X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 18. Interfacial Interactions between Phenolic Resin and Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and Their Effect on Oxidation Behavior

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The interfacial interactions between a carbon fiber electrochemically oxidized in 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, together with the effect that several different coupling agents had on this interaction. Valence band XPS, interpreted by spectra generated by ab initio molecular orbital calculations based upon particular chemical interaction models, proved valuable in understanding the nature of this chemical interaction. Model calculations suggested that the most likely chemical linkage is an ether linkage formed directly between the oxidized fiber and the resin and that the use of glutaraldehyde as a coupling agent led to probable hemiacetal cross-linking between the oxidized fiber and the resin. 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 in cases where interfacial chemical reaction occurred between the resin and fiber.

Introduction

Carbon–carbon composites have shown great utility as structural materials in the aerospace industry. Oxidation resistance of these composites, however, is relatively poor, constituting one of the major barriers in their extensive applications in the aerospace area.[1–5] Oxidation protection has been one of the major challenges in development of carbon–carbon composites. A large number of outer protection approaches such as coatings, oxidation inhibitors, and glass sealings[6–15] have been employed in the majority of these studies, with less attention given to interface protection.

While most oxidation protection studies have used outer protection approaches, we have begun a program aimed at protecting the carbon fiber–matrix resin interface in addition to various outer coating protection approaches. The influence of interfacial bonding between a carbon fiber and the matrix resin on the oxidation behavior of the composite has been investigated by a number of workers.[6,16–21] In situ protection at the fiber–matrix interface with outer protection applied simultaneously can be expected to lead to a better oxidation resistance of composites. Interface protection has potential for the improvement of oxidation resistance because this interface plays an important role in the oxidation of the composite.

Interface protection is carried out by chemical modification of the interface at the molecular level. Improvement of interfacial bonding can be achieved by establishing fiber–resin chemical bonds. A chemically cross-linked interface can be expected to enhance the integrity of composite materials, by reducing the diffusion of oxygen along the interface into the interior of the material where more oxidation damage would occur. Such an enhanced interface can be designed by generating desirable functionalities on the carbon fiber surface to chemically interact with the matrix resin or by using coupling agents to chemically bridge between the fiber

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(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**, April 2–5, 1348.
(6) Hippo, E. J.; Murdie, N.; Hyjazie, A. *Carbon* **1989**, *27*, 689.
(7) Hippo, E. J.; Murdie, N.; Kowbel, W.; Wapner, P. G. *Ext. Abstr. Program-Bienn. Conf., Carbon* **1987**, *18*, 466.
(8) Mckee, D. W.; Spiro, C. L.; Lamby, E. J. *Carbon* **1984**, *22*, 507.
(9) Ho, C. T.; Chung, D. D. L. *Carbon* **1990**, *28*, 815.
(10) Hannache, H.; Quenisset, J. M.; Naslam, R.; Heraud, L. *J. Mater. Sci.* **1984**, *19*, 202.
(11) Sheehan, J. E. *Carbon* **1989**, *27*, 709.
(12) Mckee, D. W. *Carbon* **1987**, *25*, 551.
(13) 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; p 395.
(14) Wang, Y. Q.; Wang, Z. M.; Zhou, B. L.; Shi, C. X. *J. Mater. Sci. Lett.* **1993**, *12*, 817.
(15) Buchanan F. J.; Little, J. A. *J. Mater. Sci.* **1993**, *28*, 2324.
(16) Crocker, P.; McEnaney, B. *Carbon* **1991**, *29*, 881.
(17) Bowles, K. J.; Nowak, G. *J. Compos. Mater.* **1988**, *22*, 966.
(18) Bleay, S. M.; Scott, V. D. *Carbon* **1991**, *29*, 871.
(19) Ben-Aim, R. I.; Bonardet, J. L.; Diamy, A. M.; Fraissard, J.; Legrand, J. C. *J. Mater. Sci.* **1990**, *25*, 4113.
(20) Bowles, K. J. *35th Int. SAMPE Symp.* **1990**, April 2–5, 147.
(21) Magendie, F. J.; Seferis, J. C.; Aksay, I. A. *35th Int. SAMPE Symp.* **1990**, April 2–5, 2280.

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and resin. In previous work of this group,[22] it has been established that hydroxyl-, carbonyl-, and nitrogen-containing functionalities can be introduced on a carbon fiber surface by anodically oxidizing the fiber in ammonium carbonate solution. In this work, we have studied interfacial chemical reactions between phenolic resin and fibers electrochemically oxidized in ammonium carbonate solution. We have also examined possible routes of establishing chemical cross-linking between the surface treated fiber and phenolic resin by using coupling agents. X-ray photoelectron spectrometry (XPS), with its sampling depth of 100 Å for polymeric materials and high sensitivity to the chemical environment, is an ideal technique to probe the fiber/resin interface if a sample is prepared as a thin layer of resin coated on the fiber surface. An extensive amount of chemical information is available from the valence-band XPS because the chemical shifts in the valence region arise from changes in chemical bonding leading to different atomic orbital contributions to the molecular orbitals. The core region is also influenced by chemical bonding since this causes changes in the electronic environment around the core atom concerned. The origin of core and valence band shifts are different, and the valence-band region is sometimes more sensitive to chemical bonding changes. Molecular orbital calculations provide reliable interpretation of XPS valence-band spectra, since XPS valence-band spectra can be related to calculations of the ground-state density of states. In this work, a number of fiber–resin bonding systems were investigated with core and valence band XPS. Ab initio Hartree–Fock calculations were used to explain valence band spectral features based on model structures of the interfaces. Thermogravimetric analysis (TGA) was used to monitor the oxidation behavior of the resin coated fiber samples.

Experimental Section

The carbon fiber used in this study, E-120 high-strength and high-modulus pitch-based fiber, was provided by DuPont Co. These fibers were specially prepared with neither surface treatment or sizing. In addition no other surface contaminants were introduced onto the fiber surface (such as lubricants to assist fiber winding). We have found these fiber samples to be very resistant to the adsorption of oxygen or water. 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. The spectrum of this resin was recorded by taking the 59% (by weight) aqueous solution supplied (which had 10% phenol and 2.5% formaldehyde, both by weight) and spreading it thickly on a copper plate, drying the resin film in a vacuum oven. The resulting resin film was so thick than no underlying copper could be seen in XPS studies.

Electrochemical treatment for the carbon fiber was carried out using the approach previously developed in this laboratory.[22] A 0.5 M ammonium carbonate solution was used to anodically oxidize the fiber surface in the galvanostatic mode with a current of 0.5 A and a polarizing time of 5 min. Electrochemically treated fibers were immersed in heated (to about 60 °C) resin solution for 30 min, 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. Samples exposed to a coupling agent were immersed in an resin–acetone solution prepared as described below, to which a 16% by volume (8% for glutaraldehyde (GAL)) solution of the coupling agent in acetone was added with stirring. In the case of GAL one experiment was performed using an aqueous solution of both GAL and the resin. In cases where the solution was acidified a drop of concentrated sulfuric acid was added just before the fibers were immersed into the solution. The molecular structure of GAL is shown in Charts 2–5, and PAL is the simple aldehyde, CH_3CH_2CHO. There was no evidence for water retention (perhaps on excessive polar functional groups on the fiber surface) on the fibers after this treatment was carried out. If water retention had occurred to a significant extent, then we would have observed problems in getting a good vacuum in our XPS studies and would have been able to detect water loss in the quadrupole mass spectrometer attached to our XPS vacuum system.

