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X-ray Photoelectron Spectroscopic Study of Carbon Fiber Surfaces. 23. Interfacial Interactions between Polyvinyl Alcohol and Carbon Fibers Electrochemically Oxidized in Nitric Acid Solution

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The paper examines the interaction of a carbon fiber surface, surface-treated by galvanostatic electrochemical oxidation in nitric acid solution, with poly(vinyl alcohol) (PVA). The surface chemistry of the fiber before and after interaction was examined by core and valence band X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and atomic force microscopy (AFM). Various surface treatment conditions were applied, with the previously reported hydrogen-bridge oxide structure (HBS) being the predominant species under most conditions, with much smaller amounts of surface hydroxide, carbonyl, and carboxyl groups. The amount of surface roughening increased with the level of surface oxidation. The surface of the fibers became seriously damaged when the oxidation was conducted for prolonged periods of galvanostatic treatment (more than 60 s at 0.5 A). Interfacial chemical interaction was observed between the oxidized carbon fiber surface and the PVA, by examination of a film of PVA on the fiber surface that was sufficiently thin to allow the interface region to be examined. The valence band XPS spectrum of PVA is predicted by a band structure calculation, complemented by molecular orbital calculations based upon the polymer repeat unit. The valence band spectrum is seen to be an effective fingerprint of the PVA structure. An interfacial reaction was found to occur between the oxidized fiber and PVA involving reaction between the hydroxide group in PVA and the HBS oxide on the fiber surface. The results have a wider relevance to size molecules containing −OH functionality and adjust the interfacial bonding in composites.

Introduction

Considerable attention has been given to the interfacial adhesion between the reinforcing fibers and the matrix material in fiber-reinforced composite materials.[1−3] This interaction is important because all the properties of the resultant composites depend not only on the nature of the fibers and matrix, but also more importantly on the chemical and physical interaction between the fiber and matrix which determines the interlaminar shear stress (ILSS) behavior of the resulting composite. The fiber/matrix interaction is closely related to the structure, roughness, and surface chemistry of the carbon fiber surface. Carbon fibers are made from polyacrylonitrile (PAN), pitch, or other organic materials under very high temperature (from 1200 to over 2400 °C).[4] Untreated carbon fibers have a chemically inert surface that leads to a very low ILSS when they are incorporated into composite materials. It is thus very important to modify the carbon fiber surface to improve the interaction between the fibers and the matrix. Surface treatment of the carbon fiber surface is usually designed to introduce some chemical groups onto the surface which improve the wetting of the fiber by the matrix material, and can lead to physical and chemical interaction. The methods used are mainly oxidative in nature, including "wet" process (e.g., treating carbon fibers in an aqueous oxidative agent, such as nitric acid, chromic acid for extended periods of time at room temperature, or at elevated temperatures for a short time, or by applying electrochemical treatment for short periods of time),[5−8] and "dry" process (e.g., catalytic oxidation in air, oxygen, ozone, or plasma treatment).[9−12] Characterization of the treated carbon fiber surface has been conducted by conventional analytical chemistry and/or spectroscopy, and by surface analytical techniques such as X-ray photoelectron spectroscopy (XPS,

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or ESCA).[13] There have been extensive XPS studies of PAN- and pitch-based carbon fibers widely used in composites for more than the past 25 years.[14]

Most treatment methods lead to the introduction of chemical functionality onto the carbon fiber surface though the amount and kind of functional group varies with the experimental methods and parameters. The functional group on the treated carbon fiber surface has been distinguished by the XPS C1s chemical shifts (CS). Thus, one can distinguish between hydroxide-type (C−OH, CS: 1.5 eV, carbonyl type (C=O, CS: 3−3.6 eV), and carboxyl-type functionality (COOH, CS: 4.2 eV).[15−18] Epoxide/ether functionality (C−O−C) functionality and C−N functionality comes at the same position as hydroxide functionality (CS: 1.5 eV). In addition our group has identified a hydrogen bridge oxide structure (HBS) based upon theoretical models, and the spectrum of model compounds.[19,20] Additional, and complementary, information can be obtained from the valence band XPS spectrum, which has the capacity to distinguish between hydroxide and epoxide/ether functionality, and whose spectral features can be predicted and explained by multiple scattered wave Xα and ab initio molecular orbital calculations.[21] Both the surface chemistry and topography can influence the fiber matrix interaction, and the topography can significantly influence the interaction process,[22,23] often leading to an increase in surface area.[24]

We have successfully used a thin film of polymer matrix on an oxidized fiber surface as a means of investigating the interfacial region because XPS can probe this interfacial region for thin films.[25−28] Other workers have successfully used a similar approach.[29,30] It is important to understand the interfacial chemical reaction process which has not been well understood because of the difficulties in gaining access to this buried interface.[31,32] We have applied this approach to cases where we have reacted an oxidized carbon fiber surface with a matrix material either directly,[24] or by means of coupling agents.[28]

In this paper we report a detailed investigation of the interfacial reaction between various oxidized carbon fiber surfaces and a simple polymer material. We have chosen a simple polymer with a single functional group because such a system provides a valuable model system for the detailed analysis of interfacial interactions, many of which are relevant to matrix−fiber and size−fiber interactions. Carbon fibers are typically sized to enhance their handling characteristics, but once applied the sizes are very difficult to remove from the carbon fiber surface.[33] Sizes often contain polymeric systems with −OH groups (e.g., in phenolic compatible sizes). Sometimes PVA was used as a coating to improve the interfacial bonding in epoxy matrix composites.[34,35] Here PVA was used as the model polymer system as it has a single hydroxide group attached to a CH_2 group and another CH_2 group in its repeat unit. It also has the advantage that it dissolves in water, making thin-film formation straightforward. We have focused upon the detailed chemical and topographical changes on the carbon fiber surface that result from the galvanostatic electrochemical oxidation of polyacrylonitrile derived carbon fibers. This type of oxidation was chosen because it is most easily applied to the large-scale oxidation methods that can be applied in industrial applications. We have related these changes to the interfacial interaction between oxidized carbon fiber surfaces and PVA. The surface chemistry has been monitored by XPS and X-ray powder diffraction, and the surface topography has been monitored by atomic force microscopy (AFM).

Experimental Section

Materials. The carbon fibers used in this study were untreated and unsized E-120 high modulus pitch-based fibers with a density of 2.14 g/cm^3 and a mean filament diameter of 9.2 μm in a 3000 fiber tow provided by Dupont.

The PVA investigated in this study was purchased from the SIGMA Chemical Company and had a mean molecular weight of between 30 000 and 70 000 and a lot number of 47H1017.

Sample Preparation. The electrochemistry oxidization was carried out using a standard three-electrode glass cell and Ministat Research potentiostat (model 402R). A short section of tow (about 3000 fibers) of about 6 cm in length of carbon fibers acted as the working electrode (about 4.5 cm were immersed in the electrolyte), and a piece of platinum foil was used as the counter electrode. We have previously reported[5] that this experimental approach, using galvanostatic oxidation under the conditions described below, leads to reproducible oxidation conditions. The potential of the working electrode was measured with respect to a saturated calomel reference electrode (SCE). A 1 M nitric acid solution (A.C.S. reagent grade) was used as the electrolyte, which was prepared with quadruply distilled (4-D) water. The carbon fibers were anodically oxidized for different periods from 10 s to 15 min, under galvanostatic conditions[5] with a current of either 0.25 A or 0.5 A. The treated carbon fibers were removed from the electrolyte, washed thoroughly with 4-D water, and then dried in an oven at 70 °C for 24 h.

