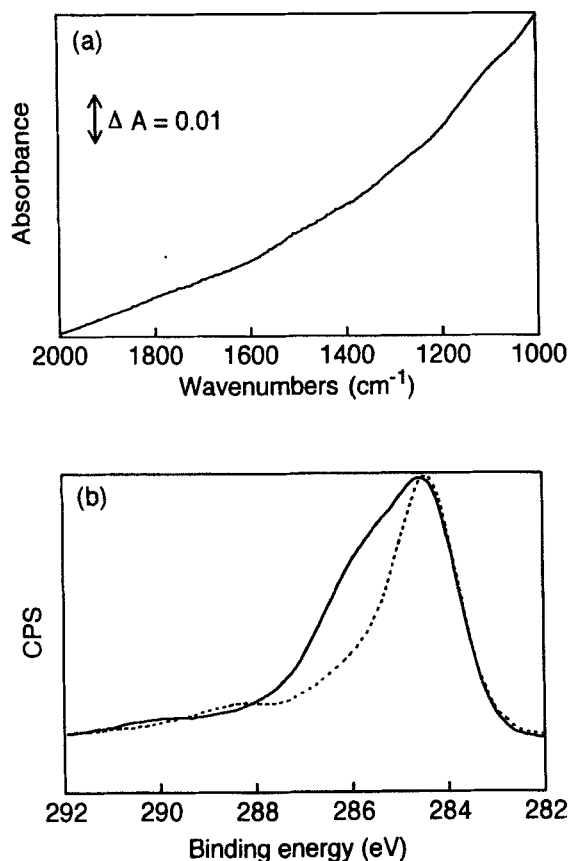
FIGURE 12 Spectra of carbon fibers reduced by $LiAlH_4$: (a) the internal reflection IR spectrum; (b) the XPS spectra of the treated fibers (solid line) and of the as-received fibers (dotted line).

IR and XPS spectra of these fibers. The O_{1S}/C_{1S} ratio of XPS, and the IR peak areas are listed in Table II and III, respectively. All the values are close to those of as-received fibers or fibers treated in ammonium bicarbonate and the reduction of the O_{1S}/C_{1S} ratio after the treatment is significant. These results also suggest the etching effect by ammonium bicarbonate.

Direct Comparison of IR and XPS data

We have been discussing the results of IR and XPS data, showing that the sensitivity of IR spectroscopy is comparable with that of XPS. At this point, it is interesting to compare these results quantitatively. To do that, a curve-fitting procedure needs to be performed on the XPS spectra of carbon fibers due to the overlapping of the C=O (carboxyl/ester), C—O (hydroxyl/ether), and graphitic carbon peaks. However, this procedure is troublesome since the C_{1S} peak of a graphite single crystal is
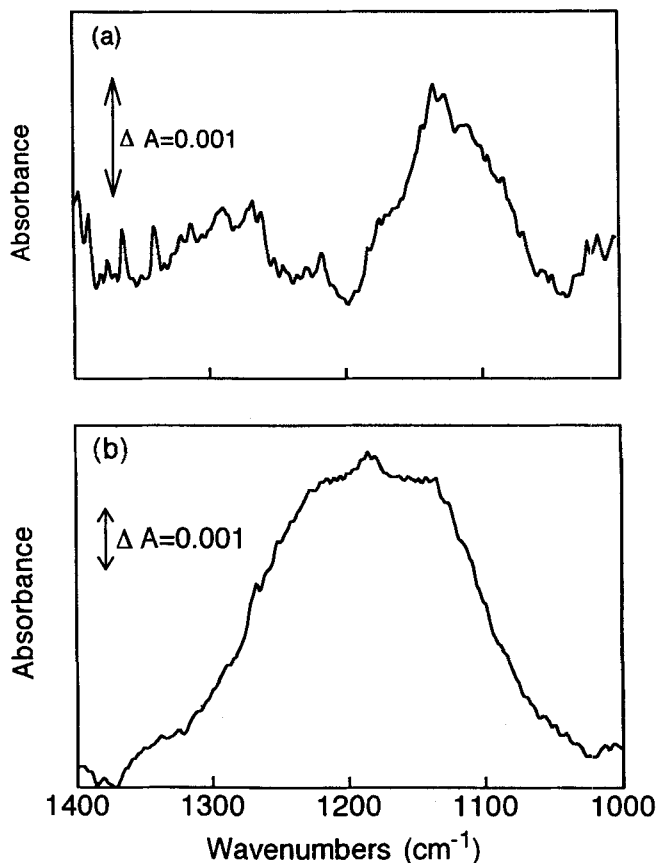

