X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 25. Interfacial Interactions between PEKK Polymer and Carbon Fibers Electrochemically Oxidized in Nitric Acid and Degradation in a Saline Solution

Yu-Qing Wang, Feng-Qiu Zhang, and Peter M. A. Sherwood*

Department of Chemistry, Willard Hall, Kansas State University,
Manhattan, Kansas 66506-3701

Received July 7, 2000. Revised Manuscript Received November 7, 2000

The interfacial interaction between surface-treated pitch-based carbon fibers and poly(ether-ketone-ketone) (PEKK) was investigated using core and valence band X-ray photoelectron spectroscopy (XPS) by using a thin film approach that allowed the buried interface to be investigated by XPS. The extent of interaction of the surface-treated fiber and the matrix material has a significant effect on the strength of the ultimate composite. This paper reports the interfacial reaction between fiber and matrix and the stability of the interface in simulated environmental conditions by exposing the PEKK-coated fibers to a saline solution. The surface chemistry of the carbon fibers was modified by electrochemical oxidation via galvanostatic treatment in nitric acid. Interfacial chemical reaction was observed mainly between the carbonyl group in PEKK and the hydrogen-bridged structure (HBS) on the fiber surface to form C−O−C bonding. When the interface was exposed to a saline solution, it was found that the PEKK polymer was degraded by this solution, together with some additional X-ray damage. It was found that there was a change in the surface functionality that suggested the replacement of C═O bonds at the interface to COOH and/or C−OH bonds. The degradation of the interfacial chemistry between the fiber and PEEK in saline solution resulted mainly from the absorption of water and the formation of COOH functionality. The valence band spectra were interpreted by spectra generated from molecular orbital calculations.

Introduction

A novel semicrystalline polymer, poly(ether-ketone-ketone) (PEKK), has been used as an effective matrix resin for advanced composites by duPont and others[1−3] because it has better thermal stability, excellent mechanical properties, improved processibility, and environmental durability[4] when compared to other thermoplastic resins, like PEEK (polyether-ether-ketone).[5] The interfacial reaction between PEKK and reinforcements, such as carbon fibers in composites, is closely related to the surface chemistry of PEKK and the reinforcing carbon fibers.[6] Thus, it is important to study this interfacial chemistry to understand the performance of advanced composites because the property of the composite depends not only on the fiber and matrix but also more importantly on the chemical and physical interaction between the fibers and matrix. The properties of the fiber-reinforced polymer composites may be degraded as a result of environmental attack during service. Previous studies have shown that the degradation resulting from environmental exposure was mainly caused by the weakening of the interfacial bonding as a result of the change of molecular structure in the interface region under attack from agents such as light, water vapor, and acid rain.[7−8] Therefore, the investigation of the chemical change of the fiber/matrix interface under the environmental conditions is necessary for the design of composites in practical applications. The surface chemistry of PEKK has been well characterized by XPS[9] and the surface modification of carbon fibers has been well investigated for many years in our laboratory,[10−11] which have usually involved surface treatment of the fibers using electrochemical polarization under potentiostatic and galvanostatic conditions.[12−13] The surface treatments have successfully

---

* To whom correspondence should be addressed.

(1) Chang, Y. *SAMPE Q.* **1988**, *19*, 29.
(2) Ke, Y. Z.; Wu, Z. W. *J. Appl. Polym*. Sci. **1998**, *67*, 659.
(3) Lin, H. R.; Advani, S. J. *Polym. Compos.* **1997**, *18*, 405.
(4) Chang, I. Y.; Hsiao, B. S. *36th Int. SAMPE Symp.* **1991**, 1587.
(5) Kausch, H. H. *Advanced Thermoplastic Composites Characterization and Processing*; Hauser and Mücher: Germany, 1992.
(6) Bradford, D.; Lease, K.; Sherwood, P. M. A. *J. Compos. Technol. Res.* **2000**, *22*, 53.
(7) McMillan, A. R.; Jones, I. A.; Rudd, C. D.; Middleton, V. *Composites Part A* **1998**, *29*, 885.
(8) Sliva, M. A.; Chu, C. C.; Adisaputro, I. A. *J. Biomed. Mater. Res.* **1997**, *36*, 469.
(9) Wang, T.; Xie, Y.; Sherwood, P. M. A. *Chem. Mater.* **1993**, *5*, 1007.
(10) Sherwood, P. M. A. *J. Electron Spectrosc.* **1996**, *81*, 319.
(11) Proctor, A.; Sherwood, P. M. A. *J. Electron Spectrosc.* **1982**, *27*, 39.
(12) Xie, Y.; Sherwood, P. M. A. *Appl. Spectrosc.* **1991**, *45*, 1158.
(13) Xie, Y.; Sherwood, P. M. A. *Appl. Spectrosc.* **1989**, *43*, 1153.

10.1021/cm000555t CCC: $20.00

introduced chemical groups onto the carbon fiber surface, which include hydroxide (C−OH), hydrogen-bridged oxide structure (HBS), carbonyl (C═O), and carboxyl (COOH) groups,[14−16] and improved the wettability and reactivity of the fibers with resin.[17−19]

XPS can be applied as an effective method for the study of the buried interface by using a thin film coating on the fiber, such that a significant signal can be observed from the interface region.[20−23] The resin/carbon fiber interfacial reaction has been successfully investigated using this approach for cases where the oxidized carbon fiber surface reacts directly with the matrix and when the reaction occurs via coupling agents.[24−25] Furthermore, ab initio calculations of molecular units that correctly model the interface have been used to predict the valence band spectra (VB) that arise in such interfacial reactions,[26] providing theoretical support for suggested chemical reaction models.

In this paper we report the detailed investigation of the interfacial reaction between carbon fibers and PEKK film and show how this interface behaves when it is exposed to a saline solution that simulates real environmental conditions. We report the use of ab initio calculations to interpret the valence band spectra that results from the interfacial region.

Experimental Section

Materials. The carbon fibers used in this study were untreated and unsized E-120 high-modulus pitch-based fibers with a density of 2.14 g/cm^3 and a mean filament diameter of 9.2 μm in a 3000 fiber tow provided by the duPont Co. The PEKK was also supplied by duPont (P11923-15501) in the form of pellets with an average diameter of about 2 mm. It is additive-free with a number-average molecular weight of 8220 (GPC) and a weight-average molecular weight of 28 500 (GPC). The glass transition temperature is less than 429 K (DSC) and the melting temperature is 578 K (DSC).