The interfacial reaction study was carried out by coating an extremely thin layer of PVA onto the fiber surface. The thickness can be controlled by the concentration of PVA solution although the exact thickness was not known. It is essential that this thickness be such that the interface lies in the region probed by XPS (which means the thickness needs to be significantly less than 100 Å). The fibers were immersed

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in PVA solution at 50 °C for 10 min and then dried in an oven at 70 °C over 30 h. These conditions did not cause any measurable decomposition of the PVA, since the deposition of PVA onto untreated carbon fibers gave an XPS spectrum that was very similar to that of PVA deposited onto copper. PVA was resolved in 4-D water at concentrations of 1, 0.5, and 0.25 wt %. The 0.25 wt % solution was found to give a suitable thickness and allowed the interface region to be examined by XPS. The pure PVA XPS spectrum was obtained by coating a copper foil with 1 wt % PVA solution at room temperature and then drying in an oven at 70 °C over 30 h. These conditions did not cause any measurable decomposition of the PVA, since the deposition of PVA onto untreated carbon fibers gave an XPS spectrum that was very similar to that of PVA deposited onto copper, and the spectrum agreed with the expected PVA spectrum obtained from calculations (vide infra).

Surface Analysis. Most of the spectra were collected using achromatic X-radiation from an AEI (Kratos) ES200B X-ray photoelectron spectrometer operated in the FRR (fixed retardation ratio) mode (with a retardation ratio of 23) using achromatic Mg Kα X-radiation at a power of 240 W. Monochromatic XPS spectra for PVA were collected on a VSW HA150 spectrometer (150-mm hemispherical analyzer) operated in the FAT (fixed analyzer transmission) mode with a pass energy of 22 eV, equipped with a 16-plate multichannel detector system and Al Kα X-radiation (240 W) produced from a 32 quartz crystal VSW monochromator providing an X-ray line width of better than 0.2 eV. The base pressure of both instruments were 10^{-9} Torr or better. The spectrometer energy scales were calibrated[36] using an argon ion etched copper plate and all spectra were referenced against the C1s peak of adventitious hydrocarbon at 284.6 eV. The fibers were mounted into the ES200B spectrometer on a holder as a short length (45 mm) of a fiber tow whose axis was at 90° to the incident X-ray beam and whose end was wrapped with aluminum foil to prevent “splaying out” at the end. The aluminum foil was positioned so that no XPS signal could be seen from the aluminum foil, or the sample holder. We have previously discussed[37] the possible alignment methods for carbon fibers, and a schematic diagram of our fiber arrangement is given in Figure 1b and c of this reference. The sample was grounded and positioned so that no signal from the sample holder could be detected in the spectrum. Data collection time was limited to minimize sample decomposition.[38,39] The typical time of data collection was about 15 min for the C1s region, 20 min for the O1s region, 30 min for the overall region, and 13−20 h for valence band spectrum, respectively. We have shown that oxidized carbon fibers suffer no significant decomposition when monochromatic X-ray light is used.[20] We have also shown that the valence band region (because the kinetic energy of the electrons are greater than the core regions and thus the depth probed is greater) is less affected by decomposition than the core XPS regions for oxidized carbon fiber exposed to achromatic X-ray light.[38]

The curve fitting of the XPS spectrum was carried out using a nonlinear-least-squares curve-fitting program with a Gaussian/Lorentzian Product Function.[40,41] The Gaussian/Lorentzian mixture was taken as 0.5, except for the graphite carbon peak which was taken as 0.84 with an exponential tail. The C1s binding energy of the graphite peak was fixed at 284.6 eV for the calibration purposes. The background shape used in the curve fitting, and the spectral smoothing methods used have been reported previously.[42,43]

Topographic and Structural Analysis. Atomic force microprobe images were obtained using a Wyko SPM 30 scanning probe microprobe. Carbon fibers were loaded on the holder above the piezzoelectric crystal using double-sided tape. The AFM images were obtained using the constant force mode with a tip force of 6 nN and a speed of 0.5 Hz across the carbon fiber.

XRD studies were carried out by using a Scintag XRD 2000 instrument to investigate the change of bulk structure of the carbon fibers. Cu Kα was used as the X-ray radiation source.

Calculations. A band structure calculation was carried out using an extensively modified version of the program CRYSTAL[44] which allowed this low-symmetry material to be studied. Crystallographic information was taken from a literature reference.[45] This structure is a deficient structure, and so a larger unit cell was generated with tetragonal symmetry that contained all the atoms including the hydrogen atoms. Calculated spectra were generated from the band structure by adjusting the density of states in the valence band for each orbital symmetry type (C2s, C2p, H1s, O2s, and O2p) by the appropriate Scofield atomic photoelectron cross section.[46] This density of states was then convoluted with a 50% mixed Gaussian/Lorentzian product function.[40,41] The ab initio Hartree−Fock calculations used a modified version of the program HONDO (copyright IBM) using an STO-3G basis set. The calculated spectra were generated by adding together the component peaks (represented by the 50% mixed Gaussian/Lorentzian product function described above) for each of the calculated energy levels, with each peak having a position corresponding to the calculated energy level and an intensity (area) corresponding to the number of electrons in the energy level multiplied by the atomic population (net atomic population for the ab initio calculations) for the level, adjusted by the appropriate atomic photoelectron cross-section. All calculations were performed on an IBM RISC/6000 computer.

Results and Discussion

The details of the surface treatment of the fibers and the monitoring of the surface chemical and topographical changes will be discussed first. The interfacial chemical reactions that occur when these surface-treated fibers are reacted with PVA will then be discussed.

XPS Studies of the Oxidized Carbon Fiber Surface. Figure 1 presents the overall (I), C1s (II), and O1s (III) XPS data for the carbon fibers before and after electrochemical oxidation using galvanostatic treatment using currents of 0.25 and 0.5 A for various times.

Overall Scan Region. Column I in Figure 1 shows the XPS overall spectra of the carbon fibers. All samples showed a strong C1s peak at a binding energy of 284.6 eV. A low intensity feature seen at about 1000 eV corresponds to the C (KVV) Auger peaks. The as-received fibers show only a very low intensity O1s signal. This signal increases substantially after oxidation for 10 s and increases in relative intensity as the level of oxidation is increased. When the oxidation time was over 5 min, the relative intensity of the O1s signal remained constant. The O(KVV) Auger peak is apparent in all the oxidized samples.