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

coupling agent system	sample code	sample preparation
no coupling agent	0-a	untreated carbon fiber E-120
	0-b	phenolic resin 337T28
	0-c	untreated fiber with resin coating
	0-d	electrochemically treated carbon fiber
	0-e	treated fiber with resin coating
glutaraldehyde (GAL)	1-a	treated fiber exposed to GAL
	1-b	treated fiber with resin coating (GAL added)
	1-c	treated fiber exposed to GAL[a]
	1-d	treated fiber with resin coating (GAL added)[a]
propionaldehyde (PAL)	2-a	treated fiber exposed to PAL
	2-b	treated fiber with resin coating (PAL added)
	2-c	treated fiber exposed to PAL[a]
	2-d	treated fiber with resin coating (PAL added)[a]
diisocyanate (DIB and DIH)	3-a	treated fiber exposed to DIB
	3-b	treated fiber with resin coating (DIB added)
	3-c	treated fiber exposed to DIH
	3-d	treated fiber with resin coating (DIH added)

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

Table 1 lists a description of the samples studied and the method used for preparing the samples. In an attempt to produce interfacial chemical reactions, four types of coupling agents were used, namely, GAL, propionaldehyde (PAL), diisobutacyanate (DIB), and diisohexacyanate (DIH). They were purchased from Aldrich and were of analytical grade purity. GAL was supplied as a 50% aqueous solution, so the acetone solution in the GAL case was 8% by volume of GAL and 8% by volume of water. To study the interfacial cross-linking, the electrochemically oxidized fibers were immersed in resin solution mixed with the coupling agents. To see if the coupling agents directly reacted with the oxidized fibers, the oxidized fibers were also exposed to acetone solutions of the coupling agents alone.

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 0.25 wt % resin solution was found to be a suitable concentration to give a thickness that met these criteria. This concentration was prepared by dissolving 1.0 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

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[22] Xie, Y.; Wang, T.; Franklin, O.; Sherwood, P. M. A. *Appl. Spectrosc.* **1992**, *46*, 645.

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.[23] The typical data collection times were as follows: C1s, 20 minutes; O1s, 30 min; N1s, 1 h; valence band 7−15 h. 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 tow was mounted with the fiber axis normal to the X-ray direction. This arrangement also gave no obvious takeoff angle because of the approximately cylindrical nature of the tow. The sample was positioned so that no aluminum metal from ends of the tow could be detected. The spectra were examined for sample decomposition. This could be done since the data displayed the spectrum in real time as it was being collected, and thus decomposition could be noticed as the new spectral points show significant change as they are added to the previously stored data. Monitoring decomposition is important as we have found this to be a problem in carbon fiber systems (ref 22 and the references therein).

Curve fitting was performed using a nonlinear least-squares curve-fitting program with a Gaussian/Lorentzian product function.[24] 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 the C1s region was taken as 284.6 eV for the calibration purpose. No charging shifts were found in the spectra studied, so no alignment problems were experienced when spectra were added together.

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.

Ab initio Hartree−Fock SCF calculations were performed to calculate the XPS valence-band spectra. These calculations used the HONDO program with a STO-3G minimal basis set[25] and were performed on an IBM RISC/6000 computer. The calculated spectra were generated by combining peaks placed at the positions 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[26] adjusted by the Scofield atomic photoelectron cross section.[27] Each component peak in the generated spectrum is represented by a 50% mixed Gaussian/Lorentzian product function[24] with each peak having the same full width at half-maximum (fwhm) of about 1 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 always exaggerate the spread of valence band energy levels by a factor of 1.3. This approach has been successfully used in other polymer systems.[28,29]

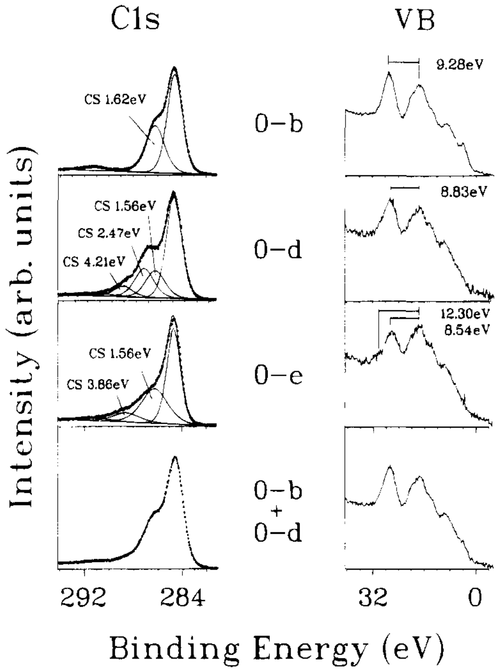

Figure 1. XPS spectra of C1s and valence band regions for phenolic resin 337T28 (0-b), carbon fiber electrochemically oxidized in ammonium carbonate solution (0-d), the oxidized fiber coated with the resin (0-e), and the 1:1 addition of spectrum 0-b and 0-d.

The 337T28 resin used has the structural repeat unit published previously.[29] In the resin used there are also some methylol groups ($-CH_2OH$) as well as the C−OH groups and $-CH_2-$ methylene bridge groups in the polymer.

Results and Discussion

Coating of the Untreated Fiber with Phenolic Resin. Our previous work[29] showed that there was no chemical interaction between the untreated fiber and resin.

Coating of Electrochemically Oxidized Fibers with Phenolic Resin. Our previous studies[22] have shown that oxidization of this carbon fiber in ammonium carbonate solution generates surface functionalities such as hydroxyl-, carbonyl-, and nitrogen-containing groups. These functional groups can act as reactive sites for chemical bonding with the resin. When the surface treated fiber was coated with resin, the nitrogen 1s signal, resulting from the surface oxidation, was still detectable at a binding energy of 400 eV, and weak Si2s and Si2p signals were also seen at binding energies of 152 and 101 eV, respectively. The detection of nitrogen under the resin coating shows that the thin film technique that is used here effectively probes the interface region that lies under the surface resin film. 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. We also found silicon present when the fibers were exposed to coupling agents (GAL or PAL) alone and believe that some silicon-containing impurity is also present in the coupling agents. The presence of silicon will cause a slight increase in the amount of oxygen (assuming the silicon present as Si/O compounds). Some structure was

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

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

(25) 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.

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

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

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

(29) Wang, T.; Sherwood, P. M. A. *Chem. Mater.* **1994**, *6*, 788.

Table 2. Chemical Shift (C.S.), Relative Peak Area, and Peak Width in the 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	67.2	1.12	1.68	24.5	1.96	4.10	2.9	1.96	6.60	5.4	2.80			
0-d	284.6	53.5	1.48	1.56	18.1	1.86	2.47	19.0	1.84	4.21	6.9	1.84	6.30	2.6	3.10
0-e	284.6	51.3	1.30	1.56	35.7	2.50	3.86	9.7	2.50	6.39	3.3	2.98			
1-a	284.6	52.5	1.26	1.49	35.2	2.46	4.08	10.4	2.46	6.81	2.0	2.00			
1-b	284.6	57.1	1.44	1.59	24.2	2.06	3.51	14.7	2.72	6.34	3.9	2.58			
1-c	284.6	56.2	1.58	1.91	30.9	2.14	3.77	11.8	2.62	6.53	1.2	2.40			
1-d	284.6	53.8	1.46	1.79	35.2	2.40	3.99	9.7	2.60	6.53	1.2	2.20			
2-a	284.6	57.1	1.54	1.63	26.5	2.02	3.70	14.4	2.58	6.28	2.1	3.62			
2-b	284.6	56.8	1.44	1.70	27.8	1.98	3.71	14.7	2.68	6.50	0.8	1.96			
2-c	284.6	57.6	1.32	1.50	28.6	2.20	3.95	12.3	2.96	6.73	1.5	2.30			
2-d	284.6	55.1	1.48	1.91	35.6	2.38	4.09	7.6	2.20	6.28	1.8	2.64			
3-a	284.6	63.5	1.78	1.54	21.6	1.72	3.97	14.0	2.06	6.40	0.9	3.86			
3-b	284.6	52.5	1.50	1.70	35.3	2.30	3.93	10.8	2.42	6.44	1.4	2.84			
3-c	284.6	67.3	1.72	1.52	19.4	1.72	4.00	13.3	1.98	6.32	0.0	2.74			
3-d	284.6	64.6	1.62	1.53	23.6	1.86	4.09	10.6	2.18	6.83	1.3	3.96			