Pretreatment of Carbon Fibers. The electrochemical oxidization was carried out using a standard three-electrode glass cell and Ministat Research Potentiostat (Model 402R).[19] A bundle of carbon fibers acted as the working electrode, and a piece of platinum foil was used as the counter electrode. The potential of the working electrode was measured with respect to a saturated calomel reference electrode (SCE); 1 M HNO_3 (ACS reagent grade) was used as the electrolyte, which was prepared with quadruply distilled (4-D) water. The carbon fibers were anodically oxidized for different periods from 10 s to 10 min, under galvanostatic conditions[22] with a current of 0.5 A, respectively. The treated carbon fibers were removed from the electrolyte, washed thoroughly with 4-D water, and then dried in an oven at 70 °C for 24 h.

Fabrication of Carbon Fiber Coated with PEKK. The interfacial reaction study was carried out by coating an extremely thin layer of PEKK onto the fiber surface. The thickness can be controlled by the concentration of the PEKK solution. The solution consisting of a 1:1 mixture of phenol and 1,2,4-trichlorobenzene was used to dissolve the PEKK pellets at 373−393 K under stirring.[9] The PEKK solution of 1 wt % was used to cast the pure PEKK film and pure PEKK coating onto a copper sheet; 0.25 wt % solution was used to coat the fibers. The fibers were heated to 323 K before coating and then were kept in solution for 10 min. After taking fibers out from the PEKK solution, the coated fibers were put on Kimwipes[7] paper tissue to remove the nonbond resin. The coated copper and fibers were dried in a oven for 1 week at 353 K and then dried in a vacuum oven for a week at 363 K to remove the solvents.

Treatment of PEKK and PEKK-Coated Fibers in Saline Solution and under Exposure to X-Radiation. To investigate the properties of composites in a practical application, saline solution kept at high temperature is usually used for accelerating media.[27] PEKK film and PEKK-coated carbon fibers were put into a flask containing 0.9 wt % NaCl solution and kept at 365 ± 1 K. The samples were kept for 5 and 10 days, respectively, and taken out, thoroughly washed with the 4-D water, and then dried in an oven at 363 K over 24 h. Recording the XPS spectra necessitated the exposure of the samples to X-radiation, which corresponded to the Mg Kα X-ray radiation of the used achromatic source that had a power of 240 W.

Surface Analysis and Data Interpretation. Most of the spectra were collected in an AEI (Kratos) ES200B X-ray spectrometer in the FAT (fixed analyzer transmission) mode with a pass energy of 50 eV, using achromatic Mg Kα as the X-ray radiation source with a line width of about 0.8 eV. Monochromatic XPS spectra for PEKK film were collected on a VSW HA150 spectrometer operated in the FAT mode with a pass energy of 22 eV, with an X-ray line width of better than 0.2 eV. The base pressure of both instruments were 10^{-9} Torr or better. The energy scales of the spectrometer were calibrated using an argon-ion-etched copper plate according to the ASTM standard.[28] The fibers were mounted into the spectrometer on a holder as a short length (45 mm) of a fiber tow. The sample was ground and positioned so that no signal from the sample holder could be detected in the spectrum. Data collection time was limited to minimize sample decomposition.[29,30] The typical time of data collection was about 15 min for the C 1s region, 20 min for the O 1s region, 30 min for the overall region, and 13−20 h for the valance band spectrum, respectively.

The curve fitting of the XPS spectrum was carried out using a nonlinear-least-squares curve-fitting program with a Gaussian/Lorentzian product function.[31,32] The Gaussian/Lorentzian mixture was taken as 0.5, except for the graphite carbon peak, which was taken as 0.84 with an exponential tail. The C 1s binding energy of the graphite peak was fixed at 284.6 eV for the calibration purposes. The background shape used in the curve fitting and the spectral smoothing methods used have been reported previously.[33,34] Ab initio Hartree−Fock calculations were performed to obtain the XPS valence band spectra. These calculations used a modified version of the program HONDO (copyright IBM) with an STO-3G minimal basis set.[35]

---

(14) Xie, Y.; Wang, T.; Rooke, M. A.; Sherwood, P. M. A. *Surf. Sci. Spectra* **1992**, *2*, 210.

(15) Xie, Y.; Sherwood, P. M. A. *Surf. Sci. Spectra* **1993**, *3*, 265.

(16) Viswanathan, H.; Rooke, M. A.; Sherwood, P. M. A. *Surf. Interface Anal.* **1997**, *25*, 409.

(17) DeVilbiss, T. A.; Wightman, J. P. *Composite Interface*; Ishida, H., Koeing, J. L., Eds.; Elsevier Science: New York, 1986; p 307.

(18) Kalnin, I. L.; Jager, H. *Carbon Fibres and Their Composites*; Fitzer, E., Ed.; Springer-Verlag: New York, 1985; p 62.

(19) Wang, Y.-Q.; Viswanathan, H.; Audi, A. A.; Sherwood, P. M. A. *Chem. Mater.* **2000**, *12*, 1100.

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

(21) Weitzsacher, C. L.; Xie, M.; Drzal, L. T. *Surf. Anal.* **1997**, *25*, 53.

(22) Gardner, C. U.; Singamsetty, C. S. K.; Booth, G. L.; He, G. R. *Carbon* **1995**, 33, 587.

(23) Wang, Y. Q.; Zhang, F. Q.; Sherwood, P. M. A. *Chem. Mater.* **1999**, *11*, 2573.

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

(25) Wang, T.; Sherwood, P. M. A. *Chem. Mater.* **1995**, *7*, 1031.

(26) Sherwood, P. M. A. *J. Vac. Sci. Technol.* **1992**, *A10*, 2783.

(27) Kenneth, J. R. St. In *Biocompatible Polymer, Metal and Composites*; Szycher, M., Eds.; Technomic Publishing Co.: Lancaster, 1983; p 861.

(28) Seah, M. P.; Gilmore, I. S.; Beamson, G. *Surf. Interface Anal.* **1998**, *26*, 642.

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

(30) Blythe, A. R.; Briggs, D.; Rance, D. J.; Zichy, V. J. I. *Polymer* **1978**, *19*, 1273.

(31) 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.

(32) Ansell, R. O.; Dickinson, T.; Povery, A. F.; Sherwood, P. M. A *Electroanal. Chem.* **1979**, *98***,** 79.

(33) Proctor, A; Sherwood, P. M. A *Anal. Chem.* **1980**, *52*, 2315.

(34) Proctor, A; Sherwood, P. M. A *Anal. Chem.* **1982**, *54*, 13.