C1s Region. Column II in Figure 1 shows the curve-fitted C1s region, with the fitting details being given in

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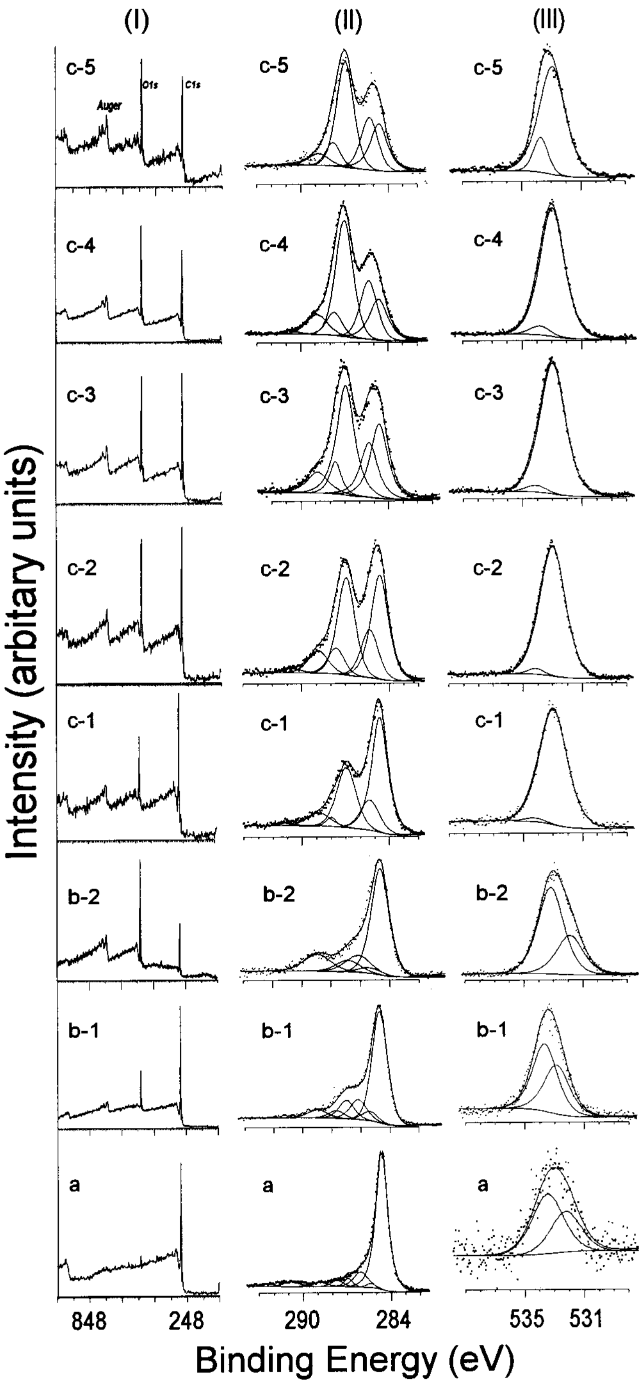

Figure 1. XPS spectra of carbon fibers treated electrochemically in 1 M HNO_3 with different parameters: (a) as-received; (b-1) 0.25 A for 10 s; (b-2) 0.25 A for 40 s; (c-1) 0.5 A for 10 s; (c-2) 0.5 A for 30 s; (c-3) 0.5 A for 1 min; (c-4) 0.5 A for 5 min; and (c-5) 0.5 A for 15 min.

Table 1. In general, oxidized carbon peaks increased in relative intensity with an increase of the oxidation time. The peaks due to oxidized carbon were assigned on the basis of previous studies[13] as the graphite carbon (peak 1), β-carbon (peak 2), hydroxide (C−OH) (peak 3), HBS oxide groups (peak 4), carbonyl (C=O) (peak 5), and carboxyl (COOH) (peak 6) as well as $\pi-\pi^*$ shake-up satellites (peak 7). The HBS group (shown in Figure 2) is positioned between those hydroxide and carbonyl groups[20] and is seen in many studies of carbon fiber oxidation.[47,48] The β-carbon atom that results from the HBS group is fitted to all the spectra, with its intensity fixed as half of that of the HBS group (since there are two HBS carbons for each β-carbon). Beamson and Briggs[49] have suggested that the β-carbon atom should have a chemical shift between 0.2 and 0.4 eV, except where the carbon atom is attached to two −C=O carbon atoms (very similar to the β-carbon atom in the HBS Group), when the value would be closer to 0.9 eV. From our curve fitting, the shift of the β-carbon was about 0.7 eV. We believe that the HBS group is the principal oxidized feature on electrochemically oxidized carbon fibers under the galvanostatic conditions.

Low levels of surface oxidation are found on as-received fibers with an intensity and composition that varies with the type of fiber and the manufacturer. The principal form of oxidized carbon on the as-received fiber was the hydroxide group (C−OH, CS: 1.5 eV), representing 9.4% of the C1s intensity. In the oxidation process at 0.25 A, all forms of oxidized carbon on the carbon fiber surface increased in intensity and the peak area ratio of the oxide ($C_{\text{oxide}}/C_{\text{total}}$) rose from 21.5% to 37.5% for 10-s treatment and to 39.7% with 40-s treatment. The fwhm of the graphite carbon peak became wider from 0.96 to 1.44 eV in the oxidation process, suggesting that disordering of the carbon lattice might result from the oxidation process. This is because the C1s peak increases in width as the form of carbon becomes more disordered.[47]

After oxidization at 0.5 A, the hydroxide group disappeared, which shows that this functional group is not stable in this electrochemical oxidation condition and is probably converted into HBS groups. The proportion of the C1s region due to graphite carbon peak (peak 1) was gradually decreased from 77% to 17.6% as the oxidation time increased up to 5 min. After 5-min treatment, the graphitic carbon peak showed a slight increase in intensity, which implies that the surface was saturated with oxides at that time and any further electrochemical reaction on the surface could not occur. The fwhm of the graphite peak also increases in width from about 0.94 to 1.6 eV as the oxidation time increased, indicating an increase in disorder with oxidation. The increase in the amount of HBS functionality and its associated β-carbon features increased rapidly during the first 10-s oxidation, and then the rate of the increase became smaller. After 5 min of oxidation there was no obvious increase on the amount of the oxide. It will be seen later from the XRD results that longer oxidation times correspond to bulk changes as indicated by the XRD results. The fwhm of the HBS peak remained generally at about 1.4 eV after oxidization. The carbonyl group reduced in intensity during first 10-s oxidation, and then increased up to the maximum of 8.4% at 15 min of oxidation, which is consistent with the conversion of some of the carbonyl group into HBS functionality during the first 10 s of the oxidation process. The relative intensity of the carboxyl group steadily increased with oxidation time. We have discussed a possible reaction scheme for this type of process in an earlier publication.[48]

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Table 1. Chemical Shift (CS, eV), FWHM (eV), and Relative Area (%) of C1s XPS of Carbon Fibers Electrochemically Treated in 1 M HNO_3[a]

