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X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 20. Interfacial Interactions between Phenolic Resin and Electrochemically Oxidized Carbon Fibers Using Titanium Alkoxide Coupling Agents and Their Effect on Oxidation Behavior

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The interfacial interactions between a carbon fiber electrochemically oxidized in phosphoric acid, nitric acid, and ammonium carbonate solution and a phenolic resin were investigated by core and valence-band X-ray photoelectron spectroscopic studies (XPS) of a very thin resin layer on the surface of the fiber. The work continues a study related to the need to improve the oxidation stability of carbon–carbon composites by an investigation of this first step in their formation, and the possibility of preferential oxidation at the fiber–matrix interface. The interaction between the surface treated fiber and the resin was investigated in the presence of titanium alkoxide coupling agents. The effect of air oxidation on the resin coated fibers (with or without coupling agents and fiber surface treatment) was examined by thermogravimetric analysis. The results show that improved oxidation behavior can be achieved for titanate coupling agents, and that tetrakis(2-ethylhexyl)titanate (TOT) is the most effective coupling agent in providing oxidation resistance. Valence band photoelectron spectroscopic data interpreted by multiple scattered wave Xα calculations are consistent with a $-OTi(OR)_2-O-$ chemically bonded bridge between the oxidized fiber surface and the phenolic resin.

Introduction

Carbon–carbon composites are of significant interest to the aerospace industry for use in high-temperature environments for certain critical applications where no other material can serve. In the development of oxidation resistant carbon–carbon composites, it is important to design a carbon fiber/resin interface that also has oxidation resistance in addition to using the normal outer protective layers or matrix oxidation inhibitors.[1–6] However, there have been few reports of the investigation of chemical modifications of the fiber–matrix interface, few studies that reveal how the interface chemistry influences the oxidation behavior, and few reports of how to achieve inherent oxidation stability by enhancement of the oxidation resistance of this interface.

Oxidation resistance at the fiber–matrix interface can be enhanced by chemical interaction between the fiber and the matrix. We have previously studied the chemical modification of this interface either by using direct chemical reaction between a surface treated fiber and a resin or by inducing reaction between treated fiber and resin with the use of coupling agents.[7,8] We find that for a variety of coupling agents and surface treated fibers *chemical* interaction between fiber and matrix (either directly or via coupling agents) leads to a significant improvement in the oxidation resistance.

In this paper, titanium alkoxide coupling agents were used in an attempt to enhance carbon fiber/resin chemical interactions. The interface between a phenolic resin and carbon fibers electrochemically oxidized in phosphoric acid, nitric acid, and ammonium carbonate solution was investigated by X-ray photoelectron spectroscopic (XPS) studies of a thin layer of resin coating on the fiber surface. Thermogravimetric analysis was performed on the resin coated carbon fibers to examine the effect of titanium alkoxide coupling agents on the oxidation stability.

Experimental Section

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

Electrochemical treatment for the carbon fiber was carried out using the approach previously developed in this laboratory.[7,9–13] Nitric acid (1.0 M), 1.0 M orthophosphoric acid (1.0 M), and ammonium carbonate (0.5 M) solutions were used

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to anodically oxidize the fiber surface in the galvanostatic mode with a current of 0.5 A and a polarizing time of 30 s in the acidic electrolytes and 5 min in the ammonium carbonate electrolyte. In fiber–resin interaction experiments electrochemically treated fibers were treated in one of two ways:

Method 1: Simultaneous Reaction. Electrochemically oxidized fibers were immersed in about 28 mL of resin solution to which one drop (1/40 mL) of coupling agent was added just before the fibers were dipped into the resin.

Method 2: Sequential Reaction. Electrochemically oxidized fibers were first exposed to about 28 mL of acetone containing one drop (1/40 mL) of coupling agent at 50–60 °C for 30 min, rinsed in acetone for 30 s and then immersed in resin solution without coupling agent.

In both cases, the fibers were exposed to resin solution at 50–60 °C for 30 min and then rinsed in acetone (spectroscopic grade) for 1 min to remove nonbound resin, dried in an 80 °C oven for 1 h, and finally vacuum-dried at 60 °C for 3 days.

Table 1 gives a description of the samples studied and the method used for preparing the samples. In an attempt to produce interfacial chemical reactions, three titanium alkoxides were used. The coupling agents were used in their pure liquid form (Tyzor brand) and were obtained from DuPont Chemicals, Wilmington, DE. They were tetraisopropyl titanate (TPT, 99–100% purity), tetra-*n*-butyl titanate (TBT, 95–99% purity), tetrakis(2-ethylhexyl)titanate (TOT, 95–99% purity). Impurities in the coupling agents consisted of a small amount of the corresponding alcohols, presumably resulting from hydrolysis, and small amounts of other titanium alkoxides.

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 detects not only the resin on the fiber surface, but also the carbon fiber underneath. In this way the interface chemistry could be studied. The thickness of the coating was adjusted by varying the concentration of the resin solution. A 0.5 wt % resin solution was found to be a suitable concentration to give a thickness that met these criteria. This concentration was prepared by dissolving 2.0 g of resin precursor in 400 mL of acetone (spectroscopic grade).

A VSW HA100 X-ray photoelectron spectrometer was used to perform XPS measurements under a base pressure of 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-etched copper plate according to the ASTM standard.[14] Fibers were mounted into the spectrometer as a short length (3.8 cm) of a fiber tow (3000 fibers in a tow) with each end of the tow wrapped with aluminum foil, one end of which was fixed onto the spectrometer probe. The sample was positioned so that no aluminum metal from ends of the tow could be detected.

Curve fitting was performed using a nonlinear least-squares curve-fitting program with a Gaussian/Lorentzian product function.[15] The Gaussian/Lorentzian mix was taken as 0.5 for all fitted peaks except for the graphitic C1s peak of untreated carbon fibers, 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 set as 284.6 eV, and the Ti3p peak at 39 eV for calibration purposes.

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.

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

electrochemical treatment system	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 H_3PO_4 at 0.5 A for 30 s	1-a	electrochemically treated carbon fiber
	1-b	treated fiber with resin coating
	1-c	treated fiber with resin coating with TPT
	1-d	treated fiber with resin coating with TBT
	1-e	treated fiber with resin coating with TOT
	1-f	treated fiber exposed to TPT
	1-g	treated fiber exposed to TBT
	1-h	treated fiber exposed to TOT
	1-i	treated fiber exposed to TPT and coated with resin
	1-j	treated fiber exposed to TBT and coated with resin
	1-k	treated fiber exposed to TOT and coated with resin
anodically oxidized in 1.0 M HNO_3 at 0.5 A for 30 s	2-a	electrochemically treated carbon fiber
	2-b	treated fiber with resin coating
	2-c	treated fiber with resin coating with TPT
	2-d	treated fiber with resin coating with TBT
	2-e	treated fiber with resin coating with TOT
	2-f	treated fiber exposed to TPT
	2-g	treated fiber exposed to TBT
	2-h	treated fiber exposed to TOT
	2-i	treated fiber exposed to TPT and coated with resin
	2-j	treated fiber exposed to TBT and coated with resin
	2-k	treated fiber exposed to TOT and coated with resin
anodically oxidized in 0.5 M $(NH_4)_2CO_3$ at 0.5 A for 5 min	3-a	electrochemically treated carbon fiber
	3-b	treated fiber with resin coating
	3-c	treated fiber with resin coating with TPT
	3-d	treated fiber with resin coating with TBT
	3-e	treated fiber with resin coating with TOT
	3-f	treated fiber exposed to TPT
	3-g	treated fiber exposed to TBT
	3-h	treated fiber exposed to TOT
	3-i	treated fiber exposed to TPT and coated with resin
	3-j	treated fiber exposed to TBT and coated with resin
	3-k	treated fiber exposed to TOT and coated with resin

Multiple scattered wave Xα calculations[16] used to model the valence band spectra were performed on an IBM RISC/6000 computer.

