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X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 24. Interfacial Interactions between Polyimide Resin and Electrochemically Oxidized PAN-Based Carbon Fibers

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The interfacial interaction between PAN-based IM7 carbon fibers and Avimid K3B, a thermoplastic polyimide resin was investigated using core and valence band X-ray photoelectron spectroscopy (XPS). The extent of interaction between the fiber and the matrix material has a significant effect on the strength of the ultimate composite. The fibers were treated to remove the surface treatment applied to the fibers by the manufacturer by resistive heating in a vacuum. The interaction of the detreated fiber, subjected to subsequent electrochemical treatment, with the resin was compared to the interaction of the commercially surface-treated fiber with the resin. Better interaction between the fiber and matrix was found in the case of the electrochemically surface-treated fiber than with a commercially surface-treated fiber, emphasizing the importance of tailoring the surface treatment to the matrix chemistry. Based on chemical shifts seen in the core region and differences in the valence band region, a reaction scheme is suggested for the possible interaction between the fiber and the resin.

Introduction

The development of lightweight composites, particularly for use in aerospace and construction applications, has gained importance over the past decade. A growing area of materials research has been devoted to the fabrication of carbon−plastic materials where the highly desirable mechanical properties of the carbon fiber are combined with the increased fracture resistance and toughness of a thermoplastic polymer. Over the years, attempts have been made to improve composite performance by increasing the tensile strength of the fiber and the toughness of the matrix system, but this has not necessarily translated into an increase in composite strength. It is now widely acknowledged that optimum composite performance is achieved only when there is a significant amount of interaction between the fiber and the matrix material at the interface between them. Often, the surface of the fiber is modified to produce the required level of interaction, leading to a significant improvement in composite performance. The effects of this type of treatment are well documented in the literature, both from outside[1−15] and from within this research group.[16−21]

In this paper, the interfacial interaction between a carbon fiber electrochemically oxidized in nitric acid and a thermoplastic resin, a polyimide, named Avimid K3B was studied using X-ray photoelectron spectroscopy (XPS). A thin layer of resin coated onto the fiber was used to model the composite interface. One compound was selected as a possible model to explain the main spectral features of the matrix whose actual structure is proprietary, and their structural similarities were investigated by using ab initio molecular orbital calculations. The possibility of solvent reaction with the fiber was also investigated.

Experimental Section

The carbon fibers used in this study were Hercules IM7 intermediate modulus polyacrylonitrile (PAN)-based fibers.

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The fiber surface was found to have industrial treatment and this fiber is called “as received”. This surface treatment was removed by a process of heat-treatment in a vacuum, and this fiber is designated as “detreated”. Further details of this treatment method were given in an earlier paper.[22] Pitch-based Dupont E120 fibers that had been specially prepared by DuPont with no surface treatment or size were also used in this study. The matrix material used was a thermoplastic resin, Avimid K3B, provided by the DuPont Company. The resin was obtained in the form of its precursor solution which was then converted into the final powder form by using a procedure provided by the manufacturer. The compound bismaleimide was obtained from Alfa Aesar. *N*-Methyl-2-pyrrolidinone (NMP) was obtained from Aldrich.

The detreated fibers were electrochemically oxidized in the galvanostatic mode using a standard three-electrode glass cell, details of which have been published earlier.[20−25] A 1.0 M solution of nitric acid was used as the electrolyte, and graphite rods were included in the circuit as counter electrodes. A current of 0.5 A and a polarization time of 40 s were used. The fiber was then dip-coated with a NMP solution of the resin by allowing the fiber and the resin solution to remain in contact for about 30 min at a temperature of 80 °C. The fiber sample was then dried for about 2 h in an 80 °C oven to drive off any excess solvent that may have been associated with the fiber. The thickness of the formed resin layer was adjusted to ensure that the layer was thin enough that the interfacial region could be studied using XPS. It was found that the optimum level of resin coverage was obtained by using a 2.0 wt % solution of the resin. This was prepared by dissolving 2.0 g of resin in 100 mL of spectroscopic grade NMP.