		as received (a)	0.25 A for 10 s (b-1)	0.25 A for 40 s (b-2)	0.5 A for 10 s (c-1)	0.5 A for 30 s (c-2)	0.5 A for 1 min (c-3)	0.5 A for 5 min (c-4)	0.5 A for 15 min (c-5)
peak 1	CS	0	0	0	0	0	0	0	0
(C−C)	fwhm	0.84	1.24	1.44	1.30	1.42	1.40	1.48	1.40
	area	77	62.5	60.3	48.5	35.5	25.9	17.6	20.9
		(3.1)	(3.6)	(3.8)	(2.8)	(2.1)	(1.8)	(2.1)	(2.2)
peak 2	CS	0.74	0.70	0.65	0.69	0.69	0.69	0.6	0.66
(β−C)	fwhm	0.66	1.24	1.72	1.54	1.42	1.40	1.36	1.38
	area	1.5	5.2	3.8	13.7	15.6	19.0	21.6	21.2
		(4.2)	(4.1)	(6.2)	(4.5)	(3.6)	(3.2)	(3.2)	(4.2)
peak 3	CS	1.43	1.5	1.45					
(C−OH)	fwhm	1.16	1.34	2.0					
	area	9.4	12.0	14.3					
		(10.1)	(6.7)	(5.1)					
peak 4	CS	2.30	2.30	2.2	2.30	2.30	2.30	2.32	2.32
(HBS)	fwhm	0.66	1.24	1.72	1.54	1.42	1.40	1.36	1.38
	area	3.1	10.4	7.6	27.5	31.3	38.0	43.1	42.3
peak 5	CS	3.04	3.0		3.34	2.99	2.99	3.02	3.15
(C═O)	fwhm	0.92	1.24		0.82	1.32	0.94	1.24	1.16
	area	3.2	4.3		2.2	7.9	7.5	7.7	8.4
		(7.2)	(7.2)		(5.2)	(5.2)	(5.1)	(5.3)	(6.2)
peak 6	CS	4.18	4.30	4.25	4.21	4.21	4.21	4.19	4.20
(COOH)	fwhm	1.04	1.53	2.1	1.82	1.40	1.70	1.64	1.68
	area	2.6	5.6	14.0	7.1	8.1	8.9	8.8	6.4
		(8.6)	(5.3)	(5.6)	(4.3)	(3.6)	(4.7)	(6.3)	(4.7)
peak 7	CS	6.18			6.38	6.0	5.99	6.01	6.08
(π−π*)	fwhm	1.16			1.16	1.58	1.26	1.50	1.58
	area	3.2			1.0	1.6	0.1	1.3	0.7
		(5.5)			(6.1)	(5.5)	−	−	−
area ratio	C_{ox}/C_{tot}	21.5	37.5	39.7	37.8	48.9	55.1	60.8	57.2

[a] Figures in parentheses represent the uncertainty values (%) in the relative peak area (two standard deviations for the fitted areas).

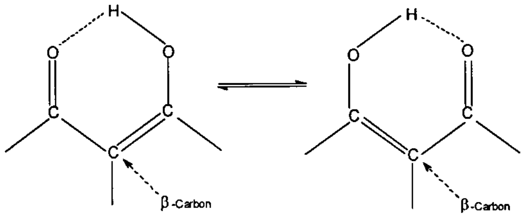

Figure 2. Representation of the hydrogen-bridged oxide structure (HBS) unit showing the location of the and β-carbon atoms.

O1s Region. Column III in Figure 1 shows the O1s region spectra fitted to two peaks for different carbon fibers. This region has been fitted in a manner consistent with our previous studies of surface-treated carbon fibers[37] without the chemisorbed oxygen signal. Consistent with the results of fitting the C1s region and recognizing that the O1s and C1s region probe different depths into the surface, the peaks can be assigned as, peak 1 (~534.0 eV) and peak 2 (~533.0 eV) corresponding to C−OH and C═O groups, respectively. Relative peak areas are shown in Table 2.

Valence Band Spectra. The complementary information provided by this region has been discussed in several papers from our group.[19,38,47,50,51] The region also probes more deeply into the carbon fiber because of the higher kinetic energy of the electrons. Figure 3 shows this region, which has been smoothed using a quadratic−cubic smooth with a 15-point smoothing interval repeated 100 times.

The changes in the valence band with oxidation follows a similar gross behavior as that which we have reported for previous studies of oxidized fibers.[19] The separation between C2p and O2s is shown in Figure 3. This separation became larger as the oxidation time increased. For the fibers oxidized at 0.25 A, the separation increased from 7.0 to 8.07 eV when oxidation time increased from 10 to 40 s. For the carbon fibers oxidized at 0.5 A, it changed from 8.49 to 8.97 eV when oxidation time rose from 10 s to 5 min When the oxidation increased to 15 min, the separation increased to 9.27 eV. In our earlier work,[52] experimental and theoretical studies showed an increase in this separation from −OH functionality to the HBS structure. The calculated O2s−C2s separation for multiple scattered wave Xα calculations for substituted coronenes with carboxyl, epoxide, carbonyl, HBS, and hydroxide group substituted coronene were 10.58, 8.92, 8.85, and 8.77 eV, respectively. The lack of splitting in the principally O2s region around 24 eV indicates that the carboxyl feature is of low intensity, as expected from the C1s region.[53] The absence of a large splitting, especially at low currents and times suggests that the −C−O−C− functionality (which would occur at the same C1s binding energy as the −OH group).

XRD Studies of the Oxidized Carbon Fiber Surface. Figure 4 shows the XRD powder diffraction spectra for carbon fibers electrochemically oxidized under different conditions. The as-received fibers show the expected graphitic spectrum normally seen for as-received fibers.[38] The oxidation process leads to an increase in the weak peak around 13° which we have

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Table 2. Binding Energy (BE, eV), FWHM (eV), and Relative Area (%) of O1s XPS of Carbon Fibers Electrochemically Treated in 1 M HNO_3[a]

		as received (a)	0.25 A for 10 s (b-1)	0.25 A for 40 s (b-2)	0.5 A for 10 s (c-1)	0.5 A for 30 s (c-2)	0.5 A for 1 min (c-3)	0.5 A for 5 min (c-4)	0.5 A for 15 min (c-5)
peak 1	BE	533.37	533.54	533.63	534.18	534.09	534.05	533.74	533.71
C−O	fwhm	2.49	1.95	2.05	1.58	1.24	1.58	1.58	1.16
	area	60.1	57.3	67.9	19.1	2.7	3.8	5.3	15.0
		(3.2)	(4.1)	(3.7)	(2.8)	(5.0)	(5.6)	(5.5)	(4.3)
peak 2	BE	532.15	532.74	532.33	532.93	532.95	532.92	532.88	532.92
C=O	fwhm	2.41	2.00	2.15	2.20	2.07	2.00	1.91	2.08
	area	39.9	42.7	32.1	80.9	97.3	96.2	94.7	85.0
		(4.7)	(5.2)	(5.7)	(4.1)	(3.4)	(2.1)	(2.4)	(2.1)

[a] Figures in parentheses represent the uncertainty values (%) in the relative peak area (two standard deviations for the fitted areas).

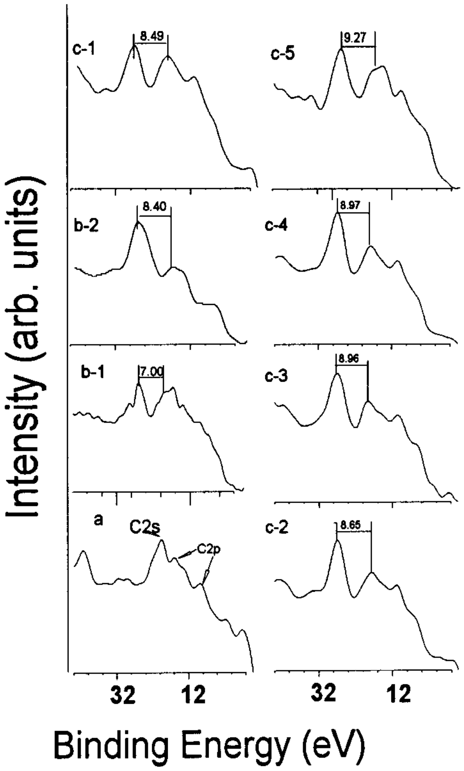

Figure 3. Valence band XPS spectra of carbon fibers treated electrochemically in 1 M HNO_3 with different parameters. (a−c are the same as in Figure 1.)