Results

Coating of the Untreated Fiber with Phenolic Resin. Our previous work[7,8] showed that there was no chemical interaction between the untreated fiber and resin.

Coating of Electrochemically Oxidized Fibers with Phenolic Resin. Our previous studies[11,13] have

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

	main peak			peak 1			peak 2			peak 3			peak 4		
sample	B.E. (eV)	area (%)	fwhm (eV)	C.S. (eV)	area (%)	fwhm (eV)	C.S. (eV)	area (%)	fwhm (eV)	C.S. (eV)	area (%)	fwhm (eV)	C.S. (eV)	area (%)	fwhm (eV)
0-a	284.6	84.8	0.82	2.01	2.6	1.30	3.03	3.1	1.30	4.39	2.4	1.30	6.42	7.1	2.84
0-b	284.6	60.0	1.44	1.62	35.9	1.82	6.56	4.1	2.80						
0-c	284.6	79.6	1.04	1.68	5.8	1.48	3.04	8.8	2.59	6.39	5.7	2.83			
1-a	284.6	48.3	1.46	2.15	41.9	2.28	4.33	7.9	2.28	6.69	1.9	2.38			
1-b	284.6	56.2	1.52	1.64	13.4	1.97	2.18	19.7	2.25	4.12	7.3	2.25	6.32	3.4	3.13
1-c	284.6	60.4	1.51	1.67	30.6	1.92	3.81	5.8	2.42	6.40	3.2	2.73			
1-d	284.6	64.7	1.55	1.62	29.2	1.69	3.75	3.8	2.46	6.48	2.3	2.39			
1-e	284.6	63.9	1.55	1.63	27.7	1.73	3.56	4.9	2.82	6.48	3.6	3.46			
1-f	284.6	58.0	1.49	2.10	33.8	2.44	4.44	4.6	1.85	6.34	3.6	2.99			
1-g	284.6	60.5	1.50	2.13	32.0	2.41	4.42	5.3	1.92	6.35	2.1	2.32			
1-h	284.6	59.5	1.51	2.05	34.5	2.48	4.47	4.2	1.57	6.32	1.8	1.81			
1-i	284.6	62.1	1.51	1.94	29.9	2.26	4.28	5.3	2.03	6.49	2.6	2.74			
1-j	284.6	63.2	1.54	1.95	25.9	2.00	3.99	8.6	2.46	6.50	2.3	2.65			
1-k	284.6	60.4	1.54	1.91	33.1	2.32	4.38	5.0	2.04	6.50	1.5	1.86			
2-a	284.6	48.8	1.62	1.98	39.5	1.72	3.20	4.0	1.72	4.26	4.7	1.80	6.24	2.9	3.42
2-b	284.6	55.5	1.64	2.01	32.8	1.84	2.89	5.8	1.84	4.47	4.3	1.84	6.69	1.6	2.01
2-c	284.6	57.1	1.66	2.05	35.0	1.94	4.10	5.5	2.22	6.44	2.5	2.74			
2-d	284.6	61.1	1.68	1.89	30.8	1.92	3.84	5.8	2.50	6.27	2.3	2.28			
2-e	284.6	63.2	1.59	1.74	30.0	1.75	3.86	3.1	1.80	6.42	3.7	2.60			
2-f	284.6	56.0	1.74	2.16	34.8	1.75	4.01	8.0	2.41	6.64	1.2	3.02			
2-g	284.6	55.5	1.70	2.13	36.7	1.87	4.23	5.5	1.97	6.57	2.2	3.19			
2-h	284.6	56.5	1.68	2.09	35.4	1.83	4.15	6.5	2.11	6.61	1.6	2.71			
2-i	284.6	55.4	1.79	2.15	36.3	1.86	4.11	7.1	2.46	6.61	1.3	2.06			
2-j	284.6	54.6	1.76	2.18	37.2	1.89	4.20	5.6	2.00	6.57	2.6	3.01			
2-k	284.6	58.2	1.76	2.19	36.6	1.98	4.45	3.7	1.72	6.46	1.5	2.08			
3-a	284.6	54.3	1.56	1.56	16.5	1.64	2.58	18.9	1.54	4.16	8.0	1.88	6.33	2.3	2.31
3-b	284.6	52.6	1.55	1.95	36.0	2.25	3.88	9.7	2.86	6.48	1.8	2.77			
3-c	284.6	53.9	1.38	1.64	31.3	2.14	3.59	12.1	3.06	6.82	2.7	2.51			
3-d	284.6	56.2	1.44	1.61	32.6	1.99	3.61	8.2	2.97	6.81	3.0	2.64			
3-e	284.6	55.6	1.49	1.69	37.3	2.12	4.11	4.1	2.11	6.42	3.0	2.61			
3-f	284.6	54.5	1.57	2.16	37.9	2.22	4.43	6.1	2.15	6.76	1.5	2.00			
3-g	284.6	53.5	1.45	2.09	38.0	2.53	4.31	6.8	2.48	6.75	1.7	2.12			
3-h	284.6	63.0	1.49	1.56	24.0	1.90	3.68	10.3	2.98	6.63	2.7	2.84			
3-i	284.6	51.5	1.54	2.04	39.0	2.32	4.18	7.8	2.55	6.78	1.8	2.29			
3-j	284.6	51.4	1.33	1.88	39.8	2.72	4.35	5.9	2.25	6.62	2.9	2.39			
3-k	284.6	58.0	1.46	1.63	31.2	2.07	3.74	7.9	2.79	6.53	3.0	2.97			

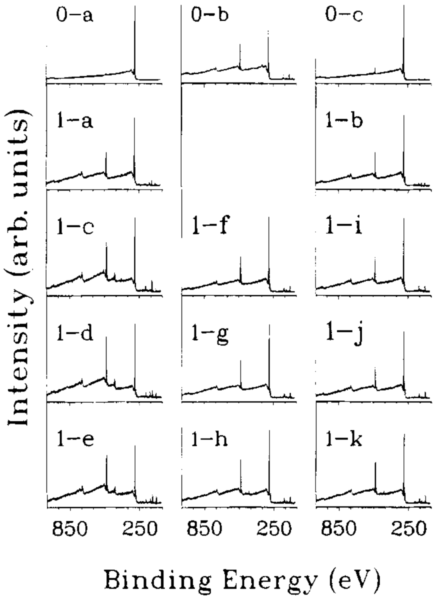

Figure 1. Overall XPS spectra of carbon fibers anodically oxidized in 1.0 M H_3PO_4 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1.

