X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 17. Interfacial Interactions between Phenolic Resin and Carbon Fibers Electrochemically Oxidized in Nitric Acid and Phosphoric Acid Solutions, and Their Effect on Oxidation Behavior

Tiejun Wang and Peter M. A. Sherwood*

Department of Chemistry, Willard Hall, Kansas State University, Manhattan, Kansas 66506

Received January 3, 1994. Revised Manuscript Received March 30, 1994®

The interactions between a carbon fiber surface, electrochemically oxidized in dilute phosphoric or dilute nitric acid, and a phenolic resin were examined. The system was chosen because of its relevance to the first step in the formation of a carbon–carbon composite and because of the possibility of preferential oxidation at the fiber–matrix interface. The interaction could be enhanced by using coupling agents, which in one case is clearly shown to form a chemical bond between the fiber and resin. The effect of air oxidation on the resin coated fiber (with or without coupling agent and fiber surface treatment) was examined by thermal gravimetric analysis (TGA). The surface chemistry of the interface region was monitored by core and valence band X-ray photoelectron spectroscopic studies of a very thin film of matrix on the surface of the fiber. The spectra were analyzed by *ab initio* molecular orbital calculations, which clearly indicated interfacial chemical interaction involving an acetal cross-linking structure for phosphoric acid-treated fibers and phenolic resin with the use of the coupling agent propionaldehyde in an acid environment. TGA results show that the resin coated samples behave differently on oxidation in air depending upon the fiber-resin interface modification. The chemically cross-linked interface using acidified propionaldehyde leads to a reduction in the oxidation rate of the coated fiber in air.

Introduction

The importance of protecting carbon-carbon composites from oxidation has been well established. In spite of their superior mechanical properties, carbon-carbon composites are subjected to oxidation in most aerospace applications.[1–5] Oxidation causes microstructural changes, leading to the degradation of mechanical properties and eventually failure.

Oxidation protection of these composites is commonly achieved by the application of an oxidation resistant outer layer, but differences in thermal expansion between this layer and the composite can cause cracking of the protective layer.[6] Once the outer protective layer has cracked oxidation may be inhibited by protective coatings on the fibers,[7] and by addition of oxidation inhibitors to the matrix,[8] and glasses to seal the cracks in the outer protective film.[6,10]

The importance of improving the oxidation resistance of the fibers in the composite has been realized,[8–15] especially as the fiber–matrix interface plays an important role in determining various physical properties of the composite. These studies have indicated that the fiber–resin interface may be selectively attacked by oxidation arising from oxygen that had diffused along this interface, and thus protection of this interface is very important. In our laboratory we are conducting research on the chemical design/modification of the fiber–resin interface. This work is aimed at establishing chemical interactions between the fiber and the resin, and studying the relationship between interface bonding and oxidation resistance of carbon fiber reinforced resin composites.

In this work, the interface between electrochemically treated carbon fibers in nitric acid and phosphoric acid solutions, and phenolic resin (a common matrix resin for carbon–carbon composites) was studied using X-ray photoelectron spectroscopy (XPS). The interface was prepared by placing a thin film of matrix resin onto the oxidized fiber so that XPS could detect the fiber, the interface region, and the resin. *Ab initio* calculations were performed to interpret spectral features in the core and valence band spectra, allowing interpretation of the interface chemistry. Thermal gravimetric analysis (TGA) was conducted on the fiber/resin composites, allowing the

---

® Abstract published in *Advance ACS Abstracts,* May 1, 1994.

(1) McKee, D. W. *Carbon* **1986,** *24,* 737.
(2) Pickup, I. M.; McEnaney, B.; Cooke, R. B. *Carbon* **1986,** *24,* 535.
(3) Zhao, J. X.; Bradt, R. C.; Walker, P. L. Jr. *Carbon* **1985,** *23,* 9.
(4) Prewo, K. M.; Batt, J. A. *J. Mater. Sci.* **1988,** *23,* 523.
(5) Bavarian, B.; Arrieta, V.; Zamanzadeh, M. *35th Int. SAMPE Symp.* **1990,** Apr 2–5, 1348.
(6) Kramer, D. P.; Magnotta, V. L.; Dyer, P. N.; Kidd, W. *NASA Conference Publication 2482, Proceedings of Joint NASA/DOD Conference, Cocoa Beach, FL, January 22–23,* **1986,** 395.
(7) Wang, Y. Q.; Wang, Z. M.; Zhou, B. L.; Shi, C. X. *J. Mater. Sci. Lett.* **1993,** *12,* 817.
(8) Hippo, E. J.; Murdie, N.; Hyjazie, A. *Carbon* **1989,** *27,* 689.
(9) Hippo, E. J.; Murdie, N.; Kowbel, W.; Wapner, P. G. *Ext. Abstr. Program-Bienn. Conf., Carbon* **1987,** *18,* 466.
(10) Buchanan, F. J.; Little, J. A. *J. Mater. Sci.* **1993,** *28,* 2324.
(11) Crocker, P.; McEnaney, B. *Carbon* **1991,** *29,* 881.
(12) Bowles, K. J. *35th Int. SAMPE Symp.* **1990,** 147.
(13) Bleay, S. M.; Scott, V. D. *Carbon* **1991,** *29,* 871.
(14) Ben-Aim, R. I.; Bonardet, J. L.; Diamy, A. M.; Fraissard, J.; Legrand, J. C. *J. Mater. Sci.* **1990,** *25,* 4113.
(15) Magendie, F. J.; Seferis, J. C.; Aksay, I. A. *35th Int. SAMPE Symp.* **1990,** 2280.

0897-4756/94/2806-0788$04.50/0

oxidation resistance to be monitored. This paper builds upon a series of papers concerned with carbon fiber surface treatment (see refs 16–19 and references therein). The focus is to understand the chemical properties of the fiber–matrix interface, in order that the interface may be optimized to enhance the oxidation resistance of carbon–carbon composites.

Experimental Section

The carbon fiber used in this study was E-120 high strength and high modulus pitch-based fiber provided by DuPont. 337T28, a phenol–formaldehyde resin from Georgia-Pacific Resins, was chosen as the matrix resin, with a number average molecular weight of 129 and a weight average molecular weight of 608.