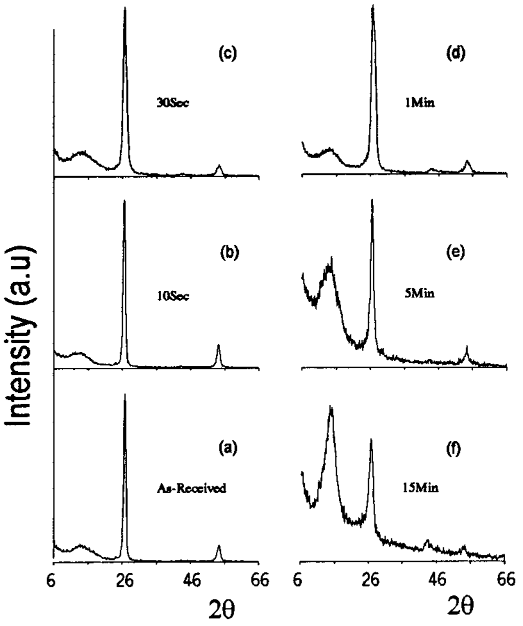

Figure 4. XRD spectra of carbon fibers treated electrochemically at 0.5 A in 1 M nitric acid for (a) 0 s, (b) 10 s, (c) 30 s, (d) 1 min, (e) 5 min, and (f) 15 min.

previously assigned to disordered bulk carbon resulting from the oxidation process.[38] After 5 min, this peak becomes very intense, and after 15 min this peak becomes the predominant feature in the spectrum. We found that the strength of treated carbon fibers was degraded by the oxidation process, the fibers being so weakened that they broke under normal handling when the oxidation process was extended beyond 15 min.

AFM Studies of the Oxidized Carbon Fiber Surface. The topographical changes that occurred on the carbon fiber surface following electrochemical oxidation were monitored by AFM. The results show a steady roughening of the fiber surface with increasing treatment time, with clear pits forming that deepened with treatment time. The roughness change during the oxidation process is indicated by the ratio of the surface area divided by the plate surface area. This ratio was 1.10 for the as-received carbon fibers, 1.14 for fibers subjected to 10 s, 1.2 for 30 s, 1.4 for 1 min, and 1.34 for fibers subjected to 15 min of oxidation. Figure 5 shows the AFM results for the as-received fiber, the fiber after 30 s and 1 min of oxidation.

Interfacial Interactions of the Oxidized Carbon Fiber Surface and PVA. The interfacial interactions between the carbon fiber surfaces and PVA was monitored by recording the XPS spectra of a thin film of PVA deposited on the oxidized carbon fiber surfaces.

XPS Spectra of Poly(vinyl alcohol). The XPS spectra of PVA using a monochromatic X-ray source is presented in Figure 6. The spectrum shows the expected features for the ($-CH_2-CHOH-$) repeat unit of the polymer and agrees well with the previously published spectrum of PVA by Beamson and Briggs.[49] Thus, the C1s region shows the one peak due to the CH_2 groups with nearly 50% of the intensity of the C1s region. There is a peak due to the C−OH group with nearly 42% of the intensity of the C1s region. We believe that the remaining approximately 8% of the C1s intensity due to −COOH functionality results from oxidation of the C−OH group during the preparation of the film. The O1s region shows a single peak due to the −OH oxygen with a low-intensity feature due to carboxyl oxygen. The fact that the O1s peak due to carboxyl oxygen represents only about 4% of the intensity in the O1s region rather than about 20% for the C1s region indicates that the carboxyl group formed by oxidation of the −OH group is not on the outer surface region since the O1s region is more

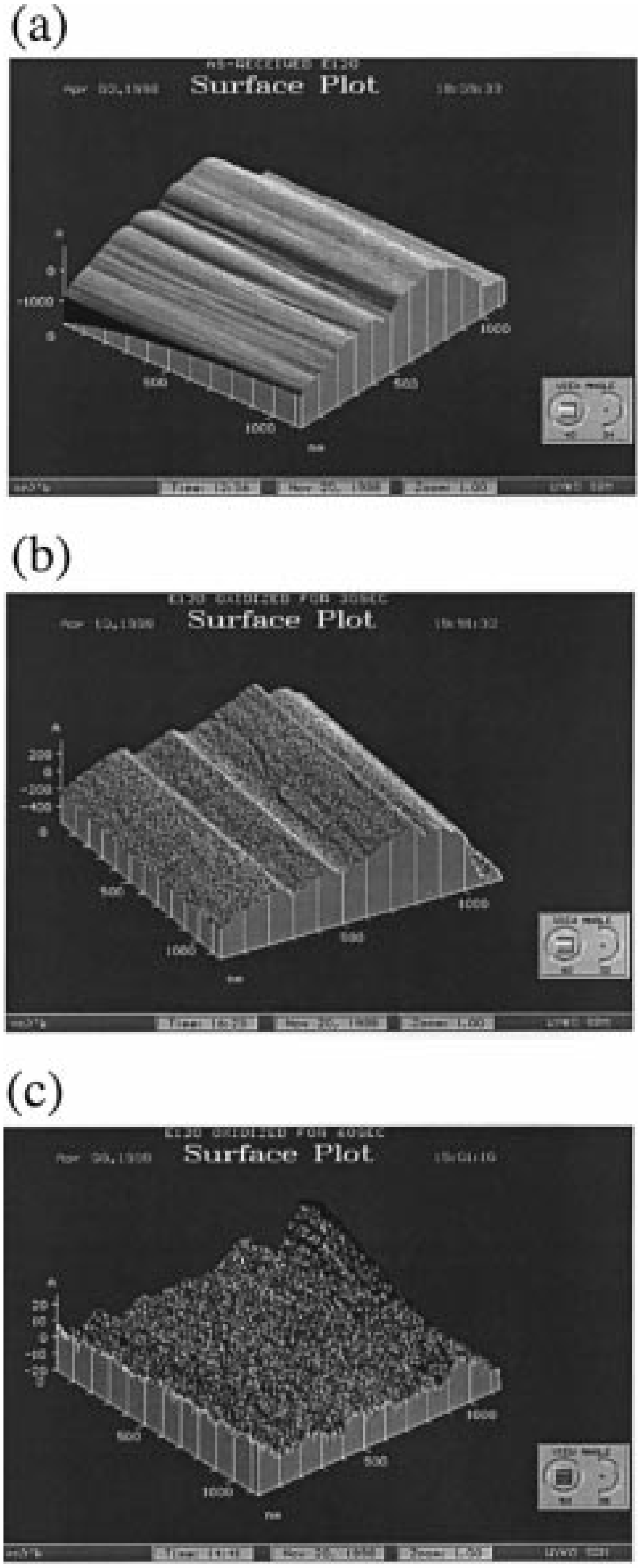

Figure 5. AFM images of (a) the as-received carbon fiber, (b) the carbon fiber electrochemically oxidized in 1 M nitric acid at 0.5 A for 10 s, and (c) same as b but oxidized for 1 min.

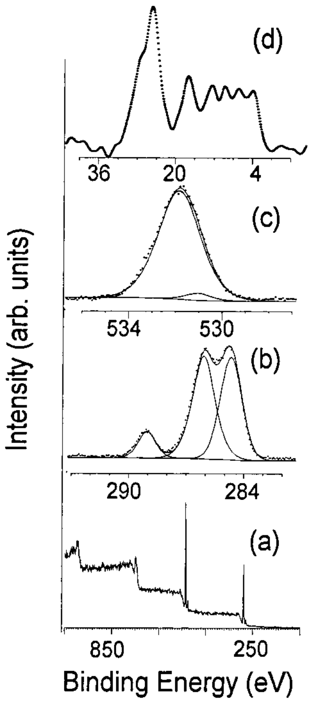

Figure 6. XPS spectra of PVA film obtained with a monochromatic Al Kα X-ray source. The overall is shown in a, the C1s region is shown in b, the O1s region in c, and the valence band region in d. The valence band region was smoothed with a 21-point quartic–quintic smooth and had a nonlinear background subtracted.