shown that oxidization of this carbon fiber in ammonium carbonate solution generates surface functionalities such as hydroxyl-, carbonyl-, and nitrogen-containing groups. In the case of the acidic electrolytes, our earlier studies[7,10,12] showed that the principal product was a bridged structure intermediate between oxide and hydroxide and phosphate groups in the case of orthophosphoric acid. These functional groups have the potential to act as reactive sites for chemical bonding with the resin and coupling agents. This earlier work showed no chemical interaction between the surface treated fiber and resin, except in the case of ammonium carbonate solution.[8] In the case of fibers electrochemically oxidized in ammonium carbonate solution a surface treated fiber coated with resin still showed a nitrogen 1s signal, resulting from surface oxidation, detectable at a binding energy of 400 eV. All the surface treated fibers coated with resin showed weak Si2s and Si2p signals at binding energies of 152 and 101 eV, respectively. The silicon-containing species originate from additives in the resin. The silicon signal can be an indicator of the presence of the resin on the fiber surface, since the resin is the only source of silicon. The curve fitting of the C1s region in all studies with oxidized fibers is shown in Table 2. The overall, C1s and valence-band spectra for fibers oxidized in phosphoric acid is shown in Figures 1–3, in nitric acid in Figures 4–6, and in ammonium carbonate solution in Figures 7–9. The Ti2p, N1s (ammonium carbonate), P2p (phosphoric acid), and O1s core regions were recorded but are not shown in the figures as there were no significant changes in these regions. The Ti2p and P2p regions showed a single peak or peaks. The N1s region did show some features that would correspond to some different nitrogen functionalities, but these features will not be discussed in this paper as they have already been discussed earlier.[8] The intensity of the Ti2p region mirrored the intensity of the Ti3p feature in the valence band. The O1s spectra were all very

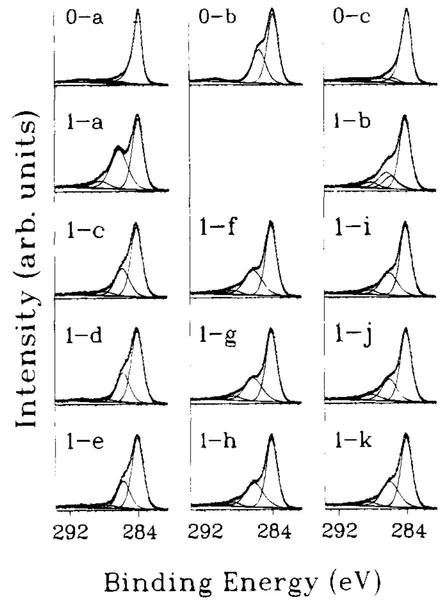

Figure 2. XPS C1s spectra of carbon fibers anodically oxidized in 1.0 M H_3PO_4 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1, and curve fitting details in Table 2.

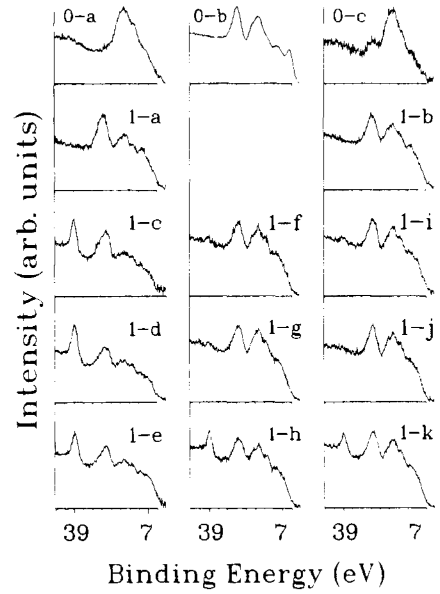

Figure 3. XPS valence band spectra of carbon fibers anodically oxidized in 1.0 M H_3PO_4 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1.

similar consisting of a single symmetrical peak, except in the case of the fibers oxidized in ammonium carbonate solution for conditons for 3-h and 3-k, and fibers oxidized in phosphoric acid for 1-c, 1-d, and 1-e. In these cases the O1s peak was asummetric. For 1-c,1-d, and 1-e this corresponded to a slight asymmetry, for 3-h and 3-k there were clearly two peaks present and the spectra were curve fitted to two peaks (area ration aporoximately 2:1 and 4:1). Figure 10 shows the atomic ratios obtained from core XPS data for all these experiments.

Oxidation Behavior of the Resin Coated Fibers. The oxidation stability of the carbon fiber coated with phenolic resin in the presence of titanium alkoxide coupling agents was examined using thermogravimetric analysis. The results of these studies are shown in Figures 11–13, and the details are described below.

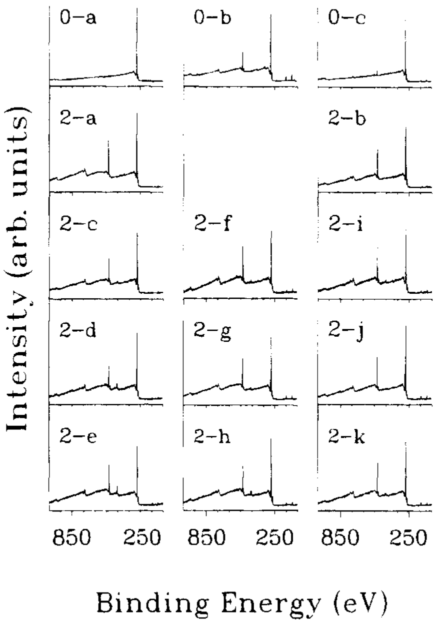

Figure 4. Overall XPS spectra of carbon fibers anodically oxidized in 1.0 M HNO_3 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1.

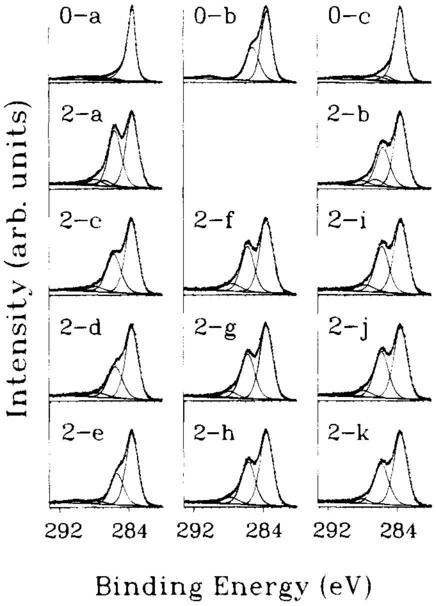

Figure 5. XPS C1s spectra of carbon fibers anodically oxidized in 1.0 M HNO_3 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1, and curve-fitting details in Table 2.

Studies of Fibers Oxidized in Phosphoric Acid. Figure 11a shows the weight loss of resin coated fibers upon heating from ambient temperature up to 1000 °C at a constant heating rate of 10 °C/min. Six types of samples were studied, namely, untreated carbon fiber, untreated fiber with resin coating, fiber electrochemically oxidized in phosphoric acid and coated with resin, oxidized fibers with resin coating with the use of the coupling agents TPT, TBT, and TOT, respectively, prepared using method 1.