Table 3. Structural Parameters Used in Constructing the Models for the ab Initio Calculations

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	O=C	1.215
C=C	1.337	C−C in O=C−aryl	1.472
N−C=	1.322	N−C	1.472
N−H	0.993		

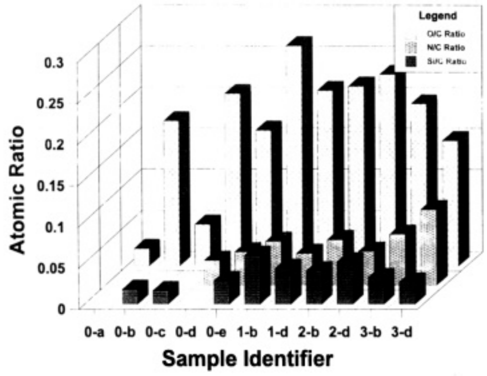

Figure 2. Atomic ratios obtained from core XPS data for carbon fiber, phenolic resin, and fibers electrochemically oxidized in ammonium carbonate solution with or without coupling agents.

found on the N1s peak after electrochemical oxidation of the fiber, but the N1s peak shape was retained for all the experiments carried out. The most intense N1s feature at 400 eV could correspond to functionalities such as NH_2, $-CONH_2$, $-CN$, and $-OCONH-$.[30,31]

Figure 1 shows a comparison between the C1s and valence region spectra for the phenolic resin 337T28 (0-b), ammonium carbonate oxidized fiber (0-d), and the oxidized fiber with the resin coating (0-e).

The curve fitting results for the C1s region are shown in Table 2. The C1s region of the resin coated fiber (0-e) has an oxide peak 1 with a chemical shift of 1.56 eV, close to that of the resin and the oxidized fiber, and an oxide peak 2 with chemical shift of 3.86 eV, corresponding to neither the resin nor the oxidized fiber. In the valence band spectrum of 0-e, a shoulder arises on the high binding energy side of the O2s region, which can be assigned to neither oxidized fiber nor the resin.

If no chemical interaction had occurred between the fiber and resin, then 0-e would be the simple addition of 0-b and 0-d. The spectrum showing the addition of 0-b and 0-d is shown in Figure 1. It can be seen that the addition spectrum can not match the experimental spectrum of 0-e. Figure 2 shows the results of atomic ratio calculations based upon the O1s, C1s, N1s and Si2p core levels. This a fall in oxygen concentration at the interface (Figure 2) which would be consistent with a condensation reaction that resulted in the loss of H_2O. In the case of a nitric acid oxidized fiber[29] where we find no evidence for chemical interaction between oxidized fiber and resin, the O/C ratio does not fall in a similar experiment. These results suggest that carbon fiber oxidized in ammonium carbonate solution has an interface chemical reaction when reacted with phenolic resin.

In an attempt to interpret the valence band spectrum of 0-e, and to account for the interfacial chemistry involved, ab initio calculations were performed. In Chart 1, two models for the interfacial cross-linking structures are proposed for the fiber/resin interactions based on the fiber surface functionalities. Ab initio Hartree−Fock SCF calculations were used to calculate the energy levels and to predict valence-band spectra based on the model structures for interfacial cross-linking using the structural parameters in Table 3. In Figure 3, the calculated spectra are compared with the experimental spectrum (0-e) after removal of a Tougaard background.[32] In the ether linkage model, the calculations indicate that 25−30 eV range of the spectrum corresponds to a mainly O2s region with the highest

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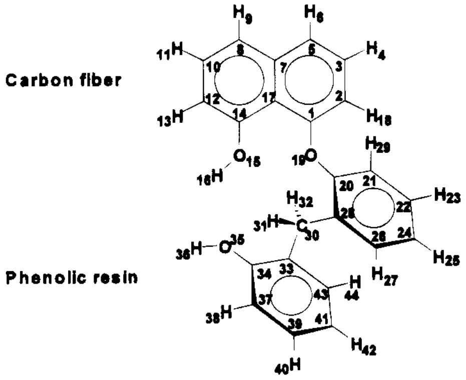
(30) Desimoni, E.; Casella, G. I.; Cataldi, T. R. I.; Salvi, A. M.; Rotunno, T.; Croce, E. Di *Surf. Interface Anal.* **1992**, *18*, 623.

(31) Briggs, D. *Practical Surface Analysis, Vol. 1: Auger and X-ray Photoelectron Spectroscopy,* 2nd ed.; Briggs, D., Seah, M. P., Eds.; Wiley: Chichester, 1990; p 445.

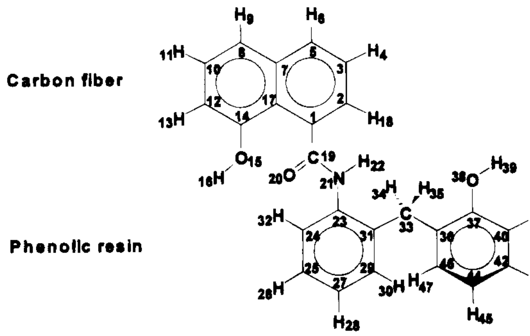
(32) Tougaard, S.; Sigmud, P. *Phys. Rev. B* **1982**, *23*, 4452.

Chart 1. Models for the Chemical Interaction between a Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and a Phenolic Resin

1. Ether linkage



2. Amide linkage



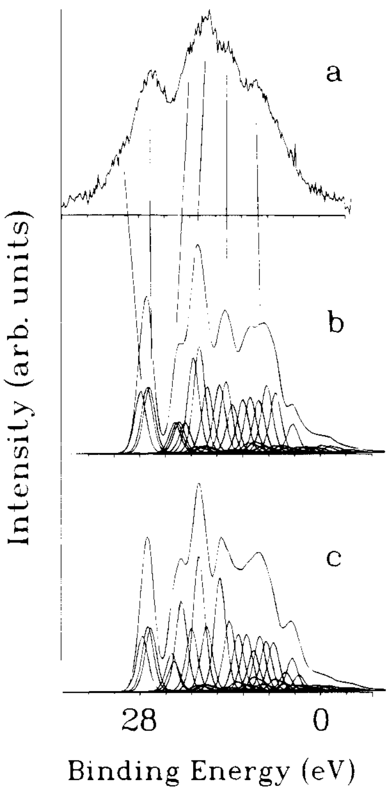


Figure 3. Comparison between experimental and calculated XPS valence-band spectra of a carbon fiber electrochemically oxidized in ammonium carbonate solution and coated with resin: (a) experimental, (b) calculated based on ether linkage model in Chart 1, and (c) calculated based on amide linkage model in Chart 1.

binding energy peak corresponding to O_{19} ($-$C$-$O$-$C), separated from the mainly $-$C$-$OH features (O_{35}, then O_{15}). In the amide linkage model, the calculations indicate that 25–30 eV range corresponds to a mainly O2s region with the highest binding energy peak corresponding to principally O_{20} ($-$C=O), separated from the mainly $-$C$-$OH features (O_{38}, then O_{15}). The main features of the experimental spectrum are all predicted in the calculated spectra. Both cross-linking models can adequately explain the features of O2s region of the experimental spectrum, making them appropriate suggestions for the interfacial chemical interaction that occurs between oxidized fiber and resin. In generating the calculated spectra, the photoelectron cross sections of O2s, O2p, N2s, and N2p were reduced to 50% of the normal Scofield[27] values to account for the very low concentration of the resin coating as compared to carbon substrate and thus a very low concentration of cross-linked components. We find that the ab initio method underestimates the separations between features in the mainly O2s region, which we discuss further in a calculation that compares ab initio and Xα calculation results.[33] This comparison shows that the calculation should predict a separation of about 3.8 eV for the two groups of peaks in Figures 3a,b, rather than the approximately 2 eV separation obtained from the spectrum obtained from ab initio calculations shown in Figure 3. It should be noted that the separation of the shoulder in Figure 3a is less than the separation of the Na2p peak from the O2s peak in Figure 4 (approximately 5 eV). The observed experimental separation between the features in the O2s region, about 3.8 eV, is more in keeping with the separation between a $-$C$-$O$-$C$-$ and a $-$C$-$OH functionality, than between a $-$C=O and $-$C$-$OH functionality,[34] though there is some variation in the position of $-$C$-$O$-$C- and $-$C=O groupings so that it is not possible to be conclusive on this assignment. The lack of any change in the N1s region after treatment of the oxidized fiber with the resin makes it more likely that the ether linkage is formed. It should be noted that the shifts in the O2s region are the opposite way around from that found in the O1s region because the former involve shifts caused by the mixing of atomic orbitals to form molecular orbitals, and the latter electrostatic interaction effects. We have previously discussed this effect.[34]