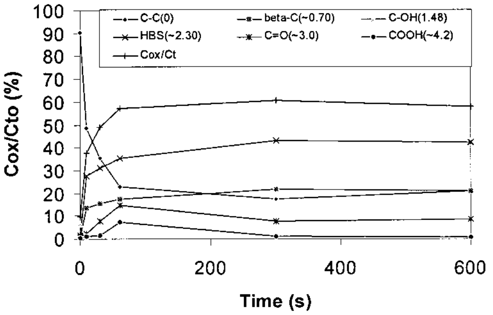

Figure 1. Area ratio for the total intensity of features associated with oxidized carbon to the total carbon intensity for the C 1s XPS spectral region for carbon fibers subjected to different times of electrochemical oxidation in 1 M HNO_3. The number in parentheses represents the chemical shift from the C 1s main peak (unit: eV).

The calculated spectra were generated by adding together the component peaks (represented by the 50% mixed Gaussian−Lorentzian product function[36]) for each of the calculated energy levels, with each peak having a position corresponding to the calculated energy level and an intensity due 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.[37] All calculations were carried out on an IBM RISC/6000 computer.

Results and Discussion

Carbon Fibers Modified Electrochemically in Nitric Acid. Figure 1 shows how the relative amounts of the different oxides change on the carbon fiber surface with increasing electrochemical oxidation time based upon the fitting of the C 1s region to the peak assignment. The results are similar to those of previous studies,[23] and so the spectral details will not be repeated here. The C−OH group only exists on the surface of as-received carbon fibers and changes into other types of oxide during electrochemical reaction. The principal oxide on the treated carbon fiber surface under the conditions reported here has been found to be a hydrogen-bridged structure oxide (HBS).[10,16] It can be seen that the amount of oxidation increases substantially with oxidation time during the first 60 s of treatment, especially over the first 10 s, and then reached a nearly constant value with increasing treatment time. We find that the oxidation level on the surface reaches a maximum level after 60 s, after which further oxidation causes changes in the interior of the graphite.[29]

PEKK Surface Chemistry and XPS Spectrum. The general structure of PEKK is well-known and has been discussed in an earlier paper.[1,9] We have already discussed the expected appeareance of the C 1s and O 1s core spectral regions in our earlier paper.[9] Figure 2 shows relevant core and valence band XPS spectra of the PEKK film obtained with monochromatic Al Kα X-radiation, which is similar to our previous study using achromatic X-radiation.[9] We have fitted the C 1s and O 1s core level spectra using our earlier peak assignment. The area ratio of the peaks is about 6.2:1.9:1:1, which is similar to the stoichiometrical atom ratio of 6:2:1:1 in the model structure of PEKK(Figure 2f). The area ratio is about 1.8:1, which is close to the expected 2:1 area ratio. The O/C ratio was 0.171, which is slightly higher that expected from the repeat unit (0.150), probably as a result of the adsorption of surface oxygen. The experimental valence band spectrum agrees well with the calculated spectrum obtained from a molecular orbital calculation using the repeat unit, as shown in Figure 2. This calculated spectrum is similar to our earlier calculation using the multiple-scattered wave Xα calculation.

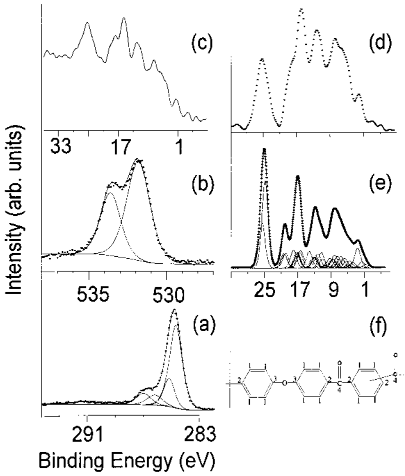

Figure 2. XPS spectra obtained using monochromatic X-radiation and repeat unit of PEKK. (a) C 1s, (b) O 1s, (c) valence band, (d) background-subtracted valence band, (e) valence band calculated from a molecular orbital calculation using the polymer repeat unit, and (f) repeat unit of PEKK.

Interaction between PEKK and Carbon Fibers. *Coating Untreated Carbon Fibers with PEKK.* The overall (I), C 1s (II), O 1s (III), and valence band (IV) XPS spectra of treated carbon fibers, PEKK coated fibers, obtained with achromatic X-radiation are presented in Figure 3. XPS analysis can be used to get a crude atomic ratio based upon the significant approximation that the surface region is homogeneous over the depth probed by XPS. Such an analysis shows the surface of these fibers to correspond to 90% graphitic carbon with a O/C ratio of about 0.022. Details of the curve fitting of the C 1s and O 1s regions for both untreated and treated fibers before and after exposure to PEKK solution, with and without removal of excess solution, is shown in Table 1.

When the untreated carbon fibers were coated with PEKK, no significant spectral changes were seen, indicating that there was no evidence for the adsorption or interaction of PEKK with the fiber surface (the spectra obtained were identical to those of Figure 3b). It was only when the fibers were not handled so that excess solution could be removed (by placing the fibers on porous paper) that any PEKK could be seen on the fibers, giving the spectra of Figure 3c. The conclusion that the PEKK had not interacted with the carbon fiber surface when excess solution was not removed from the fibers was supported by the fact that the C 1s region of Figure 3b (II) could be curve fitted to correspond to an addition of the spectrum of the untreated carbon fiber and that of PEKK. This conclusion was further supported by the addition and difference spectrum for the

---

[35] Dupuis, M.; Farazdal, A.; Karna, S. P.; Maluends, S. A. *Modern Techniques in Computational Chemistry: MOTECC-90*; Clement, E., Ed.; Escom: Leiden, 1990; Chapter 6, p 277.

[36] Ansell, R. O.; Dickinson, T.; Sherwood, P. M. A. *Electroanal. Chem.* **1979**, *98*, 79.

[37] Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

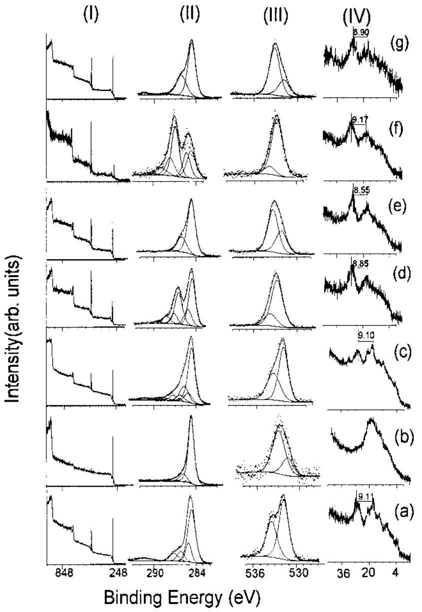

Figure 3. Overall (I), C 1s (II), O 1s (III), and valence band (IV) XPS spectra of PEKK and carbon fibers after interaction with PEKK or exposure to excess PEKK, (a) PEKK film, (b) untreated carbon fibers (or fibers after exposure to PEKK with the excess solution removed), (c) untreated carbon fibers after exposure to PEKK with the excess solution unremoved, (d) carbon fibers that have been electrochemically oxidized in nitric acid at 0.5 A for 20 s, (e) oxidized carbon fibers in (d) after exposure to PEKK with the excess solution removed, (f) carbon fibers that have been electrochemically oxidized in nitric acid at 0.5 A for 120 s, and (g) oxidized carbon fibers in (f) after exposure to PEKK with the excess solution removed.