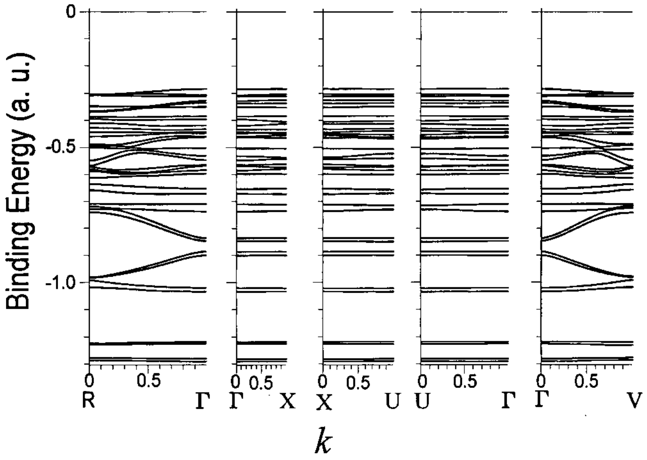

Figure 7. Dispersion relation for PVA for five directions in the first Brillouin zone for the tetragonal unit cell chosen for PVA.

surface sensitive than the C1s region. The greater surface sensitivity of the O1s region arises because the inelastic mean free path increases with electron kinetic energy, and the O1s electrons have a kinetic energy that is much less (about 960 eV rather than about 1200 eV) than the C1s electrons. To better understand the valence band region of PVA, we have carried out a band structure calculation and used this to generate a calculated spectrum using the method described. The dispersion relationship (energy against wavevector) is shown in Figure 7, which indicates that as expected, there is little dispersion (i.e., the bands are fairly flat). The spectrum calculated from the band structure calculation is in good agreement with experiment, each "peak" and "shoulder" in the calculated spectrum being reproduced in the experimental spectrum. The small amount of dispersion shown in Figure 7 suggests that a localized model (such as one based upon the polymer repeat unit terminated by hydrogen atoms) might also predict the spectrum, and we compare spectra generated from ab initio Hartree–Fock calculations on sections of a single polymer chain of increasing size with the

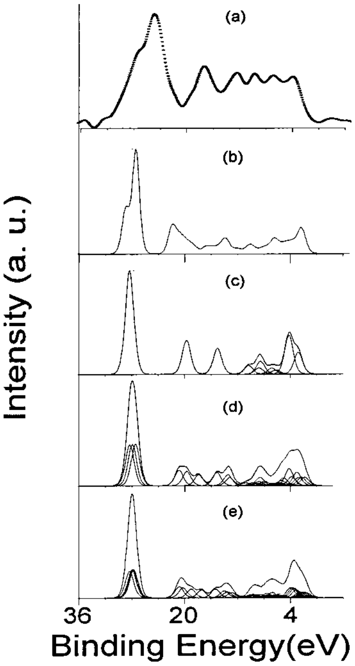

Figure 8. Comparison of the calculated and experimental valence band spectrum of PVA. The experimental spectrum shown in Figure 5c is shown in a and compared with the spectrum calculated from the band structure calculation in b. The calculated spectrum for a single chain of PVA is shown for one repeat unit in c, three repeat units in d and four repeat units in e.

experimental spectrum in Figure 8. The smallest calculated unit is the hydrogen-terminated polymer repeat unit (H−CH_2−CH(OH)−H). Increasing the number of polymer repeat unit from one to three (Figure 8d) and then four (Figure 8e) gives further improvement in the agreement. The single polymer chain seems to provide most of the spectral features, so that the hydrogen-bonded interactions between chains (included in the band structure calculation) is of less importance than interactions within a polymer chain. The main difference between Figure 8b and Figure 8e is the high binding energy asymmetry in the principally O2s region around 28 eV, and the presence of this feature in the experimental spectrum may indicate that this experimental feature is indicative of hydrogen-bonded interactions between the polymer chains.

This suggestion will be seen to be relevant when one considers the interaction of PVA with oxidized carbon fiber surfaces.

Possible Interfacial Interactions. In considering possible interfacial interactions between the oxidized carbon fiber surface and the PVA, the groups present on the PVA (alcohol (−OH) and carboxyl (CO_2H) groups) and on the carbon fiber surface (principally HBS, with a small amount of carboxyl groups or hydroxide) should be considered. A possible reaction scheme between the carbon fiber surface and PVA is shown in Figure 9. If the reaction scheme in Figure 9a occurred then the HBS and alcohol groups would be changed to carbonyl and ether functionality, and carboxyl functionality would change to ester functionality in Figure 9c. The peak at a chemical shift of 2.0−.3 eV due to HBS functionality would be replaced by two peaks with chemical shifts of 1.5 and 3.0 eV, respectively, arising from ether and carbonyl groups.

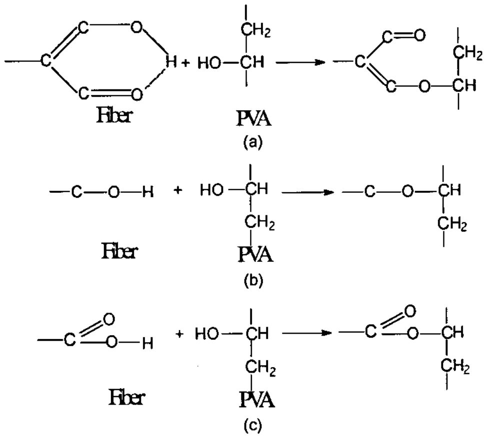

Figure 9. A possible reaction scheme between PVA and carbon fiber electrochemically oxidized in nitric acid.

XPS Spectra of Thin Films To Probe the Interfacial Region. Figure 10 shows the spectra of the oxidized fibers coated with a very thin film of PVA, so thin that the interfacial region is seen. The changes in the core XPS region are indicated by the curve-fitting results in Tables 3 and 4. The tables indicate that the spectra changes in corresponding to the scheme in Figure 9 occur. Thus, in the C1s region after coating with PVA, the peaks due to β-C and HBS are completely lost from the spectrum with only peaks due to ether (or hydroxide), carbonyl, and carboxyl present in the spectrum. These results indicate that the reaction scheme shown in Figure 9 is consistent with the observed spectral changes, and they clearly indicate *interfacial interaction between the oxidized fibers and the PVA.* While the spectra of the PVA and the PVA coated fibers (Figure 10a, c, e, and g) do not show enormous differences the differences seen are significant. It is important to note that the PVA-coated fibers need to have a peak due to >C=O groups included in their fit, and *there is no >C=O group present in the spectrum of PVA.* In addition the total O1s/C1s intensity ratios are generally smaller for the PVA-coated fibers (except in the case of the fiber oxidized at 0.25 A).