Coating of Electrochemically Oxidized Fibers with Resin and Coupling Agent GAL. GAL (glutaraldehyde) was investigated for its possible use as a coupling agent which would react with both the oxidized fiber surface and the resin to form a chemical link. Neutral and acidic conditions were used in coating the fibers. In both cases the resulting spectra indicated that chemical interaction had occurred between the fiber and resin since they could not be constructed by simple addition of the spectra of oxidized fiber and resin. In addition, treatment of the oxidized fiber with the coupling agent alone, in either neutral or acidic solution also led to chemical interaction. The results are shown

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(33) Wang, T.; Sherwood, P. M. A., to be published.

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

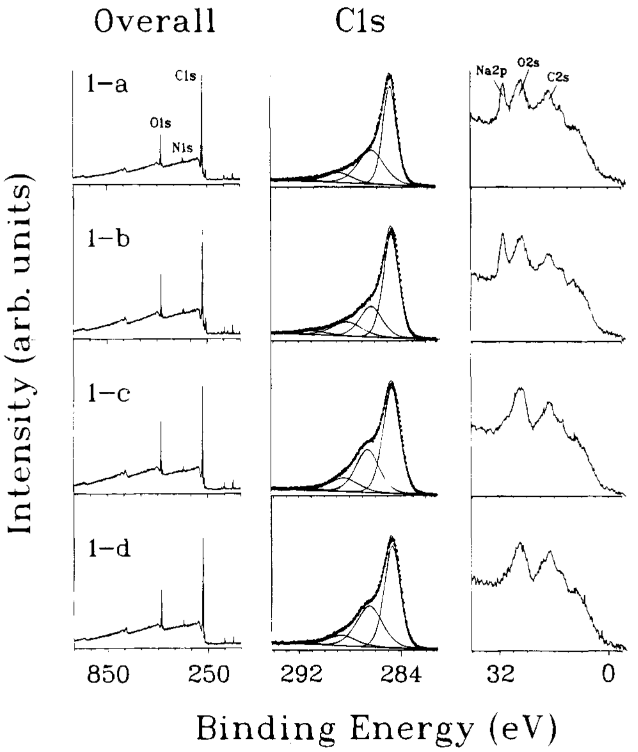

Figure 4. XPS spectra of carbon fibers electrochemically oxidized in ammonium carbonate solution and coated with resin with the coupling agent GAL: (1-a) oxidized fiber exposed to GAL, (1-b) oxidized fiber exposed to a mixture of GAL and resin, (1-c) oxidized fiber exposed to acidified GAL, and (1-d) oxidized fiber exposed to an acidified mixture of GAL and resin.

in Figure 4, which shows the overall, C1s, O1s, N1s, and valence-band XPS spectra for these four experiments.

The results indicate that there is a significant difference in the C1s and valence-band regions between the case in neutral and acidic solution. There were smaller differences in these regions for the case where the oxidized fiber was exposed to only the coupling agent, and where the oxidized fiber was exposed to coupling agent and resin both in either neutral or acidic solutions. There were no significant differences in the O1s and N1s regions, the O1s region being a single peak and the N1s region appearing identical to that of the electrochemically oxidized fiber.

The most striking difference between neutral and acidic solutions was the appearance of a narrow and intense peak at highest binding energy (31eV) in the valence-band region for the neutral solution cases. This peak was shown to be due to the Na2p peak from sodium ions, and sodium was detected as the Na $KL_{23}L_{23}$ Auger peak at 264 eV, which was absent in the spectra for acidic solutions. The presence of sodium was also detected in the solution by atomic absorption spectroscopy, which showed a sodium content of 250 ppm in the neutral solutions. Further examination of other systems showed that sodium ions have a strong tendency to attach to oxidized surfaces (both carbon and metal) in preference to being in acetone/water mixtures with a high concentration of acetone. For this to happen, the surface has to be hydroxylated, as in the present case because ammonium carbonate electrochemical oxidation leads to a high concentration of surface hydroxide. The behavior is terminated in acidic solution. Thus we find similar behavior on metal hydroxide surfaces—we have reported full details of this work in another publication,[33] and so further details will not be given in this paper. When the fiber was treated in neutral solution with an aqueous solution of GAL with no acetone present, then the spectra appeared almost identical to that of 1-c. It is clear then that the Na2p peak only appears when the solution contains a high percentage (>75% by volume in this work) of acetone, and the solution is neutral.

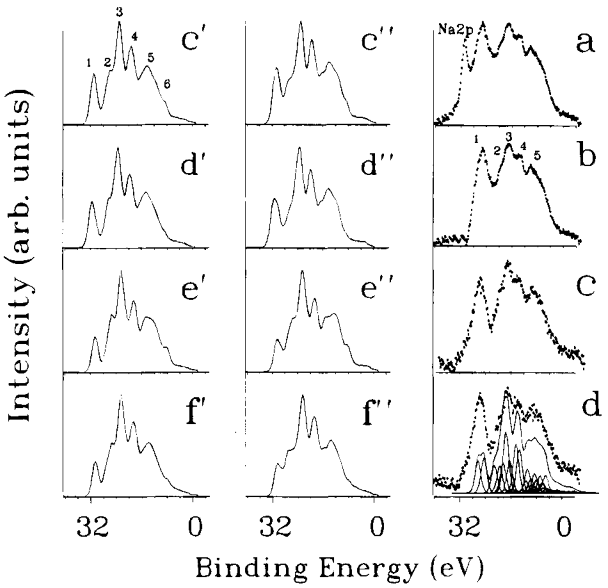

Figure 5. Comparison between experimental and calculated XPS valence band spectra of a carbon fiber electrochemically oxidized in ammonium carbonate solution and exposed to coupling agent and resin. (a) Spectrum of an oxidized fiber exposed to a neutral acetone solution of GAL and resin. (b) Spectrum (a) after removal of the Na2p peak at 31eV. (c) Spectrum of an oxidized fiber exposed to an acidic acetone solution of GAL and resin. (d) Spectrum of an oxidized fiber exposed to an acidic acetone solution of GAL alone. A calculated spectrum representing the interaction of GAL and oxidized fiber is shown below the experimental spectrum. (c′ and c″) represented calculated spectra for the model in Chart 2, (d′ and d″) the calculated spectra for the model in Chart 3, (e′ and e″) the calculated spectra for the model in Chart 4, and (f′ and f″) the calculated spectra for the model in Chart 5. The notation ′ denotes an acetal resin linkage between GAL and the resin, and ″ a hemiacetal resin linkage between GAL and the resin.