C 1s region shown in Figure 4, which indicate that the no changes could be identified that might correspond to the interaction of the carbon fiber surface with PEKK. This can also be seen from the details of the curve fitting in Tables 1 and 2, which indicate that the C 1s and O 1s spectra from the fibers exposed to PEKK without removal of excess solution are simply an addition of the two relevant spectra. Thus, in Table 2 it can be seen that the O 1s spectra of the PEKK film has more oxygen associated with the C=O components than for the C−O components (the ratio for these two functionalities being about 2:1, which is the ratio expected from the chemical structure in Figure 2f), and in the PEKK-exposed untreated carbon fibers the same ratio is found (again the ratio is about 2:1).

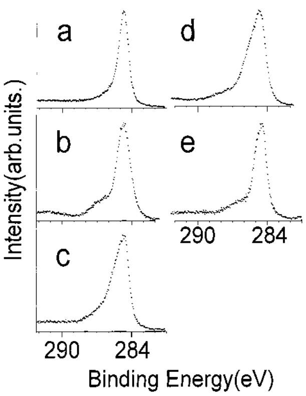

Figure 4. C 1s XPS spectra of carbon fibers. (a) shows the XPS spectrum of the untreated carbon fibers, (b) the XPS spectrum of a PEKK film, and (c) the untreated carbon fibers after exposure to PEKK with the excess solution unremoved. Spectrum (d) represents the addition spectrum of (a) and (b) and may be compared with spectrum (c). Spectrum (e) represents the difference spectrum of (c)−(a) and may be compared with the spectrum of PEKK shown in (b).

The experiment when the fibers were essentially “coated” with PEKK solution by failing to remove excess solution indicates how the interfacial region can be examined. Thus, the O/C ratio of coated carbon fibers (about 0.138) was lower than that of PEKK film (about 0.171) because of the contribution of carbon from carbon fibers. In the valence band spectrum shown in Figure 3, the relative area of the region around 18 eV, which contains significant C 2s character, in coated untreated fibers is larger than that in PEKK because of the contribution of carbon in the underlying fiber. Similarly, this valence band spectrum could be obtained from the simple addition of the carbon fiber and PEKK; thus, the separation between the principal O 2s region and the region around 18 eV is little changed (Figure 3a compared to Figure 3c). This observation shows that the

Table 1. Chemical Shift and Relative Area of C 1s XPS of Carbon Fibers Electrochemically Treated in HNO_3 at 0.5 A and Coated with PEKK

		PEKK film (a)	as-received E120 (b)	E120 + PEKK (c)	E120−20 s (d)	E120−20 s + PEKK (e)	E120−60 s (f)	E120−60 s + PEKK (g)
peak 1 (C−C)	CS (eV)	0	0	0	0	0	0	0
	fwhm (eV)	*1.29*	0.96	1.06	*1.34*	*1.29*	1.44	*1.29*
	area (%)	59.4	90.0	54.8	40.2	74.3	22.8	63.4
peak 2 (β-C)	CS (eV)	0.45	0.65	0.45	0.70		0.65	
	fwhm (eV)	*0.96*	0.86	1.34	*1.43*		1.24	
	area (%)	15.7	0.7	18.3	14.4		17.7	
peak 3 (C−O)	CS (eV)	1.55	1.48	1.55|1.10		1.40		1.50
	fwhm (eV)	*1.15*	1.24	1.34|1.34		1.48		1.67
	area (%)	9.7	6.8	6.6|21.3		24.0		30.3
peak 4 (B.S.)	CS (eV)		2.18	2.55	2.25		2.10	
	fwhm (eV)		0.86	1.43	*1.43*		1.24	
	area (%)		1.4	7.7	28.7		35.3	
peak 5 (C=O)	CS (eV)	2.55	3.03	3.15	3.0	2.90	3.0	3.00
	fwhm (eV)	*1.34*	1.53	1.43	*1.24*	*1.15*	1.43	*1.15*
	area (%)	9.4	0.6	2.8	8.1	1.7	14.6	1.1
peak 6 (COOH)	CS (eV)		4.23	4.50	4.25		4.25	4.20
	fwhm (eV)		1.53	1.53	*1.43*		1.72	*1.34*
	area (%)		0.2	3.7	6.5		7.3	1.6
peak 7 (π−π*)	CS (eV)	6.75	6.08	6.75	5.95		6.05	6.75
	fwhm (eV)	*2.39*	1.72	1.91	*1.72*		1.91	*1.91*
	area (%)	5.8	0.3	1.7	2.2		2.3	3.5

Table 2. Position, fwhm, and Relative Area of O 1s XPS of Carbon Fibers Electrochemically Treated in HNO_3 at 0.5 A and Coated with PEKK

peak no.		PEKK film (a)	as-received E120 (b)	E120 + PEKK (c)	E120−20 s (d)	E120−20 s + PEKK (e)	E120−60 s (f)	E120−60 s + PEKK (g)
peak 1 C−O	position (eV)	533.5	533.0	533.6	533.6	533.2	533.8	533.1
	fwhm (eV)	*1.86*	2.10	2.10	*2.01*	*1.72*	1.82	*1.67*
	area (%)	36.2	73.4	36.9	21.7	63.7	12.0	72.4
peak 2 O=C	position (eV)	531.7	531.8	533.3	532.7	532.1	532.7	532.1
	fwhm (eV)	*1.58*	1.82	1.53	1.86	1.82	1.91	1.81
	area (%)	63.8	26.6	63.1	78.3	36.3	88.0	27.6
O/C	atom ratio	0.171	0.022	0.138	0.377	0.269	0.584	0.250

valence band region supports the conclusions from the core region that there is no reaction between the as-received untreated carbon fibers and the PEKK polymer.