An ES200B X-ray photoelectron spectrometer was used to conduct the XPS analysis. The instrument used achromatic Mg Kα X-radiation (240 W) with a line width of 0.7 eV. Data were recorded in the FRR mode (1:23). Monochromatic XPS spectra for K3B were collected on a VSW HA150 spectrometer (150 mm hemispherical analyzer) operated in the FAT (fixed analyzer transmission) mode with a pass energy of 22 eV, equipped with a 16-plate multichannel detector system and Al Kα X-radiation (240 W) produced from a 32 quartz crystal VSW monochromator providing an X-ray line width of better than 0.2 eV. The fibers were mounted as a “brush” so that no signal was received from the sample holder. [26] NMP was recorded as a frozen solid by recording the frozen solid at liquid nitrogen temperature. Curve-fitting of the data was performed using a nonlinear least-squares method with a Gaussian−Lorentzian (G/L) product function and a nonlinear background.[27] The G/L mix was taken as 0.5 for all peaks except for the graphitic peak in the C1s core region spectra which was taken as 0.8. An exponential tail was included to represent the conduction band interactions. We find very little adventitious carbon on the surface of carbon fibers. Our evidence for this is that we find no significant build up of C1s intensity while the sample is in the spectrometer, and we often find a line width incompatible with the line width for adventitious carbon. We have previously reported that untreated fibers can give C1s line widths that have a much narrower line width than the line width found for adventitious carbon.[28]

The ab initio Closed-Shell Restricted Hartree−Fock calculations were performed using the Gaussian 98W program on a PC and a minimal STO-3G type basis set using single multiplicity and then refined using an N-31 type extended basis set[29] for the valence band. CNDO calculations were conducted using the program developed by one of us and reported earlier.[30] This program was used to perform relaxation potential model calculations for the C1s region of the NMP molecule by using Mann's integrals[31] for the $<1/r>$. IBM RISC/6000 and personal computers were used for the CNDO calculations and ab initio calculations. The calculated valence band spectra were obtained by the addition of the component peaks for each calculated energy level where the position of each peak corresponded to the theoretical energy level. The intensity of each component peak was given by the net atomic population of the energy level, adjusted by the level's photoelectric cross-section, as given by Scofield.[32] Each peak in the calculated spectrum has the same full-width at half-maximum and a G/L mixing ratio of 0.5.[27] The peak width was set to 1.15 eV for best comparison with the experimental spectra. The spectrum was linearly contracted by a factor of 1.3 to account for exaggeration of the spread of valence band energies associated with ab initio calculations. This approach has been successively applied to other polymer systems.[33]

Results and Discussion

In this paper we will discuss the possible interfacial interaction between K3B and a surface treated carbon fiber as explained in the Introduction. The purpose of this study is to see if such an interaction exists, and if so under what conditions. We will consider three systems, first the interaction of K3B with the surface treated fiber, second the interaction of a simple molecular system (*N*,*N*′-1,4-phenylenedimaleimide (PMI)), which contains many of the K3B functionalities, with the surface treated fiber, and finally an examination to see if the solvent NMP will interact with the surface treated fibers. This last experiment is very important because we have used NMP as the solvent for the K3B and the PMI. If no chemical interaction occurs at the interface the XPS data for this experiment will be simply a superimposition of the outer matrix spectrum with the inner carbon fiber spectrum, but if interaction occurs the spectrum will change to include the different chemistry associated with the interfacial interaction.