Electrochemical treatment of the carbon fibers was carried out using the approaches previously developed in this laboratory.[16-19] Nitric acid (1.0 M) and phosphoric acid (1.0 M) were used to anodically oxidize the fiber surface in the galvanostatic mode with a current of 0.5 A and a polarizing time of 30 s. Electrochemically treated fibers were immersed in heated (to about 60 °C) resin solution for 30 min, rinsed in quadruply distilled water for 1 min to remove nonbound resin, dried in an 80 °C oven for 1 h, and then vacuum-dried at 60 °C for 3 days. Samples exposed to a coupling agent were exposed to an aqueous resin solution prepared as described below, to which 16% by volume of the coupling agent was added with stirring. In cases where the solution was acidified a drop of a concentrated sulfuric acid catalyst was added just before (1–2 min) the fibers were immersed into the solution.

Table 1 provides a description of the samples studied and the method used for preparing the samples. Three different types of coupling agents were used in an attempt to produce interfacial chemical bonds, namely, formaldehyde (FAL), propionaldehyde (PAL), and glutaraldehyde (GAL). They were purchased from Aldrich and were of analytical grade purity. To study the interfacial cross-linking, the electrochemically treated fibers were immersed in an aqueous solution of the resin mixed with the coupling agents. The treated fibers were also exposed to aqueous solutions of the coupling agents alone, in order to see if the coupling agents reacted directly with the treated fibers.

The interface study was conducted by coating an extremely thin layer of resin onto the fiber surface. The resin layer was so thin that XPS can not only detect the resin on the surface of the fiber, but also the carbon fiber underneath. In this way any interface chemistry could be studied. The thickness of the coating was adjusted by varying the concentration of the resin solution. A 0.2 wt % resin solution was found to be a suitable concentration to give a thickness that met these criteria. This concentration was prepared by dissolving 0.8 g of resin precursor in 400 mL of quadruply distilled (4-D) water.

A VSW HA100 X-ray photoelectron spectrometer was used to perform XPS measurements under a base pressure of better than 10^{-9} Torr using Mg Kα X-radiation (300 W) with a line width of 0.7 eV. Spectra were recorded in FRR (fixed retardation ratio) mode with a retardation ratio of 50 for core level spectra including the overall scan, and in FAT (fixed analyzer transmission) mode with a pass energy of 25 eV for valence band spectra to achieve good instrumental resolution. The energy scale of the spectrometer was calibrated using an argon-ion-etched copper plate according to the ASTM standard.[20] Fibers were mounted into the spectrometer as a short length (3.8 cm) of a fiber tow (3000 filaments in a tow) with each end of the two wrapped with aluminum foil, one end of which was held to the spectrometer probe. The sample was positioned so that no aluminum metal from the ends of the tow was visible in the spectrometer.

Table 1. Description of Samples Studied and Methods Used for Preparing the Samples

details of electrochemical treatment	sample code	sample preparation
no treatment	0-a	untreated carbon fiber E-120
	0-b	phenolic resin 337T28
	0-c	untreated fiber with resin coating
anodically oxidized in 1.0 M HNO_3 at 0.5 A for 30 s	1-a	treated fiber
	1-b	treated fiber with resin coating
	1-c	treated fiber, rinsing in GAL[a]
	1-d	treated fiber with resin coating (GAL added)[a]
	1-e	treated fiber, rinsing in PAL[a]
	1-f	treated fiber with resin coating (PAL added)[a]
	1-g	treated fiber, rinsing in FAL[a]
	1-h	treated fiber with resin coating (FAL added)[a]
anodically oxidized in 1.0 M H_3PO_4 at 0.5 A for 30 s	2-a	treated fiber
	2-b	treated fiber with resin coating
	2-c	treated fiber, rinsing in GAL
	2-d	treated fiber with resin coating (GAL added)
	2-e	treated fiber, rinsing in GAL[a]
	2-f	treated fiber with resin coating (GAL added)[a]
	2-g	treated fiber, rinsing in PAL
	2-h	treated fiber with resin coating (PAL added)
	2-i	treated fiber, rinsing in PAL[a]
	2-j	treated fiber with resin coating (PAL added)

[a] Fibers were coated in the presence of acidic catalyst.

Curve fitting was performed using a nonlinear least-squares curve-fitting program with a Gaussian–Lorentzian product function.[21] The Gaussian/Lorentzian mix was taken as 0.5 for all peaks except for graphitic peak of untreated carbon fiber, which was taken as 0.8 with an exponential tail to represent conduction band interaction in the untreated carbon fiber. The binding energy of the most intense peak in C1s region was taken as 284.6 eV.

Measurements of oxidation behavior were carried out in a Shimadzu TGA-50 thermogravimetric analyzer in flowing dry air at a flow rate of 40 mL/min. The thermobalance has an accuracy of ±0.1 mg. About 4 mg of resin-coated carbon fiber was mounted in a platinum sample pan and heated at a programmed linear heating rate of 10 °C/min. Weight changes of the specimens were recorded as a function of temperature up to 960 °C. The mass loss of fiber due to burn off in air is characterized by the mass loss versus temperature. Another useful parameter is the temperature at which 50% of the mass of the fiber is lost.

Ab initio Hartree–Fock calculations were performed to calculate the XPS valence band spectra. These calculations used the HONDO program with an STO-3G minimal basis set[22] and were performed on an IBM RISC/6000 computer. The calculated spectra were generated by combining peaks placed at the position of all the calculated energy levels. When there were more than 20 component energy levels, some closely spaced levels are combined in order to give a total of 20 peaks. In the generated spectrum, the position of each component peak corresponds to the calculated energy level and the intensity (area) corresponds to the number of electrons in the energy level multiplied by the net atomic population of the Gelius model[23] adjusted by the

---

(16) Kozlowski, C.; Sherwood, P. M. A. *Carbon* **1987**, *25*, 751.

(17) Xie, Y.; Sherwood, P. M. A. *Chem. Mater.* **1990**, *2*, 293.

(18) Xie, Y.; Sherwood, P. M. A. *Appl. Spectrosc.* **1990**, *44*, 1621.

(19) Xie, Y.; Wang, T.; Franklin, O.; Sherwood, P. M. A. *Appl. Spectrosc.* **1992**, *46*, 645.

(20) *Surf. Interf. Anal.* **1991**, *17*, 889, ASTM E902-88.

(21) Sherwood, P. M. A. *Practical Surface Analysis*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; Wiley: Chichester, 1990, *Vol. 1*: *Auger and X-ray Photoelectron Spectroscopy*, Appendix 3.

(22) Dupuis, M.; Farazdel, A.; Karna, S. P.; Maluends, S. A. *Modern Techniques in Computational Chemistry*: *MOTECC-90*; Clement, E., Ed.; Escom: Leiden, 1990; Chapter 6, pp 277–342.

(23) Gelius, U. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *5*, 985.