FIGURE 13   The subtracted IR spectra of the carbon fibers (a) reduced by LiAlH₄, and (b) chemically oxidized for 6 hours.

asymmetric due to a relatively small band gap of the crystal.[28] To circumvent this problem, several procedures have been adopted.[4,6-10] If the degree of oxidation is not too high, the digital difference spectrum technique[7] is one of the most feasible and convenient procedures to perform. Therefore, the difference spectra were obtained by subtraction of the C_{1s} spectrum of as-received carbon fiber from those of treated carbon fibers using the appropriate weight factors leading to cancellation of the component of the main peak of the lowest binding energy. Figure 15 shows the result of the subtraction. All XPS data discussed in this study, except those for the reduced samples, were calculated to create this figure. In the figure, it is seen that the main difference caused by our oxidative treatment is in the $C{=}O$ (carboxyl/ester) peak at around 288.4 eV, and that the change of $C{-}O$ (hydroxyl/ether) peak at around 286.0 eV is quite minor. This is probably because the as-received fiber has already been oxidized. Since no major change occurred other than in the peak around 288.4 eV, the peak area (more exactly the peak area difference) of each difference spectrum was calculated and normalized using the C_{1s} peak area of the as-received carbon fiber as a reference. Figure 16 is the plot of IR peak area at
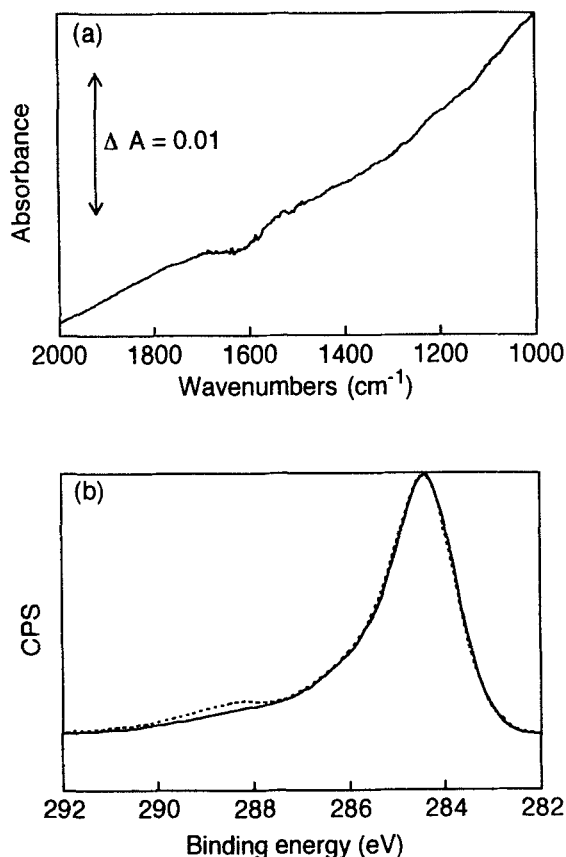

FIGURE 14   Spectra of carbon fibers re-treated in NH_4HCO_3: (a) the internal reflection IR spectrum; (b) the XPS spectra (C_{1s}) of the re-treated fibers (solid line) and for the as-received fibers.