Analysis of Avimid K3B Polyimide Resin. K3B resin, whose actual structure is proprietary, was converted from its precursor into a fine, yellow powder and analyzed using XPS. Figure 1a shows the fitted C1s core region spectrum for the prepared resin. The curve fitting procedure used the peak positions shown in Table 1. The predominant feature in the spectrum is a peak at 284.6 eV that corresponds to the C−C and C−H groups present in the resin. In addition, there are also other peaks present to the higher binding energy side of this

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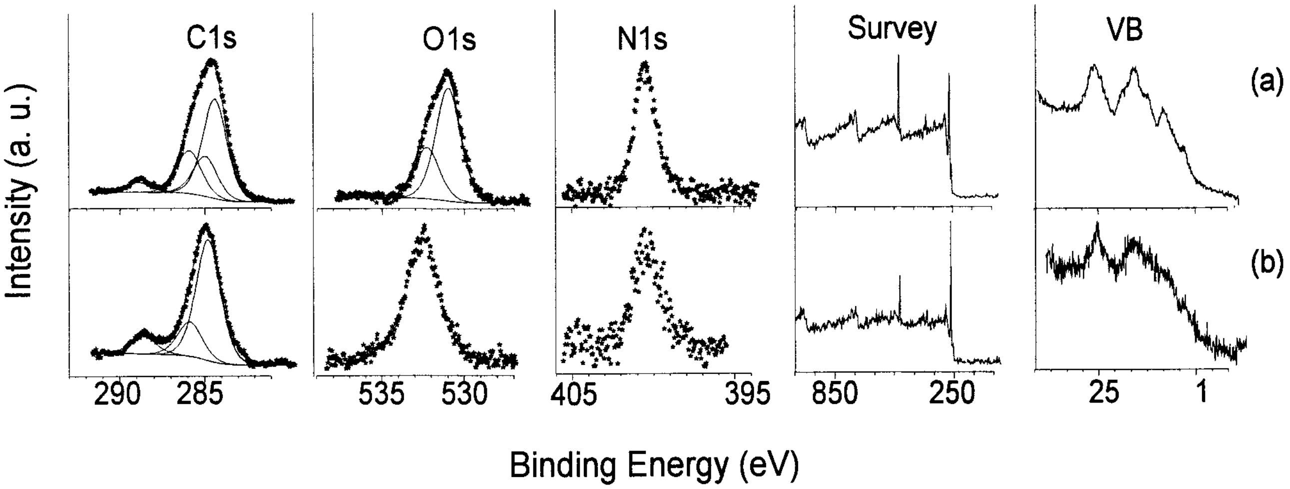

Figure 1. XPS core region spectra and valence band spectra of (a) K3B with (b) *N,N′*-1,4-phenylenedimaleimide (PMI).

Table 1. Component Peak Positions Used in C1s Curve Fitting

peak no.	functionality	binding energy (eV)
1	graphitic carbon	284.6
2	β-carbon, −C−N	285.4
2	−C−OH, −C−O−C−	286.1
3	bridged structure	286.6−287.9
4	C=O	288.6
5	COOH, COOR	289.1
6	CO_3^{2-}	289.6−290.1

main peak. The peaks present at a chemical shift of 0.8 and 1.5 eV from the main peak correspond to C−N and C−OH type functionality, respectively. In addition, another fairly intense feature at a separation of about 4.2 eV is seen which is indicative of C=O functionality present in the resin. The O1s core region spectrum of the resin consists of two component peaks that indicate the resin contains two types of C/O linkage, but the N1s spectrum only consists of a single peak and shows the resin contains one type of C−N linkage.

Analysis of the Possible Structure of K3B. To understand any chemistry that is taking place between the matrix and the carbon fibers, it is necessary to develop a model that can be used as the basis for calculations to interpret the valence band spectrum in the interface region. On the basis of a search of the literature and patents published by Du Pont[34−37] and our XPS analysis interpreted by ab initio calculations, a possible simple model for the K3B copolymer is shown in Figure 2a. It was found that the calculated and experimental valence band spectra showed significant agreement, as shown in Figure 3.