It is clearly seen that untreated fiber, when coated with phenolic resin, burns off fastest among all the samples, even faster than untreated fiber alone. This shows that coating resin on untreated fiber leads to poorer oxidation resistance. This result is expected since we have previously shown that there is no chemi-

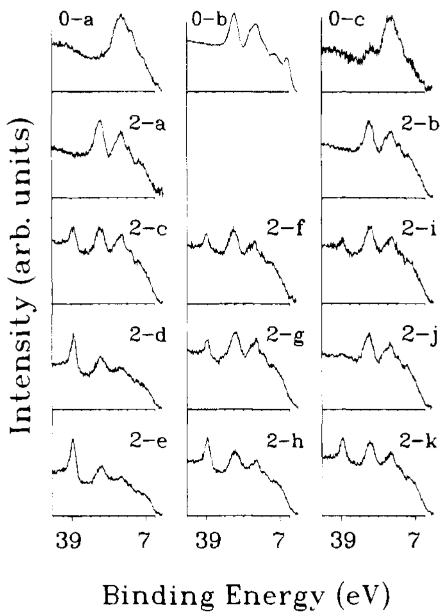

Figure 6. XPS valence band spectra of carbon fibers anodically oxidized in 1.0 M HNO_3 at 0.5 A for 30 s exposed to coupling agents and resin. Sample descriptions are given in Table 1.

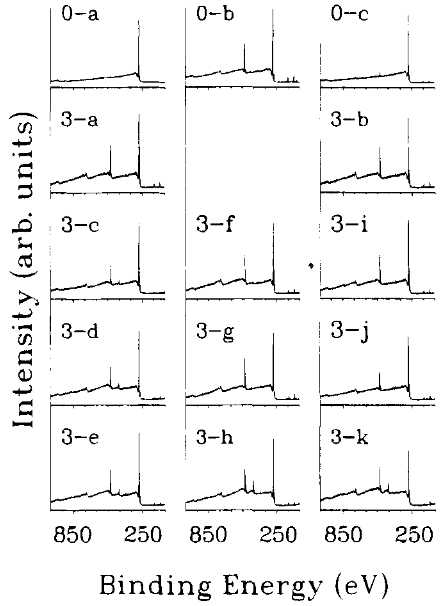

Figure 7. Overall XPS spectra of carbon fibers anodically oxidized in 0.5M $(NH_4)_2CO_3$ at 0.5A for 5 min exposed to coupling agents and resin. Sample descriptions are given in Table 1.

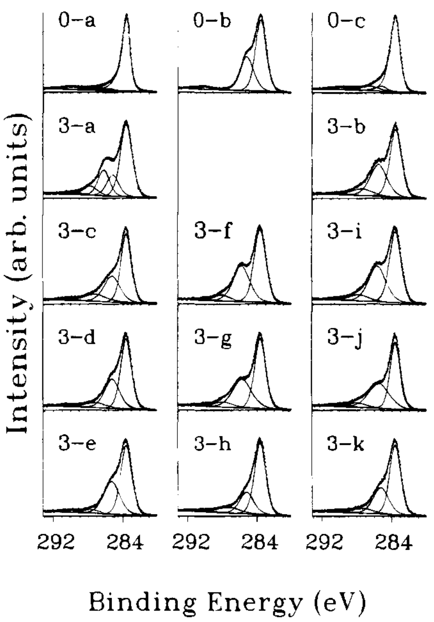

Figure 8. XPS C1s spectra of carbon fibers anodically oxidized in 0.5 M $(NH_4)_2CO_3$ at 0.5 A for 5 min exposed to coupling agents and resin. Sample descriptions are given in Table 1, and curve-fitting details in Table 2.

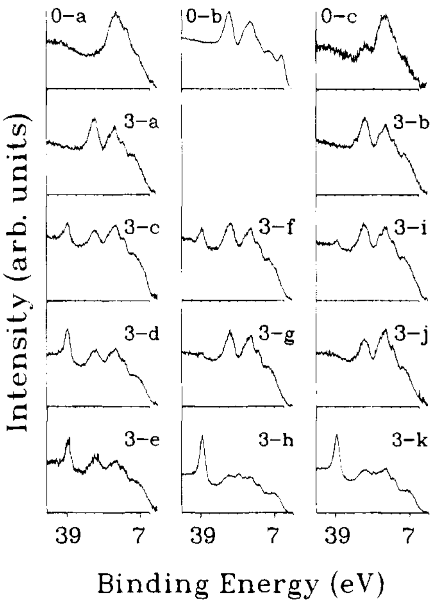

Figure 9. XPS valence-band spectra of carbon fibers anodically oxidized in 0.5 M $(NH_4)_2CO_3$ at 0.5 A for 5 min exposed to coupling agents and resin. Sample descriptions are given in Table 1.

cal interaction between untreated fiber and the resin.[7] When the surface-oxidized fiber is coated with resin, the oxidation resistance shows significant improvement. This is probably caused by the improved wetting of fiber by resin following fiber surface treatment, which we[7] and others[17] have reported. When the surface-treated fibers are exposed to the titanium alkoxide coupling agents following the simultaneous reaction approach of method 1, then substantial improvement in the oxidation resistance occurs.

Among the three samples using coupling agents, the sequence of oxidation stability increases in the order TPT, TBT, and TOT. It is interesting to note that this sequence is consistent with the intensities in the Ti2p core level and the Ti3p peak intensity in the valence-band region. In the discussion below it will be suggested that the higher the concentration of alkoxide bridged coupling between fiber and resin, then the better the oxidation resistance.

Figure 11b shows the comparison between the two methods for applying the coupling agents. Method 1 shows somewhat better oxidation resistance than method 2.

Studies of Fibers Oxidized in Nitric Acid. Figure 12 shows that all the surface treated fibers, with or without using coupling agent with a resin coating, show poorer oxidation resistance than pure untreated fiber and untreated fiber with resin coating. Surface-treated

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[17] Li, T.; Yang, Z.; Qiao, S.; Zheng, X. *Carbon* **1993**, *31*, 1361.