The C1s region showed more C/O functionality in acidic solution or for neutral solution with no acetone present. In neutral solution with acetone present the oxidized fiber–GAL–resin system (1-b, Table 1) has an oxide component 1 with a chemical shift of 1.59 eV, close to that of the resin and the oxidized fiber, and an oxide 2 peak with a chemical shift of 3.51 eV, corresponding to neither the resin nor the oxidized fiber. In acidic solution, or in neutral solution with no acetone present, the oxidized fiber–GAL–resin system (1-d) has an oxide component 1 with a chemical shift of 1.79 eV, significantly different from that of either fiber and resin, and an oxide 2 peak with a chemical shift of 4.0 eV, again different from either the resin or fiber. The reasons for the greater amount of C/O functionality in acidic solution or in a neutral solution with no acetone present are discussed below.

Figure 5 compares the valence band regions (after removal of a nonlinear background) for the neutral and acidic solutions with calculated valence band spectra for a range of possible interactions mechanisms shown in Charts 2–5. Figure 5a shows the valence band region in the oxidized fiber–GAL–resin system for the neutral acetone solution case, and Figure 5b shows the same spectrum with the Na2p region subtracted out. Figure 5c shows the valence band region in the oxidized fiber–GAL–resin system for the acidic acetone solution case, and Figure 5d shows the valence band region for the oxidized fiber exposed to a neutral aqueous solution of GAL. It is possible to identify six features in the valence-band region, five features are shown in the experimental spectrum (Figure 5b), and six in the calculated spectrum (Figure 5c′). Feature 1 is the mainly O2s region, features 2, 3, and 4 correspond to the mainly C2s region and are characteristic of an aromatic grouping, and features 5 and 6 arise from O2p/C2p contributions. The experimental spectra of Figure 5c,d are very similar with a separation between peaks 1 and 3 of 8.80 eV. We do believe that both parts c and d of Figure 5 are different from that of the oxidized fiber alone. Thus comparison of 0d in Figure 1 (oxidized fiber alone), and 1b and 1c in Figure 4 show small but significant differences in the C1s and valence band regions. The experimental spectrum of Figure 5b is similar to the other experimental spectra, though the separation between peaks 1 and 3 is smaller (8.25 eV). Figure 5d has a calculated spectrum corresponding to the fragment in bold in Chart 3 omitting the right half of the molecule, i.e., to a carbon fiber with a GAL group attached. Two features are seen in the O2s region (peak 1) corresponding to C–O–C at the higher binding energy and –C–OH at the lower binding energy. It is not possible to resolve such features in the experimental spectrum. The component peaks of the calculated spectrum correspond to the positions of the calculated energy levels grouped together to give 20 peaks (see above).

A series of calculated spectra will now be constructed. In generating these spectra, we have considered reactions with various groups that we know to occur on the oxidized carbon fiber surface. These surface groups are amide, amine and hydroxide (–OH). The spectrum of the oxidized fiber does not make it possible to unambiguously distinguish between these groups.[22] As a result of this uncertainty, one cannot expect an exact match with the calculated spectrum for any one reaction mechanism.

The calculated spectra are separated into two columns, the one on the left (indicated by ′) involving an acetal linkage between the phenolic resin and GAL (the upper of the two structures in the charts), and the one in the center (indicated by ″) corresponding to a hemiacetal linkage between the phenolic resin and GAL (the lower of the two structures in the charts). Details of the mainly O2s region of the spectrum for an acetal and hemiacetal linkage, and an alkylidene linkage is shown in Figure 6. In the acetal linkage case there are two O–C–O features, one at high binding energy (O–C–O bonding) and one at low binding energy (O–C–O nonbonding). No component peaks are shown in Figure 5, as the spectra were obtained by combining two molecular fragments to give the total fragment shown as a bold outline in the charts. Four reaction schemes are given:

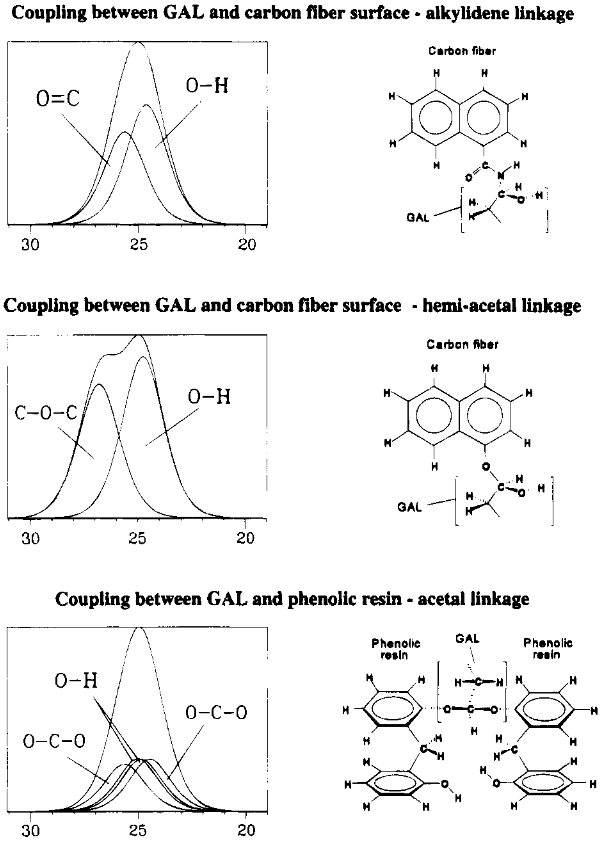

Figure 6. O2s region XPS spectra calculated by ab initio Hartree–Fock calculations for parts of the coupling models for the coupling agent GAL bonding an oxidized carbon fiber surface with a phenolic resin.

(a) Chart 2: reaction with an amide grouping on the oxidized fiber to give an alkylidene linkage between the fiber and the resin.

(b) Chart 3: reaction with an –OH grouping to give a hemiacetal linkage with the oxidized fiber.

(c) Chart 4: reaction with an amine group on the oxidized fiber to give an imine linkage with the oxidized fiber.

(d) Chart 5: reaction with an amine group on the oxidized fiber to give an enamine linkage with the oxidized fiber.

Another possible reaction scheme, namely one where the GAL bonds to the carbon fiber to form loops (i.e., both –C=O groups react with the fiber surface) was not investigated. Such a structure has been suggested to be the predominant interaction process in reactions between carbon fibers and diamines.[35,36] However if this type of grouping is formed then there will be no reaction with the resin. If this grouping is formed then the spectrum will probably appear similar to the calculated spectrum in Figure 5d.

The calculated spectra in Figure 5 all appear fairly similar, with some slight differences. On the basis of these calculated spectra it can be seen that valence band XPS is not easily able to distinguish between these four possible mechanisms. However closer examination indicates that feature 6 is lost for the hemiacetal linkage (d′ and d″) with the –OH grouping on the fiber shown

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(35) Barbier, B.; Pinson, J.; Desarmot, G.; Sanchez, M. *J. Electrochem. Soc.* **1990**, *137*, 1757.

(36) Murray, R. W. *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, 1984; Vol. 13, pp 191–368.