***N,N′*-1,4-Phenylenedimaleimide (PMI).** To compare how a molecule with many of the functionalities of the K3B polymer might interact with the fibers, we examined the interfacial chemistry associated with the exposure of the surface treated fibers to PMI, a molecule with a known and simple molecule structure shown in Figure 2b, using the same reaction procedure that was used for K3B. PMI has a distinct core and valence band spectrum as indicated in Figure 1b. One notes that only one O1s feature is seen at a binding energy corresponding to >C=O oxygen as expected from the structure shown in Figure 2b. Likewise, only one N1s feature is seen. Three principal C1s features can be seen, one corresponding to the carbon backbone, one >C−N carbon, and one corresponding to >C=O carbon atoms, though the full details of the shifts require a more complex analysis. The bismaleimide spectrum is compared with the K3B core and valence band spectrum in Figure 1. One notes the double features in the O1s region corresponding to the two types of oxygen seen in K3B indicated by the structure in Figure 2a with the expected intensity ratio of 1:2. The N1s region of K3B shows the expected single peak, and the C1s region, as expected from the structure in Figure 2a, is complex. There are, as expected, some significant differences in the valence band spectrum of K3B and PMI.

***N*-Methyl-2-pyrrolidinone (NMP).** The XPS of the core and valence band region of a frozen sample of NMP at liquid nitrogen temperature was studied in order to be able to characterize the presence of any surface NMP in our experiments. We compared our experimental data for NMP with a calculated spectrum to enhance our confidence in the experimental data, a consideration which is always important in any surface analysis, but especially important when a frozen solid is studied when other compounds can condense on the surface of the frozen solid. The C1s region is shown in Figure 4 which compares the spectrum with the spectrum calculated by using a Relaxation Potential Model (RPM) for NMP. The RPM model has been discussed elsewhere [29] and includes the effects of extraatomic relation. This calculation illustrates how the C1s region will display a complex overlapping pattern for the type of chemical functionality seen in this relatively simple molecule, also indicating excellent agreement with experiment. Figure 4 shows how the calculated peaks can be assigned to different carbon atoms in the NMP molecule. The

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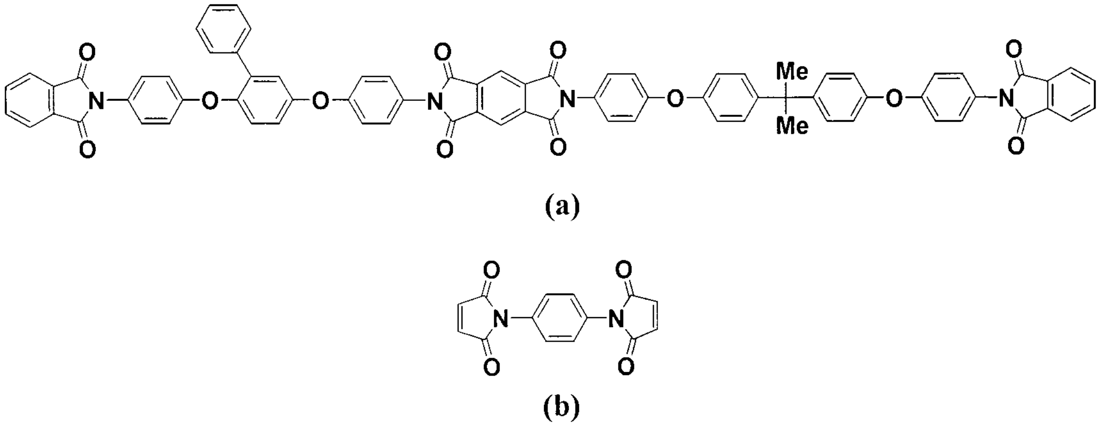

Figure 2. (a) Possible structure of the K3B based upon published data, (b) *N,N′*-1,4-phenylenedimaleimide (PMI).

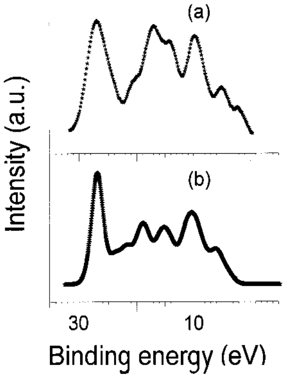

Figure 3. The comparison of (a) experimental valence band spectrum of K3B obtained with monochromatic X-radiation with (b) the calculated valence band spectra obtained using the K3B model molecule shown in Figure 2a.