From the fitting results of O1s spectrum, as shown in Table 4, PVA consists of principally one peak at 532.8 eV due to −O−H, and oxidized carbon fibers could be fit to two peaks with binding energies of 533.4 and 531.4 eV due to −OH and C=O, respectively. The spectra of the PVA-coated oxidized fibers could be fit to three peaks at 533.0, 532.2, and 531.5 eV peaks due to C−O−R, −OH, and C=O, respectively. After coating with PVA, we believe that the HBS group (which can be seen in the C1s spectrum) on the oxidized fibers reacted with C−OH group in PVA to form the functionality shown in Figure 8a. Such a functionality would result in two peaks in the C1s spectrum, one at a CS of about 1.5 eV due to −C−O−R, and another at 3.0 eV due to >C=O. In addition, the relevant peak due to carbonyl group and ether group were also seen separately in O1s region, with the principal contribution (ab out 70%) coming from the C−O−R grouping.

The use of addition and difference spectra can be used to establish the presence of a reaction at the PVA-oxidized fiber interface. The principle here is that the addition spectrum of PVA and the oxidized fiber will be the same (when added in the correct proportion) as

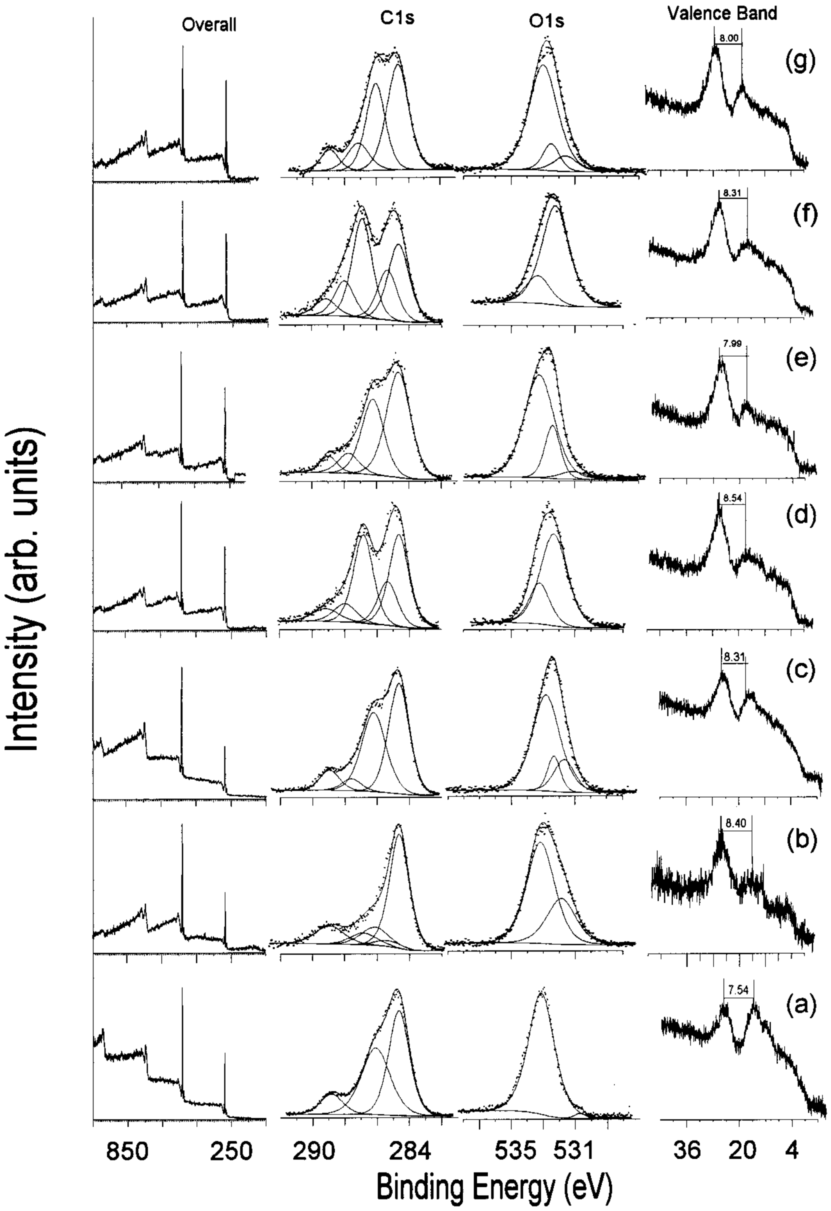

Figure 10. XPS spectra of carbon fibers treated electrochemically at in 1 M nitric acid with and without a PVA coating: (a) PVA; (b) 0.25 A for 10 s; (c) 0.25 A for 40 s with PVA; (d) 0.5 A for 40 s; (e) 0.5 A for 40 s with PV A; (f) 0.5 A for 2 min; and (g) 0.5 A for 2 min with PVA.

the spectrum of the coated fiber if no reaction has occurred at the interface. Differences, especially those where peak positions change, in this addition spectrum and the spectrum of the coated fiber indicate reaction at the oxidized fiber−PVA interface. Any differences in these two spectra will be revealed in a difference spectrum. Parts a, b, and c of Figure 11 are the experimental spectra of PVA, the oxidized carbon fibers, and PVA-coated fibers, respectively. Figure 11d was from the addition of PVA spectrum a to the spectrum of the oxidized carbon fibers (b). It is clear that the addition spectrum in Figure 11d is actually different to the spectrum of the coated fibers (Figure 11c having a substantial difference in the separation of the two main peaks (1.59 in Figure 11c and about 2.0 eV in Figure 11d)). This difference is demonstrated by subtracting the spectrum of the coated fibers (Figure 11c) from the addition spectrum (Figure 11d) to give the difference spectrum shown in Figure 11e. In fact, if the no reaction occurred between the oxidized fibers and PVA, the experimental spectrum (Figure 11c) should be the same as the addition spectrum (Figure 11d) and the difference spectrum should be a flat line. The fact that the difference spectrum in Figure 11e has a negative and positive peak reflects the difference in the separation of the main peaks in both spectra and other differences, providing strong evidence for chemical interaction at the interface. After the smoothing of the difference spectrum, the feature can be seen more clearly, as shown in Figure 11f. The positive peak at the binding energy of 286.2 eV is the principal functional group in the reacted interface, which represents the C−O−R group in the interface that did not existed in the addition spectrum. The negative peaks observed at the binding energy of 285 and 287.5 eV are features of the unreacted oxidized carbon fiber, corresponding to the HBS group and β-C group, respectively. The negative value means that these peaks did not exist in the reacted interface, but in the addition spectrum of the PVA and the oxidized fiber. These observations provide strong evi-

Table 3. Chemical Shift (CS, eV), FWHM (eV), and Relative Area (%) of C1s XPS of Carbon Fibers Electrochemically Treated in 1 M HNO_3 and Coated with PVA[a]