Chart 2. Scheme for the Interfacial Reaction Involving an Alkylidene Linkage between a Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and a Phenolic Resin in the Presence of GAL

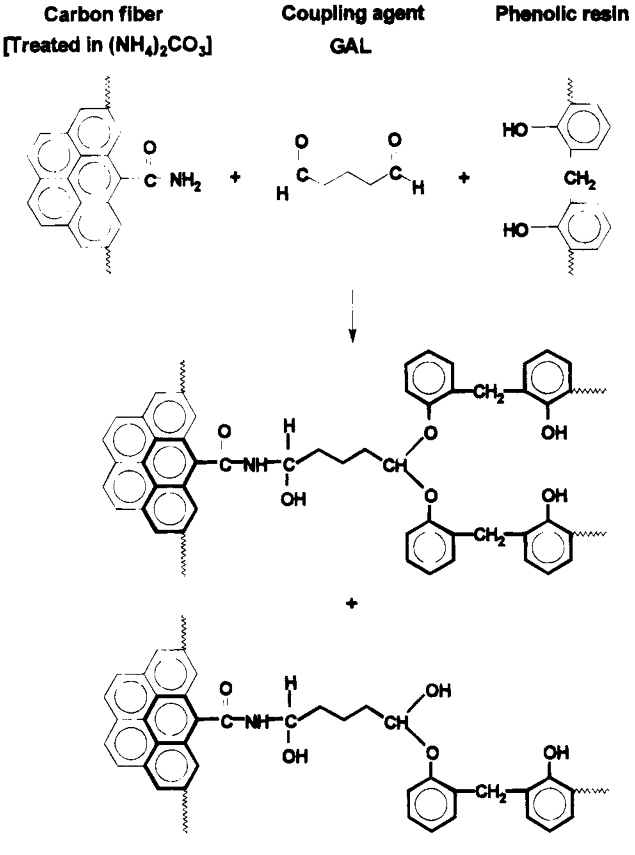
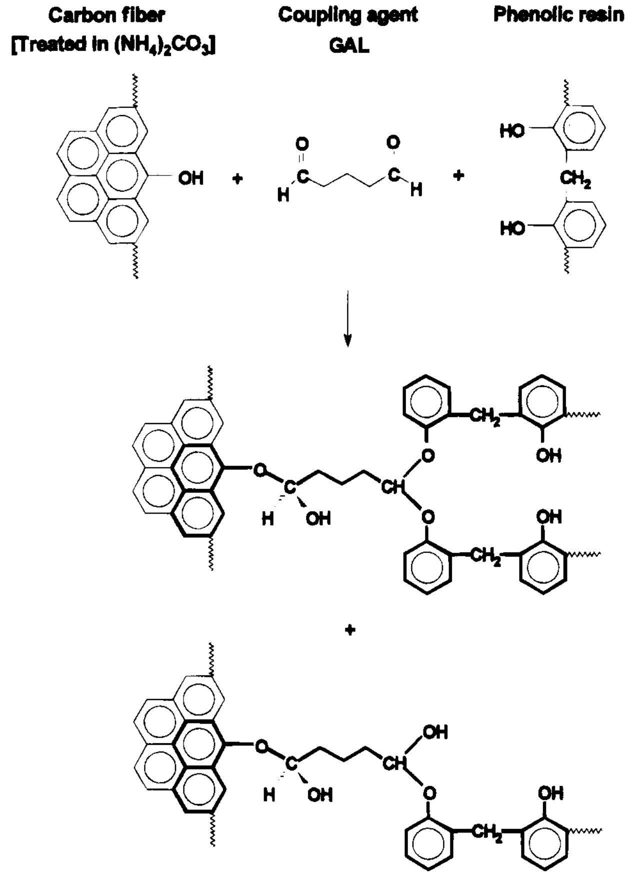


Chart 3. Scheme for the Interfacial Reaction Involving a Hemiacetal Linkage between a Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and a Phenolic Resin in the Presence of GAL

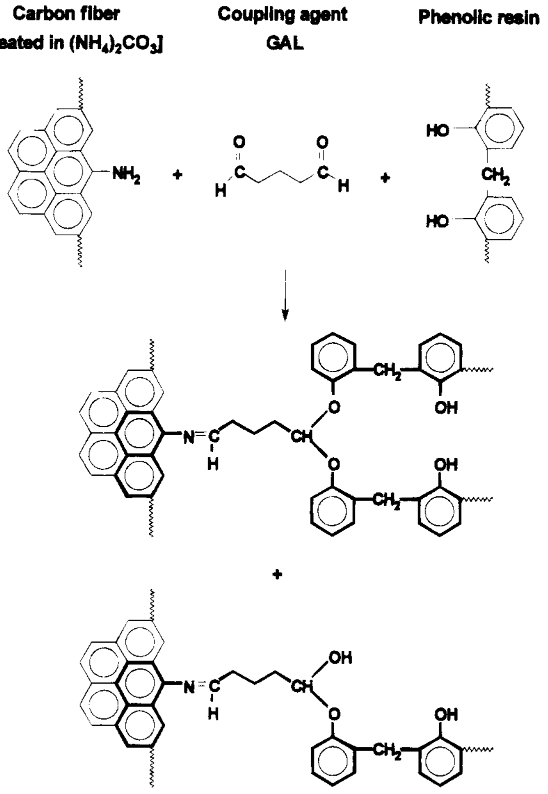


in Chart 3. This would agree with the absence of a feature 6 in the experimental spectra. However there is some uncertainty here as there is also a reduction in the amount of feature 6 in c″, f″, and f′. One also notes that there was no change in the N1s spectra, which would be consistent again with the choice of the scheme in Chart 3, as all the other schemes involve reaction with amide or amine grouping on the fiber surface. Thus the hemiacetal linkage scheme with −OH groups on the fiber seems the most likely reaction route, a suggestion that is also consistent with the fact that −OH groups are the most predominant grouping on the fiber surface after electrochemical oxidation in the ammonium carbonate electrolyte. The strong adsorption of sodium ions is consistent with the presence of surface −OH groups, and this is discussed further below.

The differences in the peak 1−3 separation between the neutral acetone solution (Figure 5b) and acidic/neutral aqueous solution cases (Figures 5c and d) may well arise as a result of a different relative amount of −C−O−C− (which would give a higher O2s binding energy and thus greater 1−3 separation) and −C−OH groupings at the interface. Both −C−O−C- and −C−OH features would give rise to the same peak (shifted about 1.6 eV) in the C1s region. A higher level of −C−O−C− groupings in 1-c and 1-d would be consistent with the explanation to be presented below.

The higher C/O functionality for the C1s region in acidic solutions or solutions where no acetone is present can be understood by further examination of the data. The atomic ratios shown in Figure 2 (see definitions in Table 1) show that treatment under neutral acetone solution conditions (1-b) led to a significant increase in the O/C ratio over either the oxidized fiber (0-d) or the resin (0-b). Figure 2 shows that treatment under acidic conditions (1-d) leads to little change in the O/C ratio as compared to either 0-d or 0-b. The increasing amount of oxygen in neutral acetone solution must be the result of some adsorbed oxygen containing non-carbon species that acts as a counter ion, and this is almost certainly hydroxide ions present in the GAL solution. The greater C/O functionality in the C1s region in 1-c and 1-d is consistent with a model where the GAL first reacts with the oxidized fiber surface to form a GAL group attached to the surface with a free −C=O group (as discussed above for the valence band region of 1-d (Figure 5d). This reaction is competitive with the attachment of sodium ions to the surface hydroxide groups of the fiber, and thus there are more C/O shifted features in the C1s region in acidic solutions or neutral solutions with no acetone present, since in this case sodium ions are more likely to stay in aqueous solution, and so do not compete with GAL for hydroxide sites on the fiber. In this model 1-a and 1-b would be expected to show more −C−OH groups from the underlying oxidized fiber, since it is these groups that interact with the sodium ions. In 1-c and 1-d there would be far fewer −C−OH groups and more −C−O−C− groups as the latter result from the interaction of the oxidized fiber with GAL. This is consistent with the observation above.