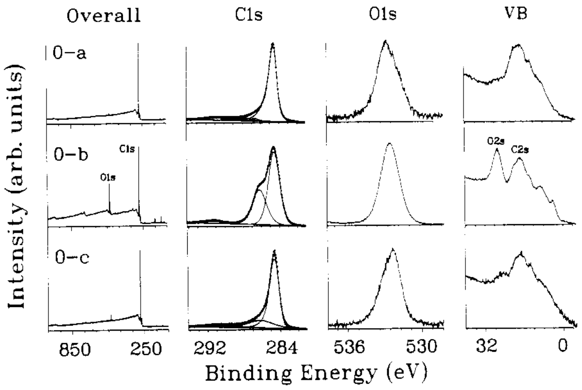


Figure 1. XPS spectra of fiber, resin, and resin-coated fiber. (O-a) untreated E120 carbon fiber, (O-b) phenol–formaldehyde 337T28 resin, (O-c) untreated E120 carbon fiber with resin coating.

Scofield atomic photoelectron cross section.[24] Each component peak in the generated spectrum is represented by a 50% mixed Gaussian/Lorentzian product function[21] with each peak having the same full width at half-maximum (fwhm) of 1.08 eV. Besides the atomic contributions to the molecular orbitals as described above, X-ray satellite features from the Mg Kα radiation were included in the calculated spectra. The resulting valence band spectrum was linearly contracted by a factor of 1.3 on the energy scale because the *ab initio* calculations typically exaggerate the spread of valence band energy levels by such an amount. This apporach has been successfully used in other polymer systems.[25]

Results and Discussion

Coating the Untreated Fiber with Phenolic Resin. Figure 1 shows XPS spectra for untreated fiber, the pure resin, and the untreated fiber coated with a thin layer of resin. The overall scan, C1s region (the curve fitting results are shown in Table 2), O1s region, and valence band regions are shown. The untreated fiber (sample O-a) gives the expected spectrum for this material,[26] showing a very weak oxygen signal which is hardly visible in the overall spectrum. The phenolic resin has a very intense oxygen signal, which can clearly be seen in the overall, O1s, and O2s regions of the valence band. There is also a weak silicon signal at binding energies of 152 and 101 eV for Si2s and Si2p, respectively, which can be identified by a weak feature in the overall spectrum. The silicon arises because of silicon-containing additives in the resin. Since the resin is the only source of silicon, the intensity of the silicon signal acts as an indicator that the sample has been exposed to resin. However, since the silicon comes from a resin additive it is possible that the additive has attached itself to the surface even if the resin has not. When the untreated fiber was coated with the resin in the manner described above the resulting spectrum (Figure 1 O-c) shows that resin is attached to the fiber surface, as indicated by the O1s and Si2p features in the overall spectrum, and the changes in the C1s and valence band regions. It is clear that the spectrum (Figure 1 O-c) results from the addition of features in Figure 1 O-a and O-b. The resin coated fiber thus has a spectrum that is the addition of the pure fiber and resin spectra, indicating that there was no chemical interaction between the fiber and the resin. The amount of resin uptaken onto the untreated fiber surface indicates that the untreated fiber had poor wettability for the resin.

Coating the Nitric Acid Oxidized Fiber with Phenolic Resin. Table 2 shows the spectral features of the oxidized fiber (discussed previously[17,27]) and the fiber coated with resin. When the surface-treated fiber was coated with the resin, the C1s oxide peak 1 shifted from a chemical shift of 2.0–1.7 eV, which is close to that of the resin, as shown in Table 2. The valence band region, which probes more deeply into the fiber surface than the core region, appeas similar to the oxidized fiber, lacking the lowest binding energy shoulder of the resin (at about 4 eV; Figure 1 O-b). The overall scan showed Si2s and Si2p signals after coating with resin, suggesting the presence of resin on the fiber. As in the case of the untreated fiber the spectrum of the coated fiber corresponded to the addition of the spectrum of the oxidized fiber and the resin, indicating no chemical interaction at the interface.

Coating the Nitric Acid Oxidized Fiber with Phenolic Resin and Coupling Agent. Table 2 (1-d, 1-f, and 1-h) shows what happens when the nitric acid oxidized fiber is coated with resin solution to which a coupling agent is added in acidified solution. All the spectra appear very similar for all regions. A parallel experiment was done in which fibers were subjected to the same treatment procedures except that no resin was added in the solution (1-c, 1-e, and 1-g). The spectra for all regions in these cases resemble those of fibers subjected to the treatment with the resin present (1-d, 1-f, and 1-h). The curve-fitting results in Table 2 show that for 1-c to 1-h peak 1 lies at almost the same chemical shift (1.9–2.0 eV), which is identical to that of the electrochemically oxidized fiber (1-a). This implies that carbon fibers electrochemically oxidized in nitric acid solution have no chemical interaction with phenolic resin in the presence of the coupling agents under the conditions used in this work. There also appears to be no resin adsorbed onto the fiber surface. It will be seen below that this result is consistent with the mechanism we propose for the action of the coupling agent in the case where interfacial chemical reaction does occur. The overall spectra in all cases show the presence of silicon, but we believe that this occurs because the silicon additive of the resin attaches itself to the surface rather than the resin.

Previous work in this laboratory has shown that the C1s oxide peak 1 with a chemical shift of around 2 eV seen here for the nitric acid treated fibers arises from a keto–enol structure.[16–18] The keto–enol group may not be as reactive as hydroxyl group because of resonance. This would explain the inertness of the nitric acid-treated carbon fiber toward reaction with the phenolic resin, with or without the presence of coupling agents.

Coating the Phosphoric Acid-Treated Fiber with Phenolic Resin. Table 2 shows the spectral features of the oxidized fiber (discussed previously[16]) and the fiber coated with resin. A small amount of phosphate is seen on the fiber surface in contrast to the nitric acid oxidation when no nitrate was seen on the surface. The changes in the C1s and valence band region are similar to the nitric acid case, except that the amount of resin on the surface seems to be less, and the same conclusions can be drawn. Thus again one concludes that no chemical reaction occurs at the interface. The smaller amount of surface resin is

---

(24) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

(25) Hamilton, L.; Sherwood, P. M. A.; Reagan, B. M. *Appl. Spectrosc.* **1993**, *47*, 139.

(26) Xie, Y.; Sherwood, P. M. A. *Surf. Sci. Spectra* **1992**, *1*, 210.

(27) Xie, Y.; Sherwood, P. M. A. *Surf. Sci. Spectra* **1992**, *1*, 265.

(28) Xie, Y.; Sherwood, P. M. A. *Chem. Mater.* **1991**, *3*, 164.