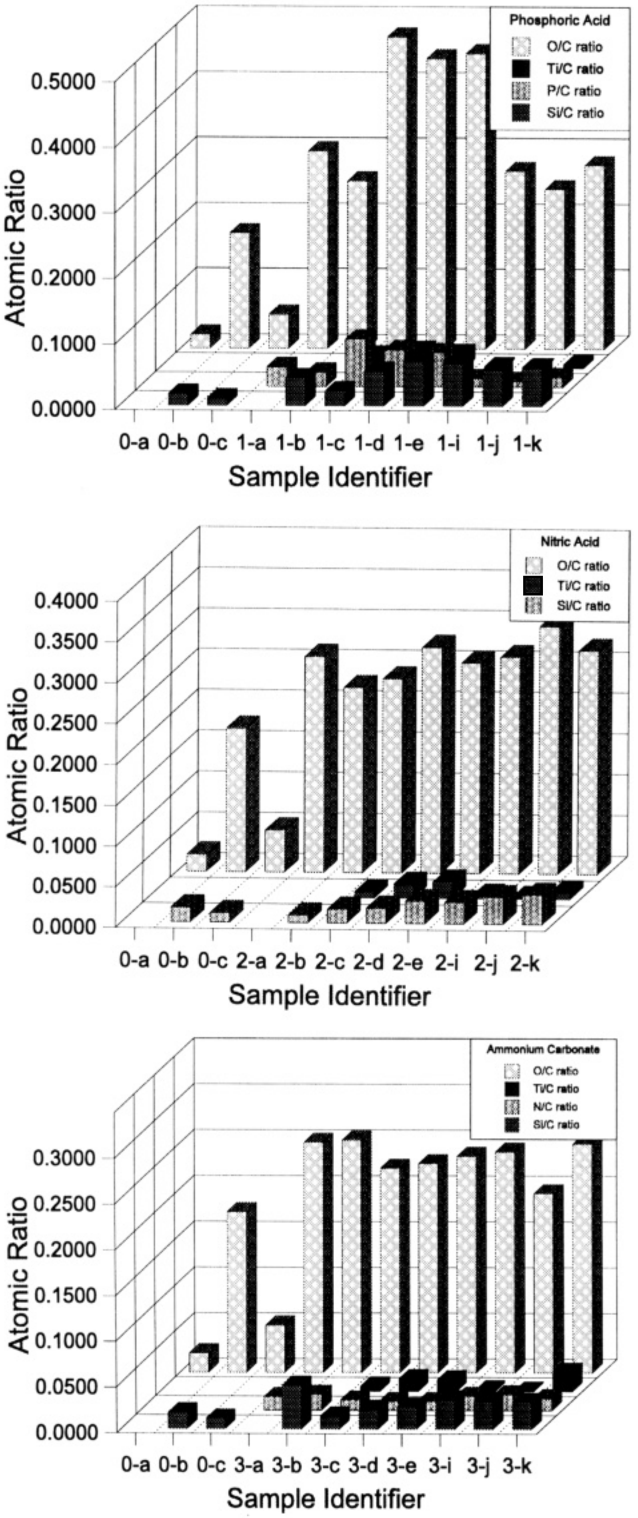

Figure 10. Atomic ratios obtained from core XPS data for carbon fiber, phenolic resin, and fibers electrochemically oxidized in various electrolytes with or without coupling agents.

fibers still show better oxidation resistance than the surface-treated fibers exposed to resin without the use of the coupling agent, and the fiber using TOT still shows better oxidation resistance than the fiber without using coupling agent, and the fiber using TOT in resin coating still shows better oxidation resistance than fibers using TPT and TBT.

Studies of Fibers Oxidized in Ammonium Carbonate. Figure 13 shows that surface treatment leads to an improvement in oxidation resistance, though the results of the method 1 treatment leads to less improvement in oxidation resistance than was found for phosphoric acid treatment. There is also a significantly better performance given by fibers treated by method 1 rather than method 2.

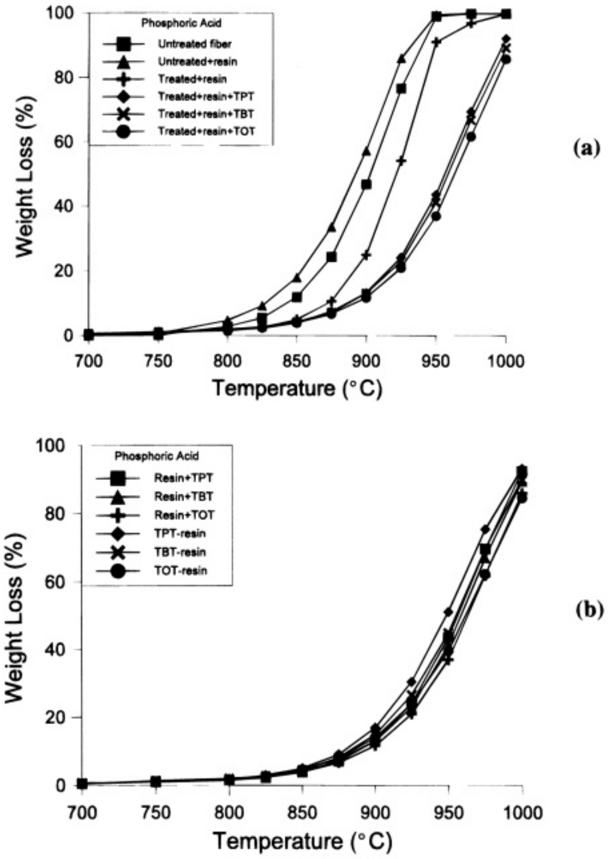

Figure 11. Thermal gravimetric analysis results indicating the oxidation behavior of carbon fibers with and without resin coatings and coupling agents, with phosphoric acid used as the electrolyte for surface treatment. (a) Results for the untreated fibers, untreated and treated fibers coated with resin, and treated fibers coated with resin and coupling agents reacted together (method 1). (b) Results for treated fibers coated with resin and coupling agents both by reacting together (method 1, shown as, e.g., "Resin+TOT") and reacting sequentially (method 2), shown as, e.g., "TOT-resin".

Discussion

Studies of Fibers Oxidized in Phosphoric Acid. The overall spectrum in Figure 1 shows that samples 1-c, 1-d, and 1-e, which were prepared by method 1, have a relatively intense Ti2p signal at a binding energy of 459 eV, a binding energy typical of oxidized titanium. For samples 1-i, 1-j, and 1-k, which were prepared by method 2, have a much less intense Ti2p signal. For 1-i and 1-j, the Ti2p signal can barely be observed from the overall spectra. Samples 1-f to 1-h, which were prepared by exposing fibers to an acetone solution containing the coupling agent without resin present, gave overall spectra similar to those of fibers treated using method 2, with the most Ti2p intensity arising from the use of the coupling agent TOT. The variations in Ti2p intensity are reflected by the changes in the valence band region for the Ti3p peak at 39 eV shown in Figure 3.

The curve fitting results for the C1s region, as presented in Table 2, indicate that the oxide component

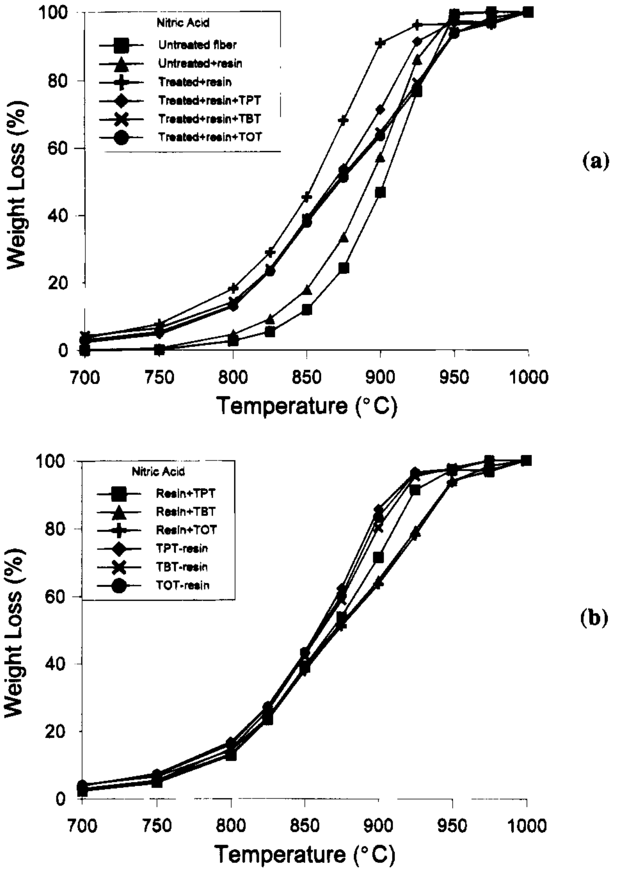

Figure 12. As in Figure 11, but for nitric acid as the electrolyte for surface treatment.