Coating of Treated Carbon Fibers with PEKK. When the oxidized carbon fibers were coated with PEKK using the procedure described above, considerable spectral changes were observed for the two different oxidation conditions used. Thus, Figures 3e and 3g, which show the spectra after PEKK coating for these two oxidation conditions, are very different from either the spectra of the oxidized fibers (Figures 3d and 3f, respectively) or of PEKK (Figure 3a). This means that significant chemical interaction has occurred since otherwise Figures 3e and 3g could be generated by adding Figures 3a and 3d (for Figure 3e) or Figures 3a and 3f (for Figure 3g) in the appropriate amounts. We have fitted the C 1s region of the spectrum of the oxidized fibers (Figures 3d and 3f) to six peaks, and the PEKK to five peaks, in both cases using the peak assignments discussed above. The spectra from the oxidized carbon fibers coated with PEKK were fitted to four peaks including the $\pi \rightarrow \pi^*$ shake-up peak, and while the peak positions selected (shown in Table 1) were very similar for both sets of oxidized fibers, the positions were significantly different from those of the oxidized fibers themselves or the PEKK. The spectra from the oxidized fibers coated with PEKK showed a peak at a chemical shift of 1.40 eV, which is consistent with the C−O−C group and a peak at a shift of 2.90 eV, which is consistent with the C=O group in addition to the principal hydrocarbon feature at 284.6 eV and the $\pi \rightarrow \pi^*$ shake-up peak at a shift of 6.75 eV. We interpret this result as being consistent with a mechanism where the HBS group on the surface of the treated fibers was lost during reaction with PEKK during the coating process. This reaction can be monitored by following the changes reported in the C 1s spectra from the coated fibers shown in Table 1. The C−O−C component in the spectra of the coated samples has 3 times as much intensity (relative to the hydrocarbon peak at 284.6 eV) as the similar feature (at a shift of 1.55 eV) in PEKK. The C 1s feature corresponding to HBS that is found for the treated fibers is absent in the spectra of the coated fibers, and the relative intensity of the C=O component is less than that of the similar feature (at a shift of 2.55 eV) in PEKK. We thus conclude that there has been a chemical reaction between the HBS groups of the treated fibers and C=O groups in PEKK, leading to the formation of C−O−C bonding at the interface.

The coating of oxidized fibers with PEKK leads to changes in the O 1s region as well as the C 1s region, as can be seen in Figure 3. The curve-fitting results for the O 1s region are shown in Table 2. We have fitted the O 1s region to two peaks due to C/O in the HBS group (or C=O group in PEKK) and C−O for all the samples. For the electrochemically oxidized carbon fibers, the relative intensity of the C/O components is greater than that of the C−O components (the ratio being about 3.6:1 for the fibers oxidized for 20 s and 7.3:1 for the fibers oxidized for 60 s). This is expected since the C 1s region indicates that the chemically shifted feature due to HBS is the most intense feature corresponding to oxidized carbon, and this feature increases in relative intensity as the oxidation time is increased from 20 to 60 s. In the case of PEKK the most intense O 1s feature is due to C=O functionality, which has about twice the relative intensity as the feature corresponding to C−O functionality. In the case of the PEKK-coated oxidized fibers the corresponding relative intensity ratio would be between 3.6:1 and 2:1 if coating led to no chemical reaction since the O 1s spectra would be the addition of the PEKK and the fiber spectrum. This is not the case, supporting the conclusion that chemical reaction between the oxidized fiber and PEKK occurs, the feature corresponding to C=O being of lower intensity in the O 1s spectrum than that due to C−O (the intensity ratio being about 1:2 for the fibers oxidized for 20 s and 1:2.5 for the fibers oxidized for 60 s). The higher the content of C/O from the HBS group on the treated carbon fiber surface, the lower the ratio of C=O to C−O−C becomes for the oxidized fibers coated with PEKK. This observation is consistent with the conclusions from the C 1s region, which indicates that the reaction leads to C/O functionality being changed to C−O−C functionality.

The O/C atom ratio is shown in Table 2 and is based upon the area ratio for the C 1s and O 1s regions. These ratios, as stated above, can be obtained if one makes the significant approximation that the region probed is homogeneous. One notes that this ratio is 0.17 for PEKK and increases to 0.38 for fibers oxidized for 20 s and 0.58 for fibers oxidized for 60 s. The coated oxidized fibers have a lower O/C ratio than the oxidized fibers, being 0.27 for PEKK-coated fibers that were oxidized for 20 s and to 0.25 for PEKK-coated fibers that were oxidized for 60 s. Again, one notes that if there were no reaction, one would certainly expect the O/C ratio to *increase* in the case of the coated fiber that had been electrochemically oxidized for the longer time period, but this is not the case. The result is consistent with oxygen loss as a result of the reaction process.

Important differences are also observed in the valence band region, which is shown in Figure 3 (IV). Thus, Figures 3e and 3g, which show the spectra after PEKK coating for these two oxidation conditions, are significantly different from either the spectra of the oxidized fibers (Figures 3d and 3f, respectively) or the spectra of PEKK (Figure 3a). This difference can be noted by comparing the separations between the two most intense peaks in the spectrum. If no chemical reaction occurred, one would anticipate a separation in the spectra for the PEKK-coated oxidized fibers of about 9.2 eV (which would result from PEKK), whereas the coated fibers have a smaller separation. Again, chemical reaction is indicated. It is interesting to note that visual differences between Figures 3g and 3f are more marked than those between Figures 3e and 3d. This is probably because the valence band region probes more deeply into the surface than the core regions and thus “see” more deeply into the interface. The more heavily oxidized fiber in Figure 3f (60-s oxidation) has more functionality to react with the PEKK than the less heavily oxidized fiber (Figure 3d), so there is probably more reaction in the former case, leading to greater spectral changes.

Possible Reactions between Treated Carbon Fibers and PEKK. As identified above, PEKK has an unsaturated bond C═O and a saturated bond C−O−C. In general, the two bonds cannot be easily reacted with other compounds except in the presence of strong oxidizing conditions. This characteristic explains why PEKK is a useful material under a range of environmental conditions including high temperatures. We show above that it is possible to cause a reaction between PEKK and the treated carbon fibers by establishing the appropriate oxidizing environment. It is clear that the surface-treated carbon fibers are chemically active and may catalyze such reactions, as suggested by other researchers.[38,39]

On the basis of our studies above we have suggested possible reaction processes between the oxidized carbon fiber surface and the PEKK. These processes have the following features: (i) the HBS group on the carbon fiber surface participates in the reaction and is lost in the reaction process; (ii) single-bonded oxygen (probably in the form of C−OH) is the main bonding form in the interface region; (iii) there is probably a small amount of C═O functionality in the interface region; (iv) some oxygen was lost during the interfacial reaction. Possible reaction schemes that fit this model are shown in Figure 5, which include the formation of (a) an ether bond and new C═O groups, (b) an ether bond and C−OH groups, and (c) only ether bonding from the breakage of HBS on the fiber surface and C═O group on PEKK because of the catalytic function of treated fibers.