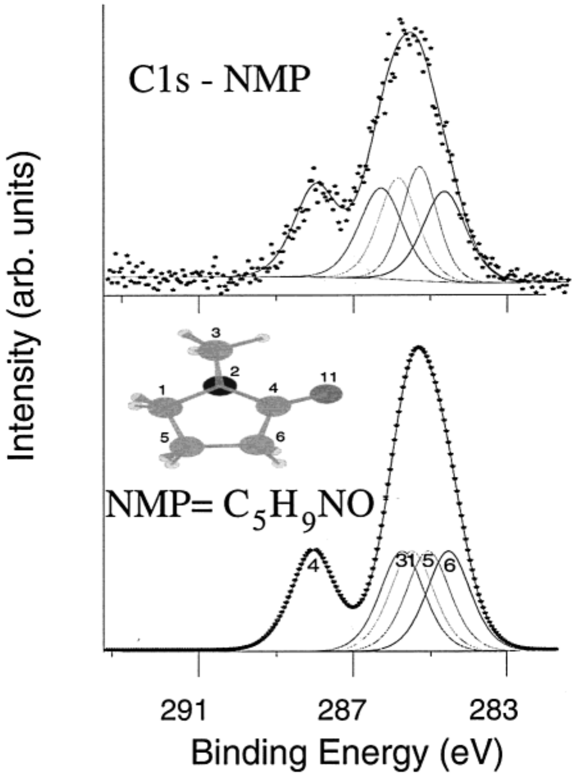

Figure 4. Comparison of (a) C1s spectrum of solid NMP at 77K with (b) calculated XPS spectrum generated with the relaxation potential model using CNDO calculations.

calculation indicates that the C1s region of NMP would be expected to exhibit five overlapping peaks corresponding to each of the five different carbon atoms in NMP (numbered 1, 3, 4, 5, 6 in the molecule structure in Figure 4). Atom 2 is the nitrogen atom, and atom 11 is oxygen. The calculation predicts the spectrum shown in Figure 4, where the peak separations of the relaxation potential model calculation were increased by 30% to improve the alignment with the experimental spectrum. The principal value of the calculation is that it indicates that the C1s peak arising from carbon atom 4 should be clearly separated from the remaining peaks. When the experimental data is fitted to five peaks whose areas were fixed and fwhm allowed to vary, one obtains a good fit to the data and an experimental spectrum that takes the form predicted by the calculation. This comparison gives us confidence that we have indeed prepared a true solid NMP surface, and that the experimental spectrum (discussed below) can be used as an appropriate standard for NMP.

The Commercially Treated Carbon Fibers. It has been shown in previous work from various workers, including our group, that untreated carbon fibers do not normally react with a given matrix material.[17] Figure 5 a shows the overall and valence band spectra for the as-received IM7 fibers. It can be seen that the fiber surface consists mainly of carbon as indicated by the intense C1s peak seen at approximately 284 eV in the overall spectrum. In addition, it appears that the treatment applied by the manufacturer has also produced a considerable amount of oxygen on the surface, confirmed by the presence of a peak at approximately 535 eV in the overall spectrum. A small amount of nitrogen was also found (Figure 6a(iii)) which we believe to be due to residual nitrogen arising from the conversion of the PAN into carbon fiber, and we have found such residual nitrogen in PAN-based fibers.[38−44] We