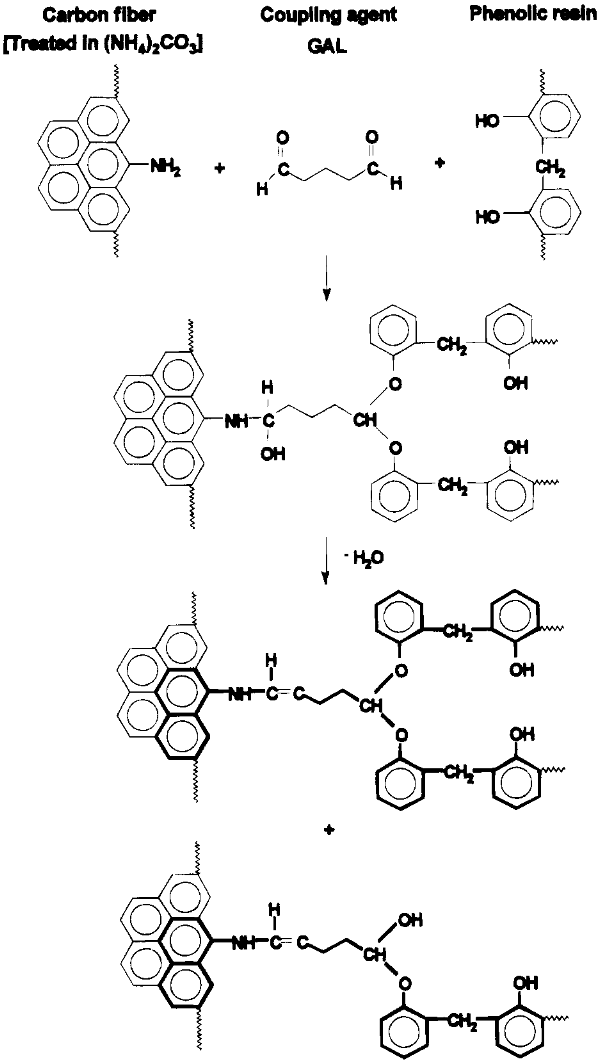
Chart 4. Scheme for the Interfacial Reaction Involving an Imine Linkage between a Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and a Phenolic Resin in the Presence of GAL



GAL, with its two $-C{=}O$ groups, is well placed to act as a coupling agent where one $-C{=}O$ group interacts with the oxidized fiber and the other with the resin. There is little change in the spectral appearence in going from the case where GAL is attached to the oxidized fiber, and where GAL is attached to both oxidized fiber and resin, i.e., 1-a to 1-b and from 1-c to 1-d. This is because the functional groups that arise in both cases are $-C-O-C-$ and $C-OH$ as indicated in Chart 3, and because the sodium ions have only a weak interaction with the resin compared with the chemical bonding that occurs with the remaining $-C{=}O$ group of GAL (after the other group interacts with the oxidized fiber). Thus the level of sodium ions is much the same for 1-a and 1-b.

The principal conclusion in this section is that GAL does act as a coupling agent that chemically bridges the oxidized fiber to the resin.

Chart 5. Scheme for the Interfacial Reaction Involving an Enamine Linkage between a Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and a Phenolic Resin in the Presence of GAL



Coating of Electrochemically Oxidized Fibers with Resin and Coupling Agent PAL. Another cross-linking agent, propanoaldehyde (PAL), was used as a possible means of chemically interacting the oxidized fiber with the resin. Neutral and acidic conditions in acetone solution were used in coating the fibers. The results are shown in Figure 7, which shows the overall, C1s, and valence-band XPS spectra for these four experiments. In both cases the resulting spectra indicated that chemical interaction had occurred between the fiber and the coupling agent since the spectrum changed from that of the oxidized fiber. However, unlike the GAL case, the spectra changed significantly in going from the case of oxidized fiber exposed to acidified PAL, and the oxidized fiber exposed to resin and acidified PAL. There was a noticeable increase in the C1s intensity of the chemically shifted features around 1.6−1.9 eV, which would be consistent with the addition of the resin spectrum to system where the PAL preferentially reacts with the fiber surface, leaving the resin unreacted with the surface. One also notes that the O/C ratio increases in going from the case of oxidized fiber/acidified PAL to oxidized fiber/acidified PAL/resin as can be seen by comparing the relative intensity of the O2s region in going from 2-c to 2-d (Table 1). In the case of PAL and oxidized fiber in neutral acetone solution some sodium ions are attached to oxidized fiber $-OH$ groups, as can be seen by the Na2p feature in the valence band of 2-a. However on using oxidized fiber/PAL (acidified or not) and resin, no Na2p feature is seen. This result is consistent with a model where the PAL has a higher affinity than GAL for the oxidized fiber surface and thus competes more effectively with sodium ions for sites on the fiber surface. This may appear contradictory as GAL has two $-C{=}O$ groups, but it may be that steric factors are important here, thus the possibility of loop structures (see the

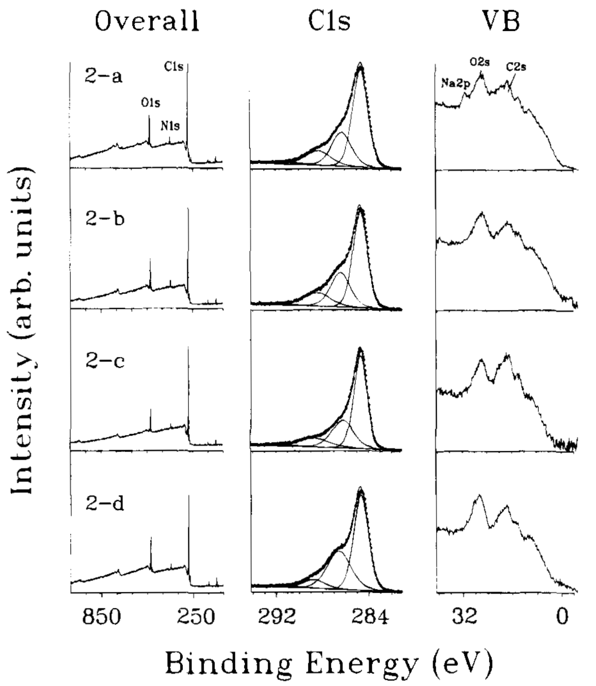


Figure 7. XPS spectra of carbon fibers electrochemically oxidized in ammonium carbonate solution and coated with resin and the coupling agent PAL: (2-a) oxidized fiber exposed to PAL, (2-b) oxidized fiber exposed to a mixture of PAL and resin, (2-c) oxidized fiber exposed to acidified PAL, and (2-d) oxidized fiber exposed to an acidified mixture of PAL and resin.

discussion above) that could form with GAL are less favored at the relatively high level of surface functionality that we for our treated fibers. Unlike GAL, however, PAL has only *one* −C=O group, which when reacted with the surface leaves a surface with little affinity for resin. When the oxidized fiber/PAL/resin system is studied, it seems that the resin weakly adheres to sodium ions attached to −OH sites on the oxidized fiber surface, thus covering the sodium ions and resulting in a spectrum (2-b) with no sodium ions present. This would be true if the peak at 284.6 eV in these spectra consisted of features from the resin alone and not the graphitic backbone of the fibers. There is no way that one can be conclusive about this because the C1s line widths are similar for the resin alone and the oxidized fiber (see Figure 1, 0-d and 0-b), and so the preceding discussion can be regarded as somewhat speculative.

The principal conclusion in this section is that PAL does not act as a coupling agent between the oxidized fiber and resin, because even though it interacts with the oxidized fiber, once such interaction occurs there is no further reaction path with the resin. The effective action of GAL is supported by the observation in dental applications that GAL has been found to be particularly effective as a bonding agent with various catalysts in producing dental resin composites with good mechanical strength.[37,38]

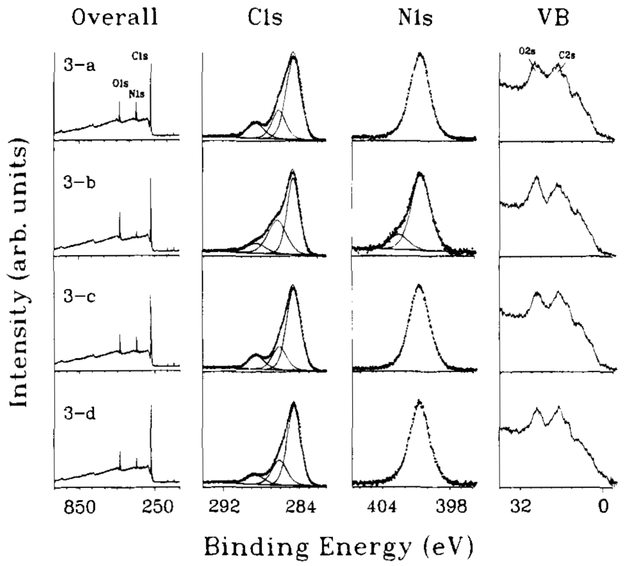


Figure 8. XPS spectra of carbon fibers electrochemically oxidized in ammonium carbonate solution and coated with resin and diisocyanate coupling agents: (3-a) oxidized fiber exposed to DIB, (3-b) oxidized fiber exposed to a mixture of DIB and resin, (3-c) oxidized fiber exposed to DIH, and (3-d) oxidized fiber exposed to a mixture of DIH and resin.