1 of samples 1-c, 1-d, and 1-e (method 1) have a chemical shift of about 1.6 eV, very close to that of the phenolic resin. Oxide peak 1 of samples 1-f, 1-g, and 1-h (fiber exposed to the coupling agent alone) has a chemical shift of about 2.1 eV. Oxide peak 1 of samples 1-i, 1-j, and 1-k (method 2) has a chemical shift of about 1.9 eV. In the last two cases, the chemical shift of oxide peak 1 revealed by curve-fitting analysis is closer to that of the oxidized fiber rather than that of the resin.

Studies of Fibers Oxidized in Nitric Acid. The overall spectrum in Figure 4 shows similar behavior with respect to titanium intensity at that found for phosphoric acid. Samples 2-f to 2-h, which were prepared by exposing fibers to an acetone solution containing the coupling agent without resin present, gave a somewhat higher titanium intensity than those of fibers treated using method 2.

The curve fitting results for the C1s region are given in Table 2. It is seen that oxide component 1 of samples 2-c, 2-d, and 2-e (method 1) has a chemical shift of 2.1, 1.9, and 1.7, respectively, with only 2-e (coupling agent TOT) having a shift (1.74 eV) close to that of the resin. Oxide peak 1 of sample 2-f, 2-g, and 2-h (fiber exposed to the coupling agent alone) has a chemical shift of about 2.1 eV. Oxide peak 1 of sample 2-i, 2-j, and 2-k (method 2) also has a chemical shift of about 2.1 eV.

Studies of Fibers Oxidized in Ammonium Carbonate. The overall spectrum in Figure 7 shows behavior with respect to titanium intensity similar to that found for phosphoric acid. Samples 3-h and 3-k have a particularly high titanium intensity when TOT is used as the coupling agent.

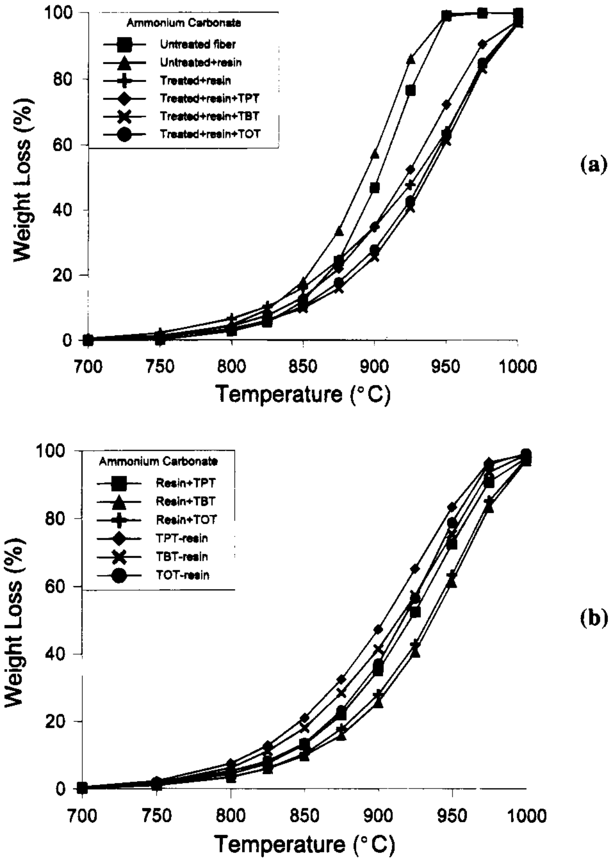

Figure 13. As in Figure 11, but for ammonium carbonate as the electrolyte for surface treatment.

The curve fitting results for the C1s region are shown in Table 2 and indicate that oxide peak 1 of samples 3-c, 3-d, and 3-e (method 1), and 3-k (method 2) has a chemical shift of about 1.6 eV, very close to that of the phenolic resin.

Interfacial Chemical Reactions. We have previously found that the experimental approach that we have taken allows us potentially to be able to identify chemical interaction at the interface. This is because the thin coating of resin is thin enough to allow information to be obtained from the interface region. Since we know the spectral features of the resin alone (0-b in Table 2 and the Figures) and of the surface treated fibers alone (1-a, 2-a, and 3-a in Table 2 and the figures), then whenever the spectrum of the resin-coated fiber does not correspond to the addition (suitably normalized for differing amounts of fiber and resin component) of the spectrum expected for the resin- and surface-treated fiber, chemical reaction in the interface region can be assumed. Of course this approach depends upon any chemical reaction at the interface region leading to different chemical features than those found in the resin and in the surface treated fiber.

Figure 14 shows reactions for both (a) simultaneous (method 1), and (b) sequential (method 2) reactions that might occur between a surface-treated carbon fiber and a phenolic resin in the presence of the titanium alkoxide coupling agents. These reaction schemes follow the reactions expected for titanium alkoxides. In addition any water present would be expected to decompose the alkoxides leading to titanium oxide (or hydroxides, or hydroxy-alkoxides):

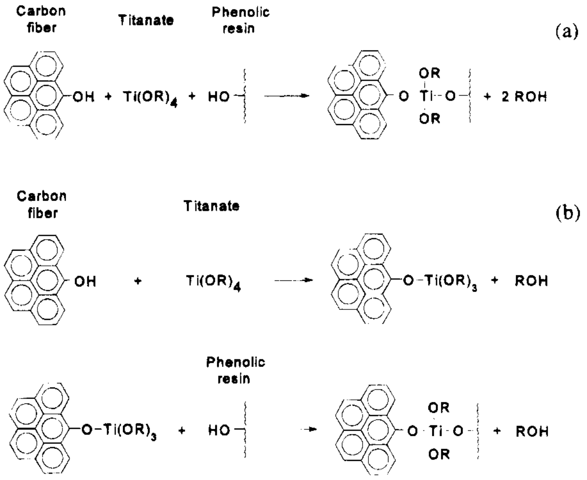

Figure 14. Reaction schemes for interfacial cross-linking reactions between the titanium alkoxide coupling agents, $Ti(OR)_4$, and the treated fibers and phenolic resin for a simultaneous reaction as in method 1, and a sequential reaction as in method 2.

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH \qquad (1)$$

In these reaction schemes it is implied that $Ti(OR)_4$ is a monomeric molecule. In fact the lower alkoxides (R = methyl, ethyl, *n*-propyl, and isopropyl) show largely polymeric units consisting of a tetramer where all titanium atoms are octahedrally coodinated to six oxygen atoms, the tetrameric unit being formed by edge sharing of four TiO_6 units.[18] In this work the titanium alkoxide coupling agents would be expected to be largely monomeric, especially TOT. The reaction schemes in Figure 14 thus seem reasonable, including the $-O-Ti(OR)_2-O-$ bridge involved in the coupling process. Chemical reaction according to Figure 14 would thus lead to the formation of $-C-OR$ groupings were R was either an alkane group or the attached carbon fiber. In both cases these groupings would be expected to lead to a peak with a binding energy shift of around 1.6 eV, the same as that found in the resin. Thus chemical reaction at the interface would not lead to a change in the C1s region with respect to the resin, though the spectrum would appear significantly different from that of the surface treated fiber. It is important to note that in the cases where the best oxidation resistance performance was found (phosphoric acid and ammonium carbonate using TOT), the C1s region showed an intense feature at a shift of 1.6 eV, consistent with the reaction model in Figure 14.

The Ti2p region did not show any evidence for chemically shifted features, but this is expected as TiO_2, the titanium alkoxides, and the $-O-Ti(OR)_2-O-$ bridge of Figure 14 would all show similar Ti2p binding energies.