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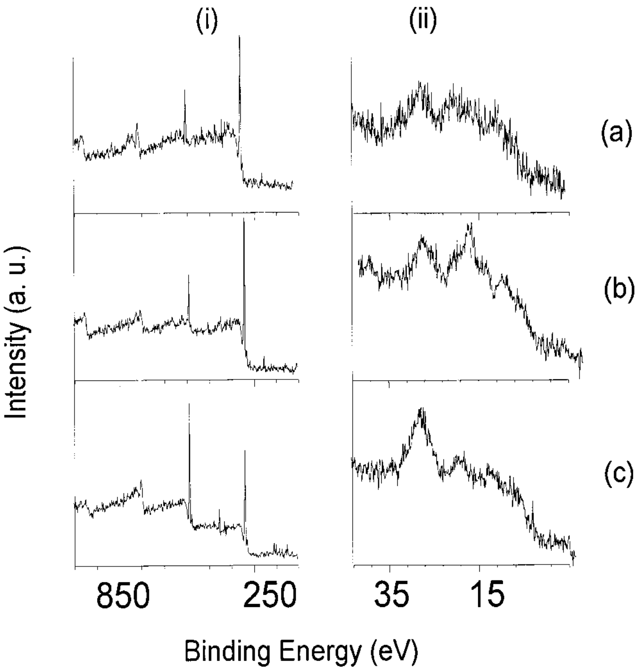

Figure 5. XPS spectra (I) survey region and (II) valence band of (a) as received IM7 fibers, (b) K3B powder, and (c) fibers dip-coated with K3B solution.

cannot rule out the possibility that some of this nitrogen came from the commercial treatment. The valence band spectra seen in Figure 5a also indicate a surface consisting of functional groups containing carbon and oxygen. Further evidence for this can be seen by a detailed examination of the core region spectra seen in Figure 6a. The main C1s peak is present at 284.6 eV and corresponds to the graphitic linkages of the carbon fiber. In addition, there are peaks present to the higher binding energy end of the main peak which correspond to oxygen-containing functional groups that have been introduced as a result of the manufacturers' surface treatment. Table 1 shows the component peaks of this spectrum and their relative positions with respect to the main peak. From the chemical shifts observed for these peaks, it is seen that COOH and C=O groups have been introduced onto the surface, in addition to C−OH type functionality. Figure 6a also shows the O1s and N1s spectra for the as-received fiber. The O1s spectrum appears to consist of two-component peaks corresponding to the presence of C=O and C−O−C. A weak N1s signal is also seen which is predominantly due to the nitrogen present in the PAN-based fiber and probably was not introduced by the commercial treatment.

Interaction of Commercially Surface-Treated Fibers with K3B. Figure 6b depicts the core spectra for the K3B resin as seen in Figure 1a. Figure 6c shows the core region spectra collected for the commercially treated fiber coated with a thin layer of resin solution. In analyzing these spectra, we assume that if there is an actual chemical interaction at the interface, then the spectrum of the coated fiber (Figure 6c) will be significantly different from the spectrum of either the uncoated fiber or the pure resin. The details of this approach have been discussed elsewhere.[46,26] The objective is to show that it is not possible to construct the spectrum of the coated fiber by adding together the spectrum of the underlying fiber and the matrix. We have monitored the maximum value in the difference spectrum (coated fiber − [a(fiber spectrum) +b(matrix spectrum)]), where a and b are fractions varying from 0 to 1. We also monitored the c^2 value[27] corresponding to a comparison of the coated fiber with [a(fiber spectrum) + b(matrix spectrum)]. We find that the smallest value of the maximum in the difference spectrum, and the smallest c^2 value correspond to a value of $a \sim b = 0.5$, i.e., approximately equal amounts of each component. The addition spectra (i.e., [a(fiber spectrum) + b(matrix spectrum)] have been normalized by setting the maximum spectral feature to be the same in the addition spectrum and the spectrum of the coated fiber. Figure 7d shows the spectrum obtained by a 1:1 addition of the fiber spectrum in Figure 7a with the resin spectrum in Figure 7b. The similarity between this addition spectrum and the spectrum for the coated fiber in Figure 7c indicates that the level of interaction between the commercially treated fiber surface and the resin solution is very low. This is further confirmed by the fact that the difference spectrum (Figure 7 e) obtained by subtracting the 1:1 addition spectrum from the experimental spectrum of the coated fiber yields a spectrum of very low intensity (almost flat). In addition, the lack of any observable shift in the N1s spectra shown in Figure 6(iii) indicates that *little or no interaction has taken place between the commercially treated fiber and the resin*. Therefore, to produce the desired level of interaction, it becomes necessary to improve the surface treatment applied by the manufacturer. It is important to point out that surface treatments can influence the mechanical properties of the fiber. For example, it has been shown that treatment may lead to the breakdown of the graphitic lattice and a consequent reduction in the mechanical strength of the fiber. This observation increases the importance of the fiber surface, so that a controlled treatment can then be applied to the detreated fiber surface.