$1720\,\mathrm{cm}^{-1}$ and XPS peak area difference at 288.4 eV. Both peaks have been assigned to C=O (carboxyl/ester) groups. All the XPS data in the previous discussion are used to create this plot except the data point from the samples that had been reduced. If a linear relationship is assumed, the correlation coefficient of Figure 16 is 0.97.
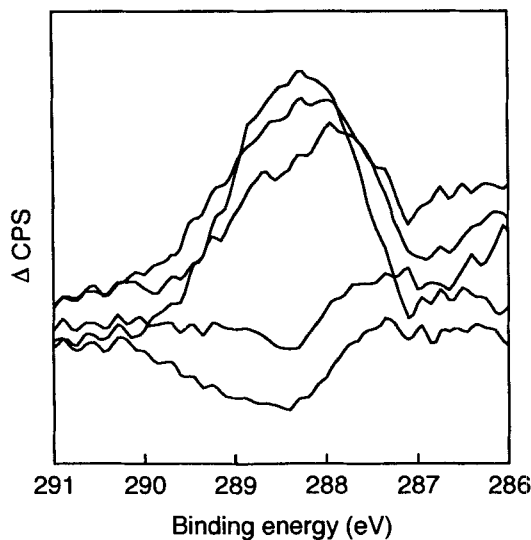

FIGURE 15   Results of substraction of the C_{1s} spectrum of the as-received fiber from those of treated carbon fibers.
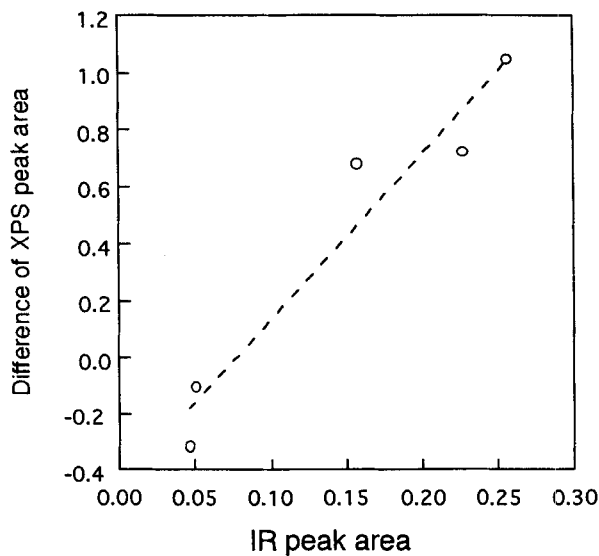

FIGURE 16   Plot of IR peak area *versus* difference of XPS peak area.

While more data points and further investigation are required to examine more closely the quantitative nature of the IR and XPS spectra of carbon fibers, it is fair to state that IR spectroscopy is sensitive enough to characterize the carbon fiber surface and to provide very similar quantitative information about the surface functionality to that produced by XPS.

CONCLUSION

The spectra of oxidized carbon fibers taken by internal reflection IR spectroscopy and XPS have been discussed. Internal reflection IR spectroscopy was found to be sensitive enough to characterize the surface of even commercially-oxidized carbon fibers. Its sensitivity is comparable with that of the XPS and titration methods. However, vibrational spectroscopy gives more detailed information than XPS, since the major bands of interest in the IR spectra of carbon fibers are isolated from each other, while those bands in XPS spectra overlap and require curve fitting which is often subjective. The amount of the surface functionality of carbon fibers increases with the oxidation time if the fibers are treated by chemical oxidation. In the case of electrochemical oxidation, the use of nitric acid or ammonium nitrate as the electrolyte will introduce several functionalities at the fiber surface, while ammonium bicarbonate only etches the surface. The comparison of IR and XPS data suggests that those techniques give the same quantitative results and are complementary in the field of carbon fiber study.

Acknowledgement

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