Table 2. Chemical Shift (CS), Relative Peak Area, and Peak Width in the C1s Region

	main peak			peak 1			peak 2			peak 3			peak 4		
sample	BE[a] (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)
0-a	284.6	84.8	0.8	2.0	2.6	1.3	3.0	3.1	1.3	4.4	2.4	1.3	6.4	7.1	2.8
0-b	284.6	60.0	1.4	1.6	35.9	1.8	6.6	4.1	2.8						
0-c	284.6	67.2	1.1	1.7	24.5	2.0	4.1	2.9	2.0	6.6	5.4	2.8			
1-a	284.6	48.8	1.6	2.0	39.5	1.7	3.2	4.0	1.7	4.3	4.7	1.8	6.2	2.9	3.4
1-b	284.6	60.9	1.6	1.7	28.3	1.7	3.0	6.0	2.2	4.4	3.5	2.2	6.5	1.3	2.2
1-c	284.6	53.2	1.5	2.0	38.8	2.0	3.0	2.6	1.7	4.2	4.2	1.7	6.2	1.2	2.0
1-d	284.6	55.3	1.6	1.9	34.0	1.8	3.0	5.2	1.8	4.3	4.5	1.8	6.4	1.0	1.9
1-e	284.6	54.9	1.6	2.0	35.5	1.8	2.9	4.0	1.8	4.2	4.3	1.6	6.2	1.3	2.1
1-f	284.6	54.9	1.6	2.0	34.5	1.8	3.0	4.8	2.0	4.3	4.5	2.0	6.5	1.3	2.2
1-g	284.6	54.6	1.7	2.0	30.9	1.6	2.9	6.5	1.6	4.2	5.4	1.7	6.2	2.6	3.3
1-h	284.6	55.2	1.6	2.0	34.3	1.9	3.0	1.5	2.1	4.2	6.8	2.1	6.4	2.1	2.3
2-a	284.6	48.3	1.5	2.1	41.9	2.3	4.3	7.9	2.3	6.7	1.9	2.4			
2-b	284.6	54.0	1.4	1.6	7.5	1.8	2.1	31.6	2.5	4.4	3.7	1.8	6.3	3.2	2.5
2-c	284.6	59.1	1.4	2.0	33.3	2.3	4.0	6.3	2.3	6.2	1.3	2.0			
2-d	284.6	56.1	1.4	2.0	34.1	2.3	3.9	7.0	2.3	6.2	2.7	2.9			
2-e	284.6	56.2	1.4	1.9	35.4	2.7	4.0	6.8	2.7	6.2	1.5	2.5			
2-f	284.6	57.8	1.3	1.5	27.3	1.9	3.2	8.3	1.5	4.5	3.4	1.5	6.4	3.2	2.3
2-g	284.6	59.1	1.5	2.1	33.5	2.2	4.2	6.3	2.2	6.8	1.1	1.8			
2-h	284.6	52.9	1.4	1.9	39.9	2.6	4.2	4.8	2.6	6.3	2.4	3.1			
2-i	284.6	50.5	1.4	1.9	42.7	2.8	4.2	5.4	2.8	6.3	1.4	2.6			
2-j	284.6	62.4	1.5	1.5	20.5	1.5	2.9	11.8	1.8	3.8	1.7	1.8	6.4	3.6	2.6

[a] Binding energy.

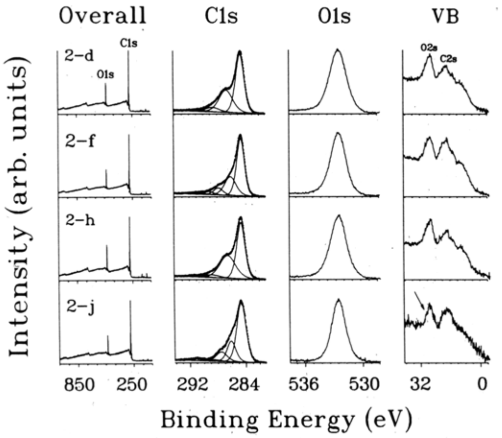


Figure 2. XPS spectra of carbon fiber electrochemically oxidized in ortho-phosphoric acid coated with resin and coupling agents. (2-d) GAL used as the coupling agent, (2-f) acidified GAL used as the coupling agent, (2-h) PAL used as the coupling agent, (2-j) acidified PAL used as the coupling agent.

suggested by the lower intensity (7.5 vs 28.3%) of the characteristic resin peak 1 features in the fitted data than in the nitric acid case (Table 2). We believe that the oxidized surface contains a phosphate group in addition to a keto–enol grouping. If we make the gross assumption that the surface composition is homogeneous, then the oxygen/phosphorus atomic ratio is 10, consistent with approximately one phosphate group per keto–enol group.

Coating the Phosphoric Acid-Treated Fiber with Phenolic Resin and Coupling Agent. Figure 2 shows what happens when the phosphoric acid oxidized fiber is coated with resin to which a coupling agent is added in both neutral and acidified solutions. The coupling agents glutaraldehyde (GAL) and propionaldehyde (PAL) were used. Figure 2 shows the XPS spectra (with the fitting results for the C1s region shown in Table 2) of the oxidized fibers with the resin coating in the presence of the coupling agents, with or without the presence of the acidic catalyst. Figure 2 and Table 2 show that the consumption of the C1s region for samples treated in the presence of acidic catalyst (2-f and 2-j) is significantly different from that of samples treated in the absence of acidic catalyst (2-d and 2-h). The samples 2-f and 2-j treated in acidic solution have a peak 1 feature with a chemical shift of 1.48 and 1.47 eV, respectively, while the samples treated in neutral solution (2-d and 2-h) have a peak 1 feature with a chemical shift between 1.9 and 2.0 eV. The results in the absence of an acidic catalyst are similar to those of the nitric acid case, indicating that the coupling agents again may inhibit or eliminate interaction with the fiber surface (because of the similarity between the spectra in 2-b, 2-d and 2-h). As in the nitric acid case, exposure of the oxidized fiber to the coupling agent alone gives very similar spectra to that of the oxidized fiber (Table 2).

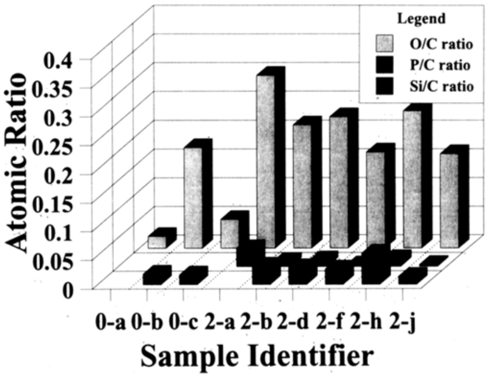


Figure 3. Atomic ratios obtained from core XPS data for fiber, resin, and fibers electrochemically oxidized in phosphoric acid with and without coupling agents.