The molecular orbital calculation for the interfacial bonding suggested in Figure 5 is used to obtain valence band spectra, as shown in Figure 6. In case (a), the region around 25 eV consists of five peaks and looks symmetrical because of the approximately equal contribution of C═O and C−O−C groups. The five peaks fall into two groups, one at higher binding energy, which have a high C−O−C character, and one at low binding energy, which have a high C═O character. The separation between O 2s and C 2s was about 7.90 eV and about 3.15 eV between C 2s and its left shoulder. In case (b) the predicted spectrum in this region is composed of five peaks, where there is a group of three equal intensity peaks at higher binding energy, which are largely associated with the C−O−C functionality, and a group of two equal intensity peaks at lower binding energy, which are largely associated with C−OH functionality. The separation between the C−O−C group of peaks and the C−OH group of peaks in (b) is significantly greater than the separation between the C−O−C group of peaks and the C═O group of peaks in (a), consistent with our previous reports[13] that the binding energy follows the order $CO_2H \sim C{-}O{-}C > C{=}O > C{-}OH$. The region around 18 eV in case (b), which largely arises from C 2s character, is wider than the corresponding region for

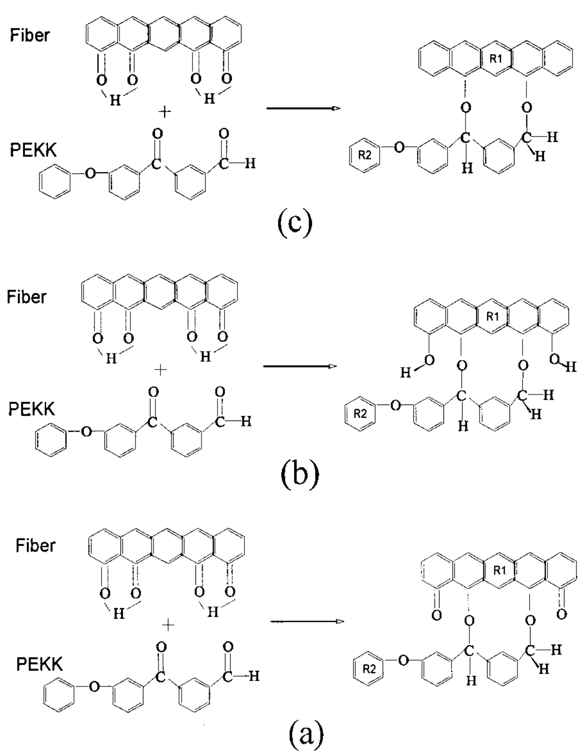

Figure 5. Three possible reaction processes between oxidized carbon fiber and PEKK, (a) with a C═O group, (b) with a COH group, and (c) with a C−O−C group. (Note: R1 ring was removed and R2 was represented by $-CH_2-CH_3$ in the ab initio calculation.)

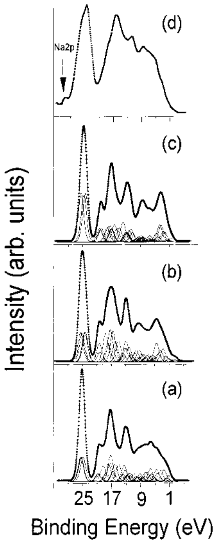

Figure 6. Comparison of valence band from calculation and experimental (where (a), (b), and (c) are the same as those in Figure 5, respectively.)

---

(38) Muller, E. A.; Gubbins, K. E. *Carbon* **1998**, *36,* 1433.

(39) Jou, G. C.-J. *Carbon* **1998**, *36,* 1643.

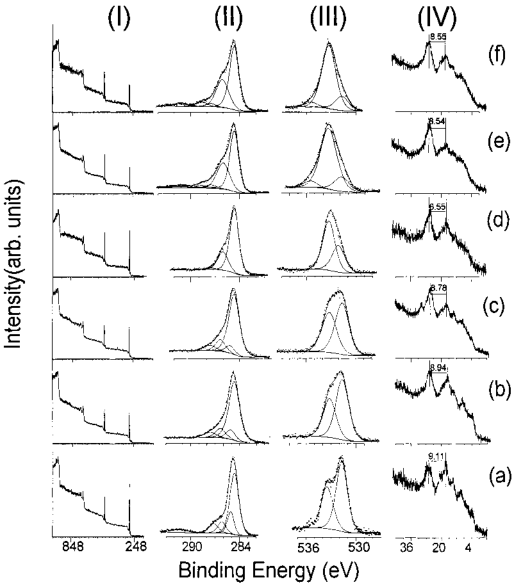

Figure 7. XPS spectra of PEKK and PEKK-coated carbon fibers holden in saline solution, (a) PEKK as cast, (b) PEKK for 5 days, (c) PEKK for 10 days, (d) PEKK-coated fibers treated for 20 s, (e) the coated fibers for 5 days, and (f) the coated fibers for 10 days.

case (a). Case (c) consists of all C−O−C links, though there are differences in the links. Two groups of peaks can be identified, the one at highest binding energy being due to C−O−C where both carbon atoms are part of an aromatic ring, the one at lower binding energy (composed of two overlapping peaks) corresponds to C−O−C where one of the carbon atoms is attached to an aliphatic group. We believe that the best agreement between theory and experiment is for the model in Figure 5c, giving the spectrum of case (c) (Figure 6). While we recognize that there are strong similarities between all the calculated spectra in Figure 6, we feel that the experimental data of Figure 6d is compatible with the model of Figure 5c and that this model is the model that is most compatible with our observed increase in the C−O−C functionality after the reaction.