It is the valence band region, and the O1s region that shows some significant differences. First our criteria for chemical interaction at the interface, namely, the difference in the spectrum from that of resin or surface treated fiber alone, is shown in the valence-band region. Thus the valence band spectra for the best oxidation resistant cases cannot be constructed by addition of the spectrum of the resin and surface treated fiber. Thus note how 1-c to 1-e in Figure 3 cannot be constructed from 1-a and 0-b, and 3-c to 3-e in Figure 9 cannot be constructed from 3-a and 0-b. This comparison *excludes* the obvious difference that the coupling agent treatment leads to a Ti3p feature at 39 eV. This difference will be demonstrated further below. At this stage however it is appropriate to comment that there are three compounds that might be present after the addition of the titanium alkoxides. TiO_2 may be formed by any reaction with water or functional groups on the fiber surface that can be "stripped off" leading to reaction 1. A true interfacial chemical reaction of the sort shown in Figure 14 may occur, and finally titanium alkoxide could be adsorbed onto the fiber surface without reaction. The latter possibility cannot be eliminated since adsorbed titanium alkoxide would be expected to give rise to the same spectral features as would be found for the interfacial chemical reaction of Figure 14. It is unlikely that the highly reactive titanium alkoxides would stay around unreacted and adsorb onto the surface without either undergoing the hydrolysis reaction shown in (1) or the coupling shown in Figure 14. In addition the fact that the differences between the valence-band region and the surface-treated fiber and resin alone are clearly apparent only in cases where good oxidation resistance imparted by method 1 is found implies that interfacial chemical reaction is a reasonable suggestion.

There is clear evidence that TiO_2 is found. Thus the O1s region of 3-h and 3-k (not shown) shows a low binding energy shoulder consistent with an inorganic oxidized titanium species. The valence band in this case (Figure 9) shows a very intense Ti3p feature, and a broad "hump" between the O2s and C2s region. The origin of this "hump" will be discussed below. The atomic ratio data of Figure 10 shows similar O/C level for treated fibers coated with resin, with or without coupling agents. However in the case of the phosphoric acid treatment all the method 1 experiments led to much higher O/C ratios. In this case it is reasonable to assume that this high ratio might arise from TiO_2 on the outer surface of the material (i.e., on top of the resin coating). Such a situation would be expected only for method 1, as method 2 would be expected to form any TiO_2 at the interface (and so its signal would be attenuated by the outer resin layer). This is reflected in a slight asymmetry to low binding energy in the O1s region (not shown) for (1-c to 1-e).

To better understand the valence-band region, we have carried out calculations to show what type of valence-band spectra would be expected for the possible titanium species that might be present. We have performed multiple scattered wave Xα calculations on three molecules, TiO_6^{8-} to represent TiO_2, and two geometries of $Ti(OCH_3)_4$. Details of these calculations are given in Table 3. The calculation for TiO_6^{8-} was performed on the charged cluster rendered neutral by a Watson sphere with an opposite positive charge on it. Transition-state calculations were not performed as previous workers have found little difference between ground- and transition-state calculations for the case of oxidized titanium.[19] $Ti(OCH_3)_4$ was used as a model for the free titanium alkoxide, and for the coupled molecules of Figure 14. It was chosen because it

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Table 3. Parameters Used and Features of the Xα Calculations

α values titanium, 0.716 95; carbon, 0.759 28;oxygen, 0.744 47; hydrogen, 0.776 54

maximum *l* values: outer and titanium 3; oxygen and carbon 1; hydrogen 1

cluster	TiO_6^{8-}	$Ti(OCH_3)_4$	$Ti(OCH_3)_4$
symmetry	O_h	D_{2d}	C_{4v}
outer α value	0.740 54	0.764 31	0.740 54
intersphere α value	0.740 54	0.764 31	0.740 54
bond lengths (Å)	1.95 Å (Ti−O)	1.98 Å (Ti−O) 1.385 Å (O−C) 1.08 Å (C−H)	1.98 Å (Ti−O) 1.385 Å (O−C) 1.08 Å (C−H)
bond angles		144.835° (Ti−O−C) 90° (O−Ti−O) 109.67° (−CH_3)	150° (Ti−O−C) 90° (O−Ti−O) 109.67° (−CH_3)
titanium sphere radius	1.273 Å	1.321 Å	1.313 Å
oxygen sphere radius	1.174 Å	0.889 Å	0.899 Å
carbon sphere radius		0.844 Å	0.856 Å
hydrogen sphere radius		0.450 Å	0.450 Å
outer sphere radius	3.132 Å	4.449 Å	4.321 Å
Watson sphere radius	1.95 Å		
virial ratio ($-2T/V$)	1.002 283	1.004 515	1.004 510

convergence	When the difference in potentials at the beginning and the end of the iteration were less than 10^{-5} of the potential at the start of the iteration. This gives energy levels that differed by less than 10^{-6} Rydbergs between the last two iterations.
core electrons	"Thawed" so that they retained atomic character while being fully included in the iterative process. Ti(1s), Ti(2s), Ti(2p), C(1s), and O(1s) electrons were treated as core electrons.

contains the TiO_4 unit, and Ti−O−C bonds found in the titanium alkoxides and the coupled molecules of Figure 14. Two geometries were chosen for the calculation. In one (D_{2d}) the titanium is surrounded by a tetrahedral arrangement of oxygen atoms. This is the arrangement taken by titanium (which is usually found in an octahedral environment) when the metal atom is surrounded by bulky groups as in TiI_2 and $TiBr_2$.[20] In the other arrangement a square-planar (C_{4v}) structure was chosen to represent a situation where steric factors might favor a square-planar coupling link in the linkage of the type shown in Figure 14 (though Figure 14 would be compatible with both a square-planar and a tetrahedral environment about the titanium atom). The two structures are illustrated in Figure 15. Bond angle and bond length data were taken from crystallographic results[18] for $Ti(OCH_3)_4$ using data for titanium atoms attached to one oxygen atom.

Calculated spectra were generated by adding together the component peaks 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 for the level, adjusted by the appropriate atomic photoelectron cross section (using the values due to Scofield[21]). Each component in the calculated spectrum was represented by an equal full width at half-maximum (1.5 eV) 50% Gaussian/Lorentzian product function peak.[15] The calculated spectra also include the $K\alpha_{3,4}$ satellite peaks for the Mg X-radiation used. The spectrum for the TiO_6^{8-} cluster was adjusted for a stoichiometry TiO_4 to give an idea of the type of spectral features that one would expect for an octahedral arrangement with TiO_4 stoichiometry. This spectrum is in excellent agreement with the published experimental spectrum.[24]

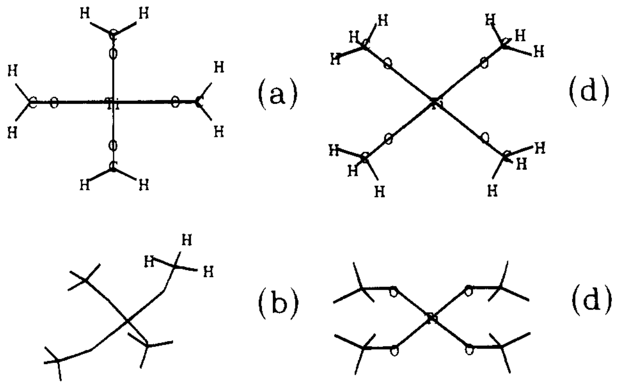

Figure 15. Geometry of the $Ti(OCH_3)_4$ molecules used for the Xα calculation. (a) "On top" view of the C_{4v} molecule where one of the C−H bonds lies over the Ti−O−C bond. (b) View in (a) after a 45° rotation about the *x* and *z* axes and a 10° rotation about the *y* axis showing the $-CH_3$ group and the bent (150°) Ti−O−C bond. (c) "On top" view of the D_{2d} molecule. (d) View in (a) after a 90° rotation about the *x* axis showing the tetrahedral arrangement about the Ti atom.