Examination of the atomic ratios of the various elements present on the fiber surface provides some useful information, even though these ratios represent an average over a surface region of changing chemical composition with depth into the surface. Figure 3 shows the atomic ratios for the phosphoric acid-treated fibers. It can be seen that a small amount of phosphorous is detected for the resin-coated fiber by XPS, as evidenced by a low P/C ratios. The detection of phosphorous underneath the resin coating justifies the thin-film technique that we are adopting to study the composite interface, showing that XPS is probing the carbon fiber/resin interface in this study. The presence of silicon has already been discussed. One also notes that the acid-catalyzed experiments (2-f and 2-j) have a lower

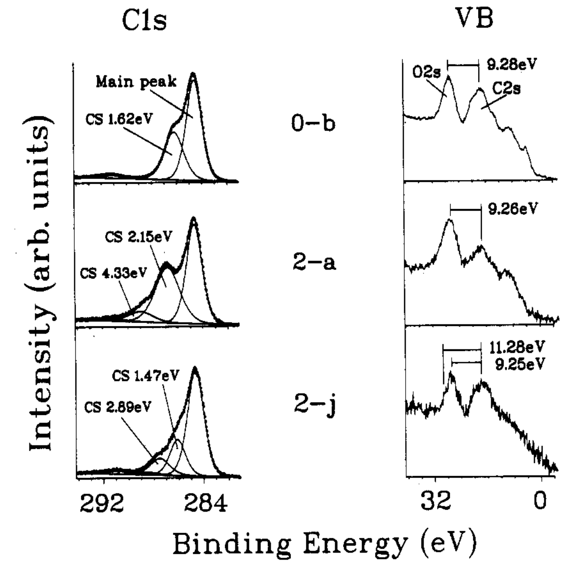


Figure 4. XPS spectra of C1s and valence band regions for 337T28 resin, carbon fiber electrochemically oxidized in phosphoric acid, and the oxidized fiber treated with acidified PAL and resin.

O/C and P/C ratio than the experiments involving coupling agents without acid being present (2-d and 2-h). This not only supports the other data indicating interfacial chemical reaction, but also is consistent with loss of phosphate in the acid-catalyzed case. In fact the O/P ratio falls from 10 in the phosphoric acid treated fiber, to more than 63 in the acid catalyzed coupling agent experiment (2-f and 2-j).

Interface Chemical Reaction in the Phosphoric Acid-Treated Fiber. Figure 4 shows a comparison between the spectra of a case where interfacial chemical interaction is suggested with the spectra of the phosphoric acid oxidized fiber and the phenolic resin. It is clear that there is no way in which the spectra in 2-j can be obtained by adding the spectra of the resin (O-b) and fiber (2-a) together. It is obvious that the chemical shifts of the component peaks in the C1s region have different binding energies. Similar conclusions can be obtained for 2-f, where chemical interaction at the interface is also suggested. The valence band region also provides support for chemical interaction in 2-j since the O2s region suggests the presence of two features, which are separated from the C2s region by 11.28 and 9.25 eV. The higher binding energy feature appears as a shoulder indicated by an arrow in Figure 2. We did try to obtain better statistics in the valence band region by recording the region for extended time periods, but there was some loss of resolution which we believe arose from surface decomposition—a problem that we have noted previously in carbon fiber systems.[29] Spectral subtraction of the intense O2s and C2s features from the spectrum showed the shoulder as a distinct feature for 2-j but not in other cases. There was no evidence for a shoulder in 2-f which may be explained by greater linewidths in this case. We discuss the origin of this shoulder below and show that its presence is consistent with the chemical interaction mechanism.

We now discuss the justification for suggesting that the phosphoric acid-treated fiber chemically interacts with GAL and PAL. We believe that this interaction goes via a reaction between the aldehyde coupling agents and –OH functionality on both the fiber and the resin to give an acetal linkage. Reactions of this sort between aldehydes and alcohols are well-known in organic chemistry.

The first step in the process is the formation of a hemiacetal. We would expect this to occur by reaction between the aldehyde coupling agent and the phenolic resin. Further reaction to form an acetal would seem less likely due to steric considerations. If this were indeed the first step then one would expect it to occur for both nitric and phosphoric acid-treated fibers. It would mean that at the time of immersion of the fiber, the fiber would be exposed to a hemiacetal functionalized phenolic resin. It is attractive to suggest that such a resin might be less easily adsorbed onto the fiber surface, and this would explain why the C1s spectrum of nitric acid or phosphoric acid-treated fibers exposed to coupling agents always resembles the oxidized fiber surface rather than the phenolic resin. This is indicated in Table 2 which shows the chemical shift of peak 1 to be around 2.0 eV in such cases in contrast to the cases where no coupling agents were used (1-b and 2-b) where the shift is around 1.6 eV. These values correspond to the oxidized fiber surface (2.0 eV/2.1 eV, 1-a and 2-a) and the phenolic resin (1.6 eV, O-b), respectively.

In the case of fiber exposed to phosphoric acid and acidified coupling agents we see a C1s region that is different from that of either the oxidized fiber, or the resin. In this situation we believe that the hemiacetal formed between the phenolic resin and the aldehyde reacts with the oxidized fiber surface. This reaction occurs because the presence of the phosphate groups on the fiber surface assists the formation of an acetal bridge between the oxidized fiber surface and the phenolic resin. The first step in the process may involve acid catalyzed loss of phosphate ions to give surface –OH functionality. This surface–OH functionality then reacts with the hemiacetal formed between the phenolic resin and the aldehyde to form an acetal bridge following the reaction scheme shown in Chart 1. The loss of phosphate ions would explain the fall in the O/P ratio from 10 in the phosphoric acid-treated fiber, to more than 63 in the acid-catalyzed coupling agent experiment (2-f and 2-j). This low O/P ratio makes it certain that the high binding energy shoulder in the valence band region of 2-j cannot be due to phosphate, since the phosphate ion, where the O/P ratio is 4, has a comparable intensity shoulder in this region. Also in the case of 2-a, the phosphoric acid-treated fiber, where the O/P ratio is 10, no shoulder is evident. The valence band region of the phosphate ion (shown for lithium phosphate, which has only phosphate contributions to the valence band) is indicated in Figure 5, which compares the experimental data (after removal of a Tougaard background[30]) with a spectrum calculated from a multiple scattered wave Xα calculation (calculation details have been previously reported[31]). The calculations indicate that the region of the spectrum around 25 eV corresponds to a mixed O2s/P3s region with the higher binding energy peak corresponding to 21.8% P3s and 73.7% O2s character, and the lower binding energy peak corresponding to 9.4% P3s character and 86.6% O2s character.