Degradation of PEKK and PEKK-Coated Carbon Fibers. *Behavior of PEKK and PEKK-Coated Fibers in Saline Solution*. The exposure of samples in a saline solution at elevated temperature is a common method for the investigation of the properties of composites used in industry or medical applications. Figure 7 presents the Overall (I), C 1s (II), O 1s (III), and valence band (IV) spectra of a PEKK film and coated carbon fibers that have been exposed to saline solution at 365 K. For the PEKK film, a new peak of low intensity due to COOH appeared, and all the peaks became wider as the exposure time to the saline solution increased (Table 3). The position for peak 2 was almost unchanged and the C−O−C peak showed little change with increasing exposure time. In contrast, the C═O showed considerable change in position with exposure time, changing from a shift of 2.55 eV (in the as-cast PEKK film) to between 2.8 and 3.1 eV with increasing exposure time. The higher binding energy C═O feature is consistent with the position found for this functional group in a number of polymer systems. The increase in oxidation that results in exposure of the PEKK and the PEKK-coated fibers to saline solution is reflected in the decrease in the percentage of peak 1, which corresponds to unoxidized carbon. While there is little change in the relative intensity of peak 4 (C═O), the remaining peaks (peaks 2 and 3) increase significantly in relative intensity with exposure time. In particular, peak 3 (C−O) doubles its relative intensity from 9.7 to 18.2% after 10 days of exposure time. While C−OH and C−O−C functionality cannot be distinguished in the core region, they can be identified from the valence band region. Previous studies[12] (and the results of our calculations below) have indicated that the C−O−C functionality would have a higher binding energy principally O 2s region around 25 eV, and thus we conclude that the functionality is probably C−O−C. The valence band spectra are consistent with the conclusions based upon the core region and clearly indicate the significant increase of oxygen on the surface as well as the change in C/O functionality with exposure time. One needs to be careful about quantification in this region because of the mixing between atomic orbitals resulting from chemical interaction, which means that there is no simple O 2s and C 2s region, for example. One of us has discussed this elsewhere in some detail;[40] nevertheless, it can be seen how the peak around 25 eV, which has a high O 2s content, increases in relative intensity with exposure time, which is quantified in Table 3. The separation between this region and the largely C 2s region at some 8−9 eV lower binding energy can be seen to fall with increasing exposure time to the saline solution.

The observations in the core and valence band regions provide strong evidence for chemical reaction between the functional groups on the PEKK surface in the saline solution and a reaction that increases steadily with exposure time to the saline solution. When the samples are exposed to the saline solution for 10 days, sodium is detected on the surface with a significant Na 2p signal. This observation is indicative of damage to the surface of the PEKK, which allows for the strong interaction of sodium ions such that they are not removed by the normal washing process performed on all the samples after saline solution exposure.

Similar results are found for the PEKK-coated fibers upon exposure to saline solution as those found for the PEKK film. The results, shown in Figure 7 and Table 3, show steady oxidation with increasing exposure time. For the coated fibers treated in saline solution, the change trend of the spectra is similar to those of PEKK, though there is little additional change between 5 and 10 min of exposure, suggesting that the process reaches a “plateau” after 5 days. The O 1s spectra in Figure 7 have been fitted to the components discussed above and support the conclusions from the C 1s region that the −C−O−C−/C−OH peak becomes of relatively larger intensity and the −C═O peak falls in intensity with increasing exposure time. A third peak due to adsorbed water is included for the PEKK-coated fibers at 535.3 eV in the O 1s curve-fitting results shown in Figure 7 and Table 3, providing strong evidence for water penetration into the surface, possibly into the PEKK/fiber

---

(40) Sherwood, P. M. A. In *Encyclopedia of Materials: Science and Technology*; Buschow, K.H. J., Cahn, R. W., Flemings, M. C., Ilschner, B., Kramer, E. J., Mahajan,S., Eds.; Elesevier Science: New York, in press.

Table 3. Chemical Shift, fwhm, and Relative Area of C 1s and O 1s XPS of PEKK and PEKK-Coated Carbon Fibers Electrochemically Treated in HNO_3 and Relative Area of C 1s and O 1s XPS of PEKK and PEKK-Coated Carbon Fiber at 0.5 A Kept in Saline Solution at 365 K

	peak no.		as-cast (a)	5 days (b)	10 days (c)	as-cast (d)	5 days (e)	10 days (f)
C 1s	peak 1 (C−C)	CS (eV)	0	0	0	0	0	0
		fwhm (eV)	1.29	1.44	1.44	1.29	1.29	1.35
		area (%)	59.4	55.2	50.2	74.3	59.9	56.4
C 1s	peak 2 (β-C)	CS (eV)	0.45	0.45	0.48			
		fwhm (eV)	0.96	1.34	1.34			
		area (%)	15.7	21.6	21.9			
C 1s	peak 3 C−O	CS (eV)	1.55	1.60	1.65	1.40	1.40	1.45
		fwhm (eV)	1.15	1.43	1.63	1.48	1.82	1.82
		area (%)	9.7	13.8	18.2	24.0	30.4	32.2
C 1s	peak 4 C═O	CS (eV)	2.55	2.80	3.08	2.90	2.90	2.90
		fwhm (eV)	1.34	1.43	1.53	1.15	1.44	1.34
		area (%)	9.4	7.5	6.8	1.7	3.4	2.8
C 1s	peak 5 COOH	CS (eV)	none	4.10	4.10		4.0	4.0
		fwhm (eV)		1.15	1.29		1.72	1.53
		area (%)		2.0	2.9		3.4	4.5
C 1s	peak 6 (π−π*)	CS (eV)	6.75				6.6	6.6
		fwhm (eV)	2.31				1.91	1.91
		area (%)	5.8				2.9	4.0
O 1s	peak 1 H_2O	position (eV)					535.3	535.4
		fwhm (eV)					1.91	1.82
		area (%)					6.5	5.2
O 1s	peak 2 C−O	position (eV)	533.5	533.1	533.1	533.2	533.2	533.3
		fwhm (eV)	*1.86*	1.86	2.10	1.72	2.31	*1.91*
		area (%)	36.2	38.7	45.0	63.7	77.2	77.8
O 1s	peak 3 O═C	position (eV)	531.7	531.6	531.6	532.1	531.6	531.7
		fwhm (eV)	*1.58*	1.72	2.01	1.82	2.20	2.04
		area (%)	63.8	61.3	55	36.3	16.3	16.9
O/C		atom ratio	0.171	0.230	0.271	0.269	0.337	0.337
VB	O 2s/C 2s	area ratio in VB	0.60	0.757	1.44	1.09	1.53	1.34

interface as well as the probably damaged surface region. Other workers have suggested that water may be present after exposure of polymer systems to saline solutions, but previously no clear evidence could be provided to support this suggestion.[8] The "plateau" behavior after 5 days that was seen for the C 1s region is also evident in the O 1s region.

Degradation of PEKK and Coated Fiber in X-ray Radiation. A collateral result of our experiment is that we also necessarily expose the PEKK and the PEKK coated fibers to X-radiation. X-radiation could clearly cause some degradation, and indeed the potential degradation of polymers upon irradiation is an important topic. We have followed the effect of exposure time on the Mg Kα X-radiation used to collect our XPS data, and Figure 8 presents the spectra of the PEKK film and PEKK-coated carbon fibers for different X-radiation exposure times. The C 1s spectra changed little with radiation exposure time, but there was a noticeable change in the O 1s spectra for the same exposure conditions. Much larger changes are seen for the O 1s region in Figure 8, which shows an increase in C−O single-bonded species at the expense of C═O double-bonded species with exposure time. Some oxygen loss with exposure time is also indicated, as shown by the decrease in the C/O ratio with exposure.