Coating of Electrochemically Oxidized Fibers with Diisocyanate Coupling Agents. On the basis of the fact that oxidation treatment of carbon fiber in ammonium carbonate solution can generate nitrogen-containing functionalities on the fiber surface, another route was explored to establish fiber/resin chemical interaction with the use of diisocyanate as a coupling agent due to the anticipated high reactivity of isocyanate group with nitrogen-containing groups, such as primary amine and secondary amine. Diisobutacyanate (DIB), and diisohexacyanate (DIH) were used in this study. The spectra (Figure 8) indicate that in most cases the coupling agents are attached to the oxidized fiber surface, leading to a marked increase in the amount of surface nitrogen. Figures 2 and 8 indicate that the DIB/oxidized fiber/resin system has the lowest nitrogen level, and indeed in this case the spectra appear closer to those in Figure 1 and 4. In other cases the N/C ratio is so high (and the O/C ratio correspondingly lower, Figure 2) that the C1s region appears significantly different. We believe that in this case the C1s peak 1, shifted by about 1.5 eV (3-a, 3-c, and 3-d), corresponds largely to C−N functionality, and the features shifted by about 4 eV to the isocyanate group −N=C=O (see Table 1 for sample definitions). In the valence band the valley between the mainly O2s and mainly C2s region is somewhat reduced due to the presence of N2s functionality.

We believe that these results are consistent with a situation where the coupling agents react and/or adsorb onto the oxidized fiber surface. There is no evidence for the reaction of the coupling agents with the resin. The difference between 3-b and the other spectra probably arises because when resin is present it preferentially reacts with the fiber surface. The suggestion is then that 3-b should appear similar to the oxidized fiber coated with resin without coupling agent (O-e) in Figure 1. Visual comparison of O-e with 3-b for the C1s region and the valence band reveals considerable similarities. Of course *exact* agreement would not be expected.

Spectra 3-a, 3-c, and 3-d are consistent with a strong adsorption of the coupling agent rather than chemical reaction with the oxidized fiber surface. Thus in this case these coupling agents would seem to have little

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(37) Peutzfeldt, A.; Asmussen, E. *J. Dent. Res.* **1992**, *71*, 1522.
(38) Sterrett,J. D.; Sutow,E. J.; Murphy,H. J. *Quintessence Int.* **1992**, *23*, 61.

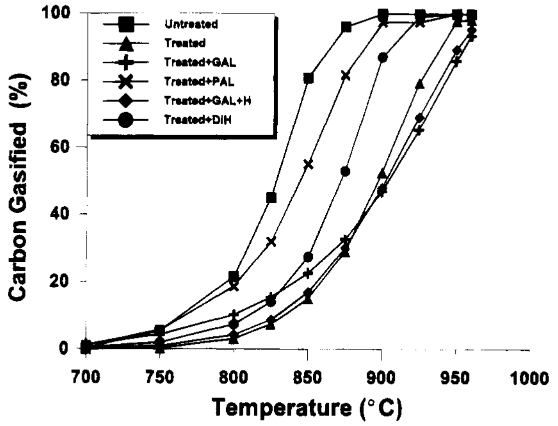

Figure 9. Thermogravimetric analysis results of oxidation behavior of resin-coated carbon fibers showing the effects of fiber surface treatment and coupling agents. The percentage of carbon gasified represents the percentage mass loss during gasification.

effect in enhancing fiber/resin interaction. The ineffective nature of these coupling agents probably arises because there is not a high enough concentration of amine groups on the oxidized fiber surface to react with these coupling agents. It may be that reaction could be induced if a suitable catalyst were used.

The principal conclusion in this section is that diisocyanate coupling agents do not act as a coupling agent between the oxidized fiber and resin.

Oxidation Behavior of Resin-Coated Fibers. Figure 9 shows the percentage mass loss of resin coated fibers due to gasification when the fiber samples are subjected to heating from ambient temperature to 1000 °C at a constant heating rate of 10 °C/min. The mass change was recorded continuously as the temperature increased linearly. Six types of sample were studied, namely, an untreated fiber with resin coating, a fiber oxidized in ammonium carbonate solution and coated with resin, oxidized fibers with resin coating in the presence of GAL, PAL, acidified GAL, and DIH, respectively. The samples for this study used the same amount of coating as those used for XPS analysis. It can been seen from Figure 9 that the untreated fiber with resin coating begins to lose weight and burns off completely before any other samples and thus has the lowest overall oxidation stability of all the samples upon heating. The surface oxidized fiber with resin coating shows a significantly improved oxidation stability. For the surface treated fiber coated with resin together with GAL, the rate of mass loss is a little faster than that of the surface oxidized fiber with resin coating before 40% of the carbon is gasified, but becoming slower after 40% carbon gasification, showing a fairly improved overall oxidation stability in later stages of the oxidation process. The relatively poor oxidation resistance in early stage and improved oxidation resistance at higher temperature stage might imply that the interfacial reaction was incomplete during the sample preparation and at higher temperature measurement environment the interaction was promoted and gradually went to completion. Such an observation would be consistent with the loss of adsorbed sodium ions in the heating process. Coating resin on the fiber together with GAL in neutral or acidic conditions leads to a similar oxidation behavior, especially at later stages in the oxidation process. The surface oxidized fiber coated with resin together with PAL, or the coated resin together with DIH, showed poorer oxidation resistance than either the oxidized fiber alone, or the fiber treated with GAL as a coupling agent.

These results show that the best oxidation resistance is found in the two cases where we consider chemical interaction between the oxidized fiber and resin to have taken place, namely the oxidized fiber and resin alone and the oxidized fiber/GAL/resin system. In the case of PAL the suggested strong interaction of the coupling agent with the oxidized fiber, leaving weak interaction between fiber and resin, results in poor oxidation resistance—only slightly better than the untreated fiber and resin. In the case of DIH the suggested adsorption of this agent onto the oxidized fiber also leads to poorer oxidation resistance than in the cases where chemical interaction between fiber and resin is indicated.

Conclusions

XPS studies show that electrochemically oxidizing carbon fibers surface in ammonium carbonate solution is an effective method for promoting chemical interactions between fiber and phenolic resins. Direct reaction of a carbon fiber, electrochemically oxidized in ammonium carbonate solution, and a phenolic resin probably leads to a $-C-O-C-$ type linkage between the fiber and resin. Use of the bifunctional ($-C{=}$)) coupling agent glutaraldehyde probably results in a hemiacetal linkage with a $-C-O-C-$ link. The experimental spectra for the interfacial region probed are consistent with spectra calculated by ab initio Hartree–Fock calculations for the suggested chemical linkages.

The results of thermogravimetric analysis suggest that electrochemical oxidation of a carbon fiber surface in ammonium carbonate solution improves the oxidation stability of resin-coated carbon fiber, by direct chemical reaction between oxidized fiber and resin, or by the use a chemically reacting coupling agents (GAL). This result is consistent with reports that fiber surface treatment in other electrolytes, such as sodium hypochlorite solution ($NaClO_3$) can improve oxidation resistance as well.[39]

Interfacial chemical reaction, with or without the use of coupling agents, clearly has a role to play in the improvement of oxidation stability. Such reactions would seem to be effective in reducing diffusion of oxygen along the interface. 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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(39) Li, T.; Yang, Z.; Qiao, S.; Zheng, X. *Carbon* **1993**, *31*, 1361