Figure 16 shows the calculated spectra for the three molecules and compares these calculated spectra with the difference spectrum between the background subtracted valence-band spectrum of a fiber treated by anodic oxidation in phosphoric acid and simultaneously coated with TOT and resin (Figure 3-1e), and the background subtracted valence-band spectrum of the anodically oxidized fiber exposed to resin alone (Figure 3-1b). The latter spectrum represents an addition of the surface-treated fiber and the resin since no chemical interaction is found in this case.[7] This difference spectrum thus shows the features in the valence-band spectrum that cannot be explained as being due to surface treated fiber and to resin. The difference spectrum was smoothed. The resulting difference spectrum shows a number of features which can be identified with features in the calculated spectra. All the spectra show a Ti3p feature at 39 eV. The calculated spectra show a feature marked "1" which corresponds to the $K\alpha_{3,4}$ X-ray satellite from the Ti3p feature at 39 ev, and this feature can be clearly seen as a shoulder in the difference spectrum. Feature "2" in the calculated spectra corresponds to principally O2s intensity. In the case of TiO_6^{8-} this feature lies at a significantly lower binding energy than in the spectra of $Ti(OCH_3)_4$. This is because in the oxide the O2s region is widely separated from the titanium regions and so is little mixed with other levels and is largely O2s. It behaves thus rather like a core level and so occurs in the low-binding-energy range (as for the O1s region). In $Ti(OCH_3)_4$ the O2s region shows significant mixing with the close C2s region (shown as "3" in the spectra of $Ti(OCH_3)_4$) leading to a shift to higher binding energy. We suggest that the intense feature in the valence-band region around 25 eV is due to O2s features from TiO_4 units from the coupling shown in Figure 14. The broad feature at lower binding energy would then correspond

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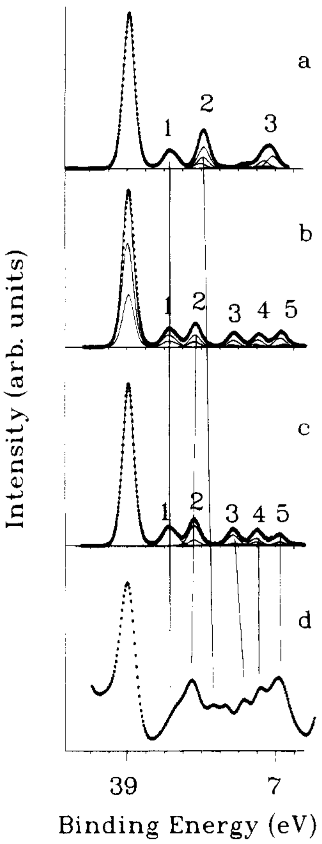

Figure 16. Difference spectrum (d) between the background subtracted valence band spectrum of a fiber treated by anodic oxidation in phosphoric acid and simultaneously coated with TOT and resin (Figure 4-1e), and the background subtracted valence band spectrum of the anodically oxidized fiber exposed to resin alone (Figure 4-1b) after a 21-point binomial smooth repeated 10 times, compared with the calculated valence-band spectrum (a) of TiO_2 (for the TiO_4 stoichiometry) and the calculated valence-band spectrum of C_{4v} (b) and D_{2d} (c) $Ti(OCH_3)_4$. The calculated spectra were obtained from Xα calculations on a TiO_6^{8-} cluster (TiO_2) and on C_{4v} and D_{2d} $Ti(OCH_3)_4$ molecules.

to O2s from oxidized titanium. Thus the calculations suggest that the presence of oxidized titanium (TiO_2) would lead to a reduction in the valley between the O2s and C2s regions in the valence-band region. This is consistent with large amounts of TiO_2 in 3-h and 3-k of Figure 9, since these figures show hardly any valley between the O2s and C2s region. The difference spectrum shows three other features compatible with features "3" (C2s), "4", and "5" (C2p and O2p) in the $Ti(OCH_3)_4$ spectra. Feature "3" in the TiO_6^{8-} spectra results from O2p intensity. Its presence in the difference band spectrum would tend to introduce a low binding energy "hump" into the spectrum as observed. The calculations suggest that there is little difference in the appearance of the spectrum for the D_{2d} and C_{4v} forms of $Ti(OCH_3)_4$ though there are differences in the relative intensities of peaks "2" and "5". These differences are too small to make any meaningful suggestions as to the stoichiometry about the titanium atom based upon our experimental data.

The calculations thus support the suggestion that chemical interaction at the interface occurs following the scheme shown in Figure 14. We believe that most of the titanium present at the interface region in those systems that give enhanced oxidation resistance arises from chemical interactions of the type shown in Figure 14. This is then another case to support our observation that it requires chemical interaction at the interface to give enhanced oxidation resistance in these systems. Method 1 is clearly superior to method 2 as it always leads to better oxidation resistance even though the differences between the performance of method 1 and method 2 are not substantial. Sequential reaction using method 2 is likely to lead to a less attractive second chemical coupling step (Figure 14) because of the presence of any TiO_2 formed at the interface in the first step, which is likely to reduce the number of coupling sites available. Our results suggest that method 2 has fewer coupling sites than method 1. The better performance of TOT over TBT and TPT is expected because the bulky 2-ethylhexyl groups present in TOT make better leaving groups than the less bulk isopropyl and *n*-butyl groups present in TPT and TBT.

The poor performance of the nitric acid treated fibers is not surprising as we have shown extensive fiber damage in high levels of surface treatment using this electrolyte.[23,24] This damage leaves large slits in the fiber surface, which provides an excellent avenue for oxygen attack. This is why the untreated fibers always give better oxidation resistant performance than the treated fibers.

Conclusions

XPS studies using core and valence-band photoemission on a thin film of resin over a surface-treated carbon fiber surface allow the interface region to be probed. These data can be compared with the oxidation resistance of the resin coated fibers, and the valence band interpreted by multiple scattered wave Xα calculations. The results show that titanium alkoxide coupling agents lead to interfacial cross-linking involving the oxidized fiber surface, the titanium alkoxide, and the phenolic resin. The greatest degree of cross-linking, and the best oxidation resistant behavior occurs when the reaction is carried out in a simultaneous manner. The use of titanium alkoxides, especially tetrakis(2-ethylhexyl)titanate (TOT), as a coupling agent leads to substantial improvements in oxidation resistance. Electrochemical oxidation in orthophosphoric acid proves to be the best fiber surface treatment for use with the titanium alkoxides as coupling agents, and this gives the best oxidation resistant performance. Ammonium carbonate is another suitable electrolyte, but nitric acid causes too much fiber damage to be effective.

Interfacial chemical reaction, with titanium alkoxide coupling agents, clearly has an important role to play in the improvement of oxidation stability. This approach promises to be a valuable approach to be used in conjunction with other methods for the improvement of the oxidation stability of carbon fibers for use in composites.

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