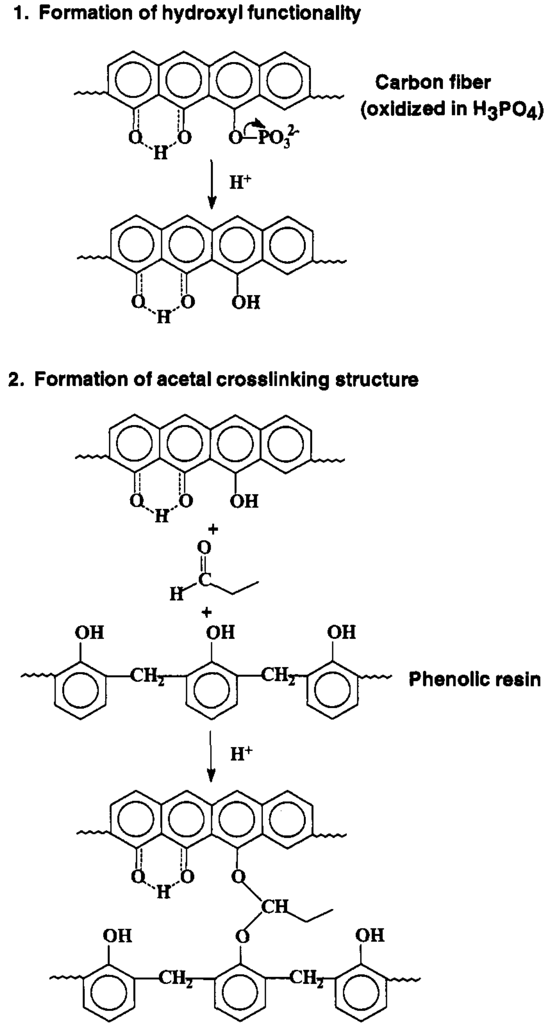
---

[29] Kozlowski, C.; Sherwood, P. M. A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2099.

[30] Tougaard, S.; Sigmund, P. *Phys. Rev. B* **1982**, *25*, 4452.

[31] Welsh, I. D.; Sherwood, P. M. A. *Chem. Mater.* **1992**, *4*, 133.

Chart 1. Scheme for the Interfacial Reaction between a Carbon Fiber Electrochemically Oxidized in Phosphoric Acid Solution and Phenolic Resin in the Presence of Acidied PAL



This type of acetal linkage has been suggested previously,[32] but not confirmed experimentally, to explain the significant improvement in mechanical properties of dental polymeric composites after using propionaldehyde as a binding agent. In the model in Chart 1, the carbon from PAL is attached to two oxygen atoms, one from oxidized carbon fiber and one from the resin. The electronic environment is equivalent to a carbonyl, which, according to Briggs and Beamson's OVP concept,[33] has a O(1s–2s) separation of about 505 eV. In our experiment, the O(1s–2s) separation for the O2s shoulder on the high-bonding-energy side is 505.2 eV, which is in good agreement with Briggs and Beamson's value.

The core and valence band XPS spectra were calculated using *ab initio* Hartree–Fock calculations for a model based upon the acetal linkage. The approach allowed us to see whether the observed spectra were consistent with an interface reaction that proceeded by the acetal linkage suggested above. We also calculated the expected spectrum for the valence band region of the phenolic resin based upon a hydrogen-terminated repeat unit for the phenolic resin shown in Chart 2. We have found that polymer systems effectively represented by a polymer repeat unit.[34,35] The model for the interfacial interaction between the resin and the oxidized fiber is based upon the acetal-bridged model shown in Chart 3. The oxidized fiber is based upon a two naphthalene unit with the propionaldehyde in the acetal bridge. Table 3 shows the parameters used in both calculations. The calculated spectra are compared with the experimental spectra, after the removal of a nonlinear background, in Figures 6 and 7. The main features of the experimental spectra are predicted in the calculated spectra.

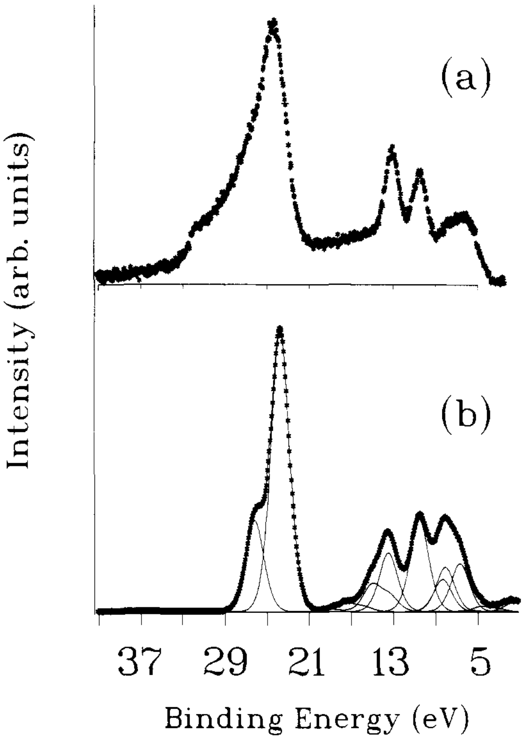
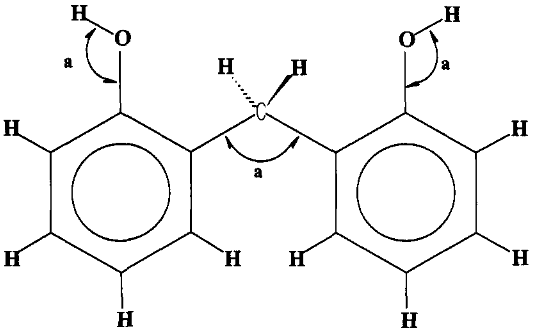


Figure 5. XPS valence band spectra of lithium phosphate (a) compared with a spectrum (b) calculated from a transition state Xα calculation. Experimental and calculation details have been previously reported.[31] A Tougaard background was subtracted from the experimental data.