Possible Degradation Reactions of PEKK and the Reacted Interface in the Saline Solution. The core XPS studies discussed above indicate that COOH and/or C−OH groups were formed for the PEKK polymer exposed to saline solution. Two possible products of the reaction of PEKK with the saline solution are shown in Figure 9, in which (a) a COOH group was formed by the oxidation of the C═O group and (b) a C−OH group is formed by the attack of water. The valence band spectra of the model compounds generated from molecular orbital calculations are presented there. The spectrum generated from model (b) has a high binding energy shoulder in the region around 25 eV, in good agreement with the experimental data. This shoulder is absent in the spectrum generated from model (a). The shoulder in from model (b) arises from the highest binding energy component, which is composed of COOH and C−O−C functionality. The shoulder is missing in model (a), which while having C−O−C functionality, lacks the additional COOH feature that causes the high

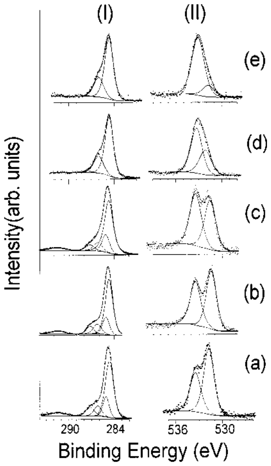

Figure 8. XPS spectra of PEKK and PEKK-coated carbon fibers in the X-ray radiation of (a) as-cast PEKK, (b) PEKK for 24 h, (c) PEKK for 48 h, (d) PEKK-coated fibers, and (e) the coated fibers for 24 h.

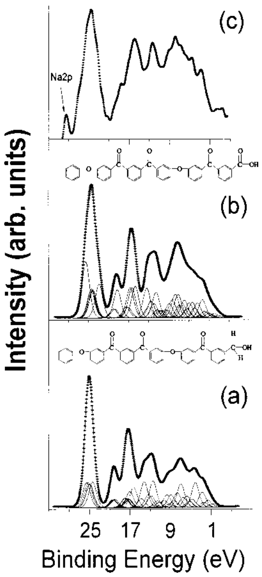

Figure 9. Model compounds for PEKK decomposition products and comparison of experimental and calculated valence bands after degradation in saline solution at 365 K, (a) with a C−OH group, (b) with a COOH group, and (c) experimental.

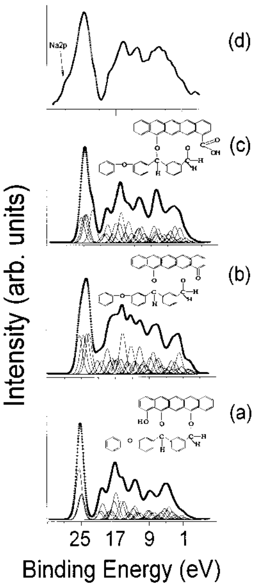

Figure 10. Model compounds for decomposition products of a PEKK film on carbon fiber surfaces and comparison of calculated and experimental valence bands of the reacted interface of PEKK/carbon fibers treated, with (a) a C−OH group, (b) a C═O group, (c) a COOH group, and (d) experimental.

binding energy area to gain in intensity and thus appears as a shoulder.

In the case of carbon fibers coated with PEKK and exposed to saline solution the spectral changes can also be understood by comparison with calculations. An additional feature of this system is that water is absorbed on the surface and perhaps also at the interface between the fiber and the PEKK. There are thus three kinds of possible functionalities present for this system that result from the degradation caused by saline solution, namely, of (a) −OH (caused by water interaction), (b) C═O (as in PEKK above), and (c) COOH (as in PEKK above). We show in Figure 10 three models that contain these functionalities and might represent the interfacial chemistry for this system and calculated VB. Each of these three models contain the C−O−C link between the carbon fiber and the PEKK since we discuss above how we believe that this group is the predominant group at the PEKK−carbon fiber interface. These models have (a) an additional OH group, (b) an additional C═O group, and (c) and additional COOH group arising from interaction with saline solution. The corresponding valence band spectra generated from molecular orbital calculations are shown in Figure 10. In the case of the model compound with a C−OH group (a), a symmetrical feature around 25 eV is obtained. In the case of (b), this region becomes asymmetrical with a shoulder at higher binding energy. In the (c) case this region is also asymmetrical, but now the shoulder is more pronounced and is at lower binding energy. A comparison with the experimental valence band in (d) indicates the best agreement with model (c), that is, the interface where decomposition has led to COOH functionality, since the experimental spectrum has a low binding energy shoulder. There is a pronounced high binding energy shoulder, but this is caused by the presence of Na 2p from adsorbed sodium ions.

Conclusions

The surface chemistry associated with the interaction of carbon fibers with PEKK polymer and the reaction between PEKK polymer and carbon fibers that were both untreated and electrochemically oxidized in nitric acid solution has been investigated. In addition, the degradation of the PEKK and the PEKK-coated fibers after exposure to saline solution and X-radiation has been monitored using a combination of core and valence band XPS, with the latter being interpreted by molecular orbital calculations. The results indicate that this approach can identify the surface chemical changes that result. The PEKK polymer film on the fibers, produced by immersion of the fibers in a solution of PEKK, has been shown to give a film of PEKK on the fibers and chemical interaction at the PEKK carbon fiber interface. The latter chemical interaction only occurs when the carbon fibers were initially oxidized by electrochemical treatment; untreated fibers do not react with the PEKK film. The reaction mainly resulted from chemical interaction between the HBS group on the treated fibers and carbonyl group in PEKK, and this interaction can be successfully modeled by molecular orbital calculations on fragments of the interface region.

Exposure of the PEKK or the carbon fibers coated with PEKK to saline solution at elevated temperatures caused degradation of the PEKK polymer due to change of a part of a carbonyl group to a carboxyl group and degradation of the reacted interface because of absorption of water and formation of some carboxyl functionality. Exposure to the X-ray radiation used to generate the XPS spectra caused the carbonyl group to be changed to C−O−C functionality. Careful analysis of the valence band spectra using spectra generated from molecular orbital calculations provided complementary information to that found in the core region and provided very strong evidence for the chemical reaction between the treated fibers and polymer and the degradation of polymer and the polymer-coated fibers.

Acknowledgment. This material was based upon work supported by the National Science Foundation under Grant CHE-9421068. The U.S. Government has certain rights in this material. We are grateful to the duPont Company for providing the carbon fibers and to Mr. Daniel Felker for his valuable assistance with this work.

CM000555T