		PVA (1)	0.25 A for 40 s (2)	0.25 A for 40 s +PVA (3)	0.5 A for 40 s (4)	0.5 A for 40 s + PVA (5)	0.5 A for 2 min (6)	0.5 A for 2 min + PVA (7)
peak 1	CS	0	0	0	0	0	0	0
(C−C)	fwhm	1.34	1.44	1.48	1.44	1.76	1.52	1.56
	area	49.6	60.3	47	35.5	51.8	29.9	41.2
		(4.3)	(3.8)	(3.2)	(2.4)	(3.3)	(3.1)	(2.6)
peak 2	CS		0.65		0.7		0.70	
(β-C)	fwhm		1.72		1.42		1.42	
	area		3.8		16.7		17.5	
			(6.2)		(5.4)		(4.7)	
peak 3	CS	1.50	1.45	1.55		1.59		1.49
(C−OH)	fwhm	1.34	2.0	1.77		1.62		1.68
	area	41.9	14.3	40		34.0		43.3
		(3.2)	(5.1)	(2.5)		(2.8)		(3.5)
peak 4	CS		2.2		2.19		2.24	
(HBS)	fwhm		1.72		1.42		1.42	
	area		7.6		33.4		34.9	
peak 5	CS			2.95	3.33	3.09	3.33	3.04
(C=O)	fwhm			1.43	1.62	1.52	1.42	2.10
	area			4.8	7.9	8.4	12.3	10.5
				(3.2)	(3.4)	(3.7)	(4.1)	(5.4)
peak 6	CS	4.20	4.25	4.3	4.18	4.21	4.21	4.21
(COOH)	fwhm	1.82	2.1	1.43	1.90	1.24	1.52	1.12
	area	8.5	14.0	8.2	6.5	5.77	6.2	5.1
		(2.1)	(5.6)	(3.2)	(4.3)	(4.2)	(3.9)	(4.6)
peak area ratio	C_{ox}/C_{tot}	51.4	39.7	53	64.5	48.2	70.1	58.8
separ[b] (eV)		7.84	8.40	8.31	8.54	7.99	8.31	8.00

[a] Figures in parentheses represent the uncertainty values (%) in the relative peak area (two standard deviations for the fitted areas). [b] The separation between O2s and C2s.

Table 4. Binding Energy (BE, eV), FWHM (eV), and Relative Area (%) of O1s XPS of Carbon Fibers Electrochemically Treated in HNO_3 and Coated with PVA[a]

		PVA (1)	0.25 A for 40 s (2)	0.25 A for 40 s +PVA (3)	0.5 A for 40 s (4)	0.5 A for 40 s + PVA (5)	0.5 A for 2 min (6)	0.5 A for 2 min + PVA (7)
peak 1	BE			532.75		533.19		532.94
(C−O−R)	fwhm			2.00		2.19		2.10
	area			70.2		74.9		78.7
				(2.4)		(1.7)		(1.9)
peak 2	BE	532.8	533.13	532.25	533.29	532.34	533.23	532.44
(C−O)	fwhm	1.91	1.95	1.05	1.52	1.15	1.81	1.28
	area	98.1	57.3	12.1	26.0	21.1	19.5	11.9
		(2.1)	(3.4)	(3.7)	(2.1)	(2.3)	(1.9)	(2.3)
peak 3	BE	530.4	531.87	531.6	532.09	531.10	532.14	531.55
(C=O)	fwhm	0.76	2.00	1.52	2.00	1.90	2.00	1.71
	area	1.9	42.7	17.7	74.0	5.0	80.5	9.4
		(5.4)	(3.2)	(4.1)	(1.8)	(2.5)	(2.3)	(2.6)
O1s/C1s		1.95	2.10	2.10	1.66	1.51	1.65	1.39

[a] Figures in parentheses represent the uncertainty values (%) in the relative peak area (two standard deviations for the fitted areas).

dence of interfacial interaction between PVA and the oxidized carbon fibers.

In the valence band spectra (shown in Figure 10), the O2s−C2s separation was ~7.5 eV for PVA (comparable to the literature value[49]), and 8.40−8.78 eV for oxidized carbon fibers. For PVA-coated carbon fibers the separation lies between that of PVA and the oxidized fibers, *but the area ratio of the O2s region around 28 eV to the C2s region around 18 eV was about* ***twice*** *that of PVA*, although slightly less than the value for the oxidized fibers. It is interesting to note that the principally O2s region around 28 eV becomes more symmetrical with less of a high binding energy tail for the oxidized fibers exposed to PVA. In the study of PVA discussed above it was noted that the high binding energy tail might be due to hydrogen-bonded interactions between PVA chains. Certainly if the possible mechanism for PVA/oxidized carbon fiber surface reaction that we have suggested is correct then this hydrogen bonding would be lost because the C−OH groups of PVA would be expected to react with the carbon fiber surface as shown in Figure 8.

It is important to note that while the C1s region shows a significant, but not substantial difference between the PVA-coated fibers and PVA, the valence band region is very different for PVA and PVA-coated fibers both in the O2s−C2s separation and in the relative intensities of the O2s and C2s regions. Since the valence band region probes more deeply into the fibers, it might be tempting to think that we are simply seeing the oxidized fibers below an unreacted PVA layer, but there are substantial differences in both the O2s−C2s separation and in the relative intensities of the O2s and the C2s regions between the coated fibers and the oxidized fibers. In any case, even the more deeply probing valence band region would see substantial contributions from an unreacted PVA surface layer, and there is no way that the valence band region can be

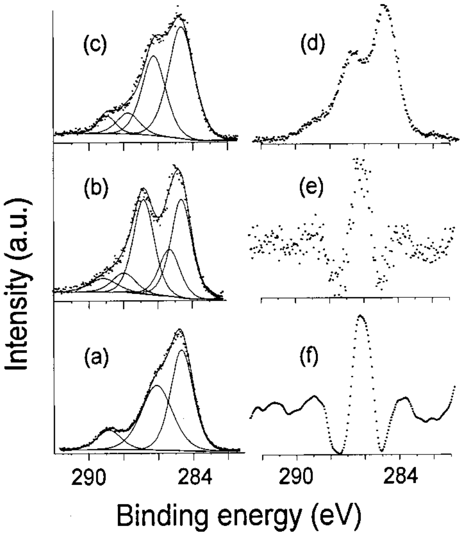

Figure 11. C1s addition spectrum and difference spectrum of carbon fibers in 1 M nitric acid for 0.5 A for 40 s and PVA: (a) PVA, (b) the oxidized carbon fibers, (c) the PVA-coated fibers, (d) addition spectrum (= a + b), (e) difference spectrum (= c − d), and (f) the spectrum d smoothed with a 21-point quartic−quintic smoothing function after the removal of a nonlinear background.

explained by adding the PVA spectrum to that of the oxidized fiber. These results are incompatible with a model where no reaction between PVA and the oxidized carbon fibers occurs.

Conclusions

Electrochemically oxidized carbon fibers are seen to chemically react with thin films of PVA to form a chemically bound interface. The importance of using both core and valence band XPS to study this surface chemistry and to take advantage of the different depth information provided by each region is illustrated. The changes in surface chemistry and topography of oxidized carbon fibers follow the expected changes for these fibers on electrochemical oxidation. In this study we show that a range of different surface treatments cause differences in the chemical composition, and we relate these chemical changes to changes in the fiber surface topography. The combination of chemical and topographical changes is very likely to enhance the wetting of the carbon fibers by the PVA films and chemical interaction between the carbon fibers and the PVA results. Careful analysis of the PVA valence band spectrum, and the following of changes in the valence band as the oxidized fibers are exposed to PVA provides complementary support for the changes in the core region and provides very strong evidence for chemical reaction between the oxidized fiber and the PVA.

It is clear that this type of interaction can readily occur between oxidized carbon fiber surfaces and polymeric materials with −OH groups present on the surface. Such chemical interaction is probably present when size is applied to fibers, and it certainly can be anticipated in sizes that contain −OH functionality of the sort found in PVA. The study complements our earlier studies that indicate that such chemical and physical interaction can occur, and underlines the importance of tailoring the carbon fiber surface to the chemistry of the matrix material.

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