Chart 2. Model of the Phenolic Resin Repeat Unit Used for the *ab Initio Calculation*



The valence band spectra show an O2s region around 25 eV with a single peak in Figure 6 and two peaks in Figure 7 (explaining the shoulder in the calculated spectrum). A triplet pattern is found between 18 and 11 eV, which is characteristic of the graphitic structure in the carbon fiber and the aromatic structure of the resin, and has been predicted by our previous Xα calculations.[34,35]

---

(32) Peutzfeldt, A.; Asmussen, E. *J. Dent. Res.* **1992**, *7*, 1522.

(33) Briggs, D.; Beamson, G. *Anal. Chem.* **1993**, *65*, 1517.

(34) Sherwood, P. M. A. *J. Vac. Sci. Technol. A* **1992**, *10*, 2783.

(35) Wang, T.; Xie, Y.; Sherwood, P. M. A. *Chem. Mater.* **1993**, *5*, 1007.

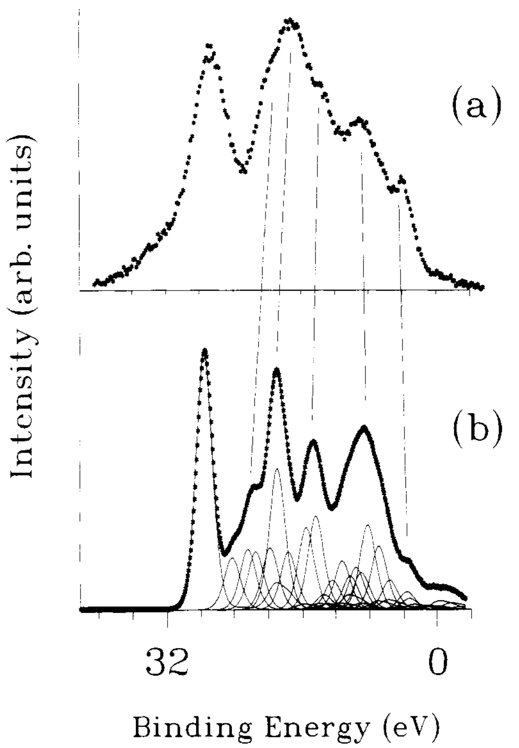
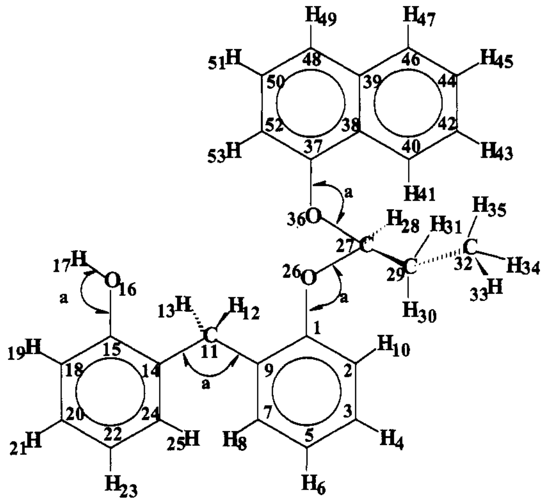


Figure 6. Comparison between experimental (a) and calculated (b) XPS valence band spectra for phenolic resin 337T28.

Chart 3. Model of the Acetal–Cross-Linking Structure between a Carbon Fiber Electrochemically Oxidized in Phosphoric Acid Solution and Phenolic Resin in the Presence of Acidified PAL Used for the *ab Initio* Calculation



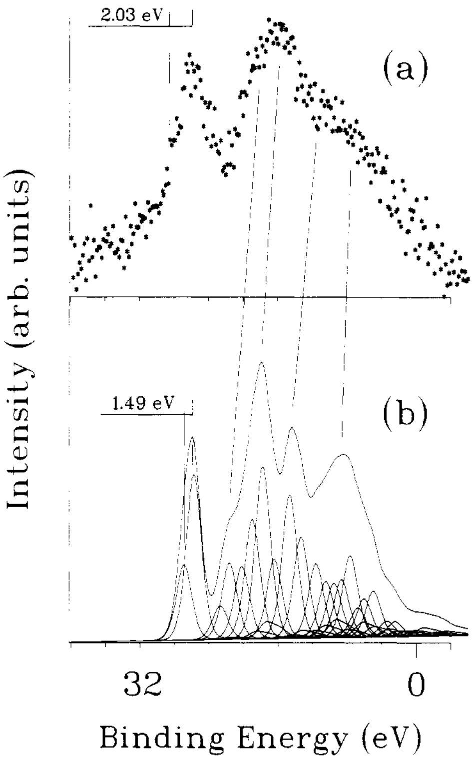


Figure 7. Comparison between experimental (a) and calculated (b) XPS valence band spectra for a carbon fiber electrochemically oxidized in phosphoric acid and exposed to acidified PAL. The calculated spectrum is based upon the acetal–cross-linking structure in Chart 3.

The low-binding-energy region is the result of overlap between mixed principally C2p and O2p atomic orbitals. In generating the calculated spectrum of the resin, the photoelectron cross sections for O2s and O2p were reduced to 50% (Figure 6) and 25% (Figure 7) of the normal Scofield values to account for the cross-linking not accounted for in the models of Charts 2 and 3. The resin has more $-CH_2-$ linkages than in the model in Chart 2, and it is likely that Chart 3 overestimates the number of acetal bridges.

The *ab initio* Hartree–Fock results for the interfacial linkage suggested by the model in Chart 3 were used to calculate the chemical shifts that would be expected in the C1s region. The results, summarized in Figure 8, show that the carbon atoms numbered 15, 1, and 37 (Chart 3) have very close binding energies with a C_{15}–C_1 separation of 0.0182 eV and a C_1–C_{37} separation of 0.161 eV. These three carbon atoms all have one singly bonded oxygen atom attached and can be assigned to oxide peak 1 with a chemical shift of 1.47 eV for sample 2-j. C_{27} is attached to two oxygen atoms and would correspond to oxide peak 2 with a chemical shift of 2.89 eV. The calculated C_{27}–C_{15} separation is 1.62 eV, while experimental separation between oxide peaks 1 and 2 is 1.42 eV. The C1s core region is thus consistent with the acetal linkage model.

Overall the calculations show that the suggested acetal linkage is compatible with the observed XPS core and valence band spectra.

Oxidation Behavior of the Resin-Coated Fibers. Figure 9 shows the percentage of the mass of resin-coated

Table 3. Structural Parameters Used in Constructing the Models for the *ab Initio* Calculations[a]

bond type	bond length (Å)	bond type	bond length (Å)
C–C (aromatic rings)	1.37	C–C (aliphatic)	1.54
C–C (aromatic–aliphatic)	1.54	(aromatic) C–O (H)	1.34
(aromatic) C–O–C (aliphatic)	1.34, 1.426	C–H	1.089
O–H	0.970		

[a] Standard bond angles are taken. Angle "a" is 109.5°. The angle between the two benzene rings in the model of the phenolic resin is 30.5°. The angle between the graphitic plane (represented by naptalene) and the resin plane in the model of the interface between fiber and resin is 109.5°.

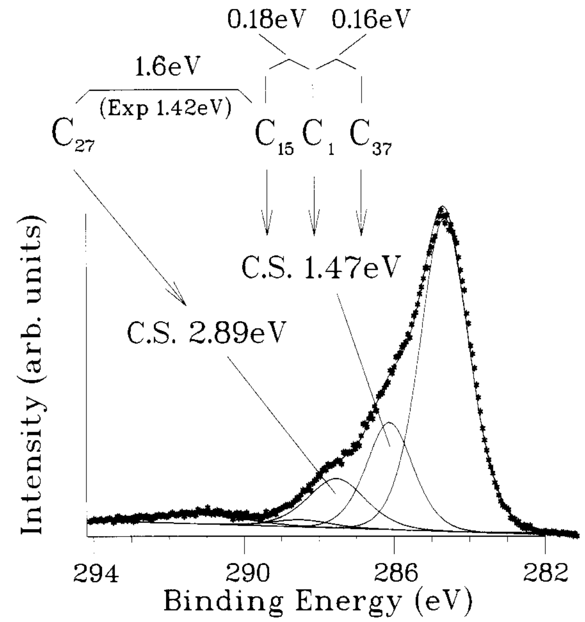


Figure 8. XPS spectra of C1s region of carbon fiber electrochemically oxidized in phosphoric acid, and the oxidized fiber treated with acidified PAL. The separations between the curve fitted component peaks are compared with the separations calculated from an *ab initio* calculation.

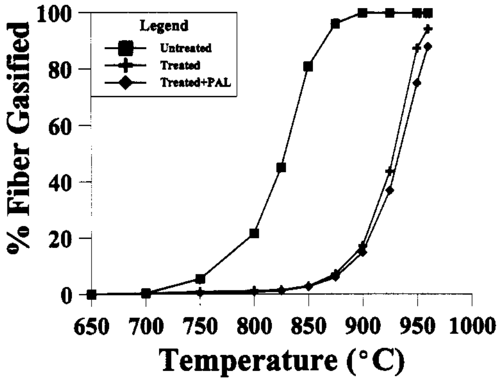


Figure 9. Thermal gravimetric analysis results indicating the oxidation behavior of carbon fibers with resin coating. The percentage burnoff indicates the percentage of mass loss of gasification.

carbon fiber that is lost to gasification for coated fibers heated in air in a thermal gravimetric analysis experiment. Three types of sample were studied, namely, an untreated carbon fiber with resin coating, a fiber oxidized in phosphoric acid with resin coating, and a phosphoric acid oxidized fiber with resin coating and acid catalyzed treatment with PAL. In these measurements, the mass change was recorded continuously as the temperature of the thermobalance was increased at a constant rate of 10 °C/min. The untreated fiber with resin coating began to lose weight at about 700 °C with a burnoff rate that became significant at higher temperatures. For the fiber electrochemically oxidized in phosphoric acid and then coated with the resin, the mass loss started at a temperature of about 820 °C and was gradually speeded up until complete gasification at about 950 °C. The electrochemically oxidized fiber with the resin coating together with acidified PAL—the situation that we have suggested gives interfacial chemical reaction—showed the lowest burnoff rate on heating in air, and did not show any significant mass loss until about 840 °C. This was the best performance of any of the fibers studied.

These studies suggest that electrochemical treatment of the carbon fiber surface improves the oxidation stability. Use of a coupling agent while coating the resin on the electrochemically oxidized fibers results in further improvement in the oxidation resistance of the carbon fiber composites. The 50% burn off temperatures $T_{50\%}$ are 833.5, 928.5, and 934.9 °C for untreated fiber with resin coating, oxidized fiber with resin coating, and oxidized fiber with resin coating and acidified PAL added, respectively. The improvement of oxidation stability with the use of a coupling agent that gives interfacial chemical interaction between the fiber surface and the phenolic resin appears to have potential as a component in the strategy for maximizing the oxidation protection of carbon-carbon composites. The surface of the fiber appears to be very important in effecting oxidation resistance at the fiber–matrix interface, since without any surface treatment much poorer oxidation behavior is found. The surface treatment may cause both physical and chemical changes on the fiber surface,[36] will improve the surface of the fiber towards wetting by the phenolic resin, and provides a surface with interfacial chemical reaction possibilities. Establishing interfacial chemical bonds between the fiber and matrix resin would be expected to be effective in reducing oxygen diffusion through the interface.

Conclusions

This work establishes the importance of carbon fiber surface treatment and interface chemical modification in the improvement in oxidation protection of carbon–carbon composites and carbon fiber reinforced polymeric composites. The carbon fiber–matrix interface must be considered when oxidation protection is developed. An approach that attempts to modify and enhance the oxidation stability of this interface is important. This may follow the methods that we have used here, as well as approaches that seek to protect the fiber itself from oxidation. We are also currently investigating the use of various protective coatings on fibers.[37,38] The carbon fiber–matrix interface thus needs to be included into an oxidation protection strategy that currently includes oxidation protection of the matrix (e.g., borate glasses) and the outer composite structure.

In this study we show that XPS can be used to reveal interfacial chemistry in the carbon fiber–matrix system. The use of propionaldehyde under acidic conditions as a coupling agent is seen to yield an interfacial chemical reaction that can be interpreted as corresponding to acetal cross-linking. The core and valence band XPS data can be interpreted by *ab initio* Hartree–Fock calculations. Air oxidation monitored by thermogravimetric analysis shows that the cross-linked samples have an enhanced oxidation resistance.

Acknowledgment. This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. F496620-92-J-0144. We are grateful to Georgia-Pacific Resins, Inc. for kindly supplying phenolic resin samples. We thank Professor K. J. Klabunde for use of his thermal gravimetric analysis facility.

---

(36) Sherwood, P. M. A. *Mat. Res. Soc. Proc.* **1992**, *270* (*Novel Forms of Carbon*), 79.

(37) Xie, Y.; Sherwood, P. M. A. *Chem. Mater.*, in press.

(38) Rooke, M. A.; Sherwood, P. M. A., submitted for publication.