Interaction of Electrochemically Oxidized Fibers with K3B. The detreated fiber surface is galvanostatically oxidized at 0.5A for 40 s in 1.0 M HNO_3. It has been observed from results reported earlier that oxidation in nitric acid produces a hydrogen-bridged structure (HBS)[17,22,45 46] (it is a keto−enol tautomerized bridged structure) as the primary oxidation related functionality (see the drawing in Figure 9). The introduction of this functional group on the surface of the fiber facilitates the reaction of the fiber with a solution of K3B resin. Figure 8a shows the curve-fitted C1s core region spectrum for the fiber oxidized in nitric acid following the detreatment procedure. The curve-fitting is carried out by using the component peaks shown in Table 1. A relatively high level of oxidation can be seen as indicated by the extremely intense feature seen at a shift of 2.8 eV from the main peak. This corresponds to the formation of the HBS, as expected for oxidation in an acidic solution. The C1s spectrum seen in Figure 7b represents the core region spectrum for K3B powder (as

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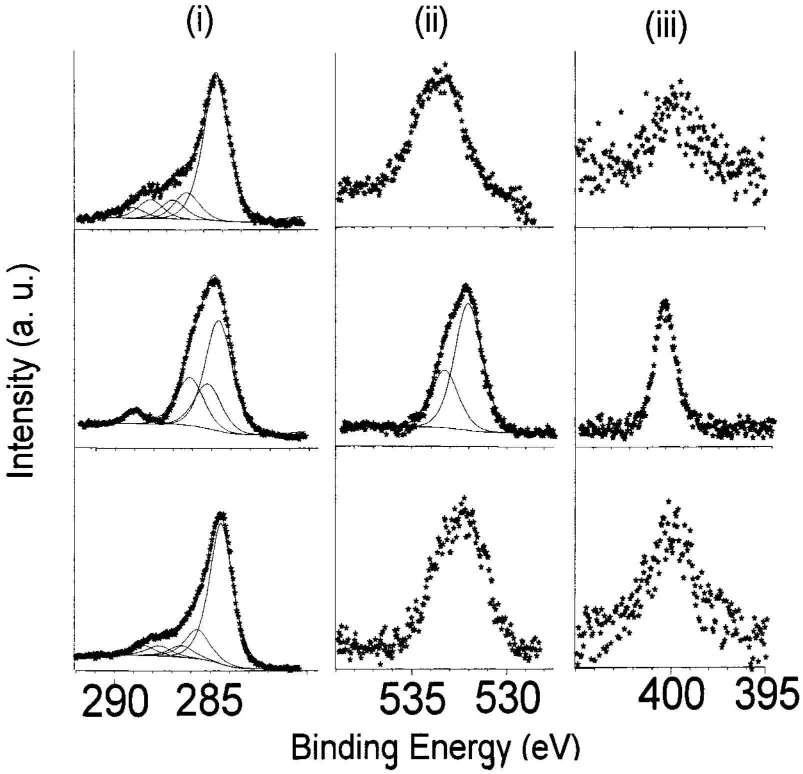

Figure 6. XPS spectra (I) C1s, (II) O1s, and (III) N1s region of (a) as received IM7 fibers, (b) K3B powder, and (c) fibers dip-coated with K3B solution. The atomic ratio of C:O:N = 1.00:0.31:0.09 for a, 1.00:0.44:0.08 for b, and 1.00:0.31:0.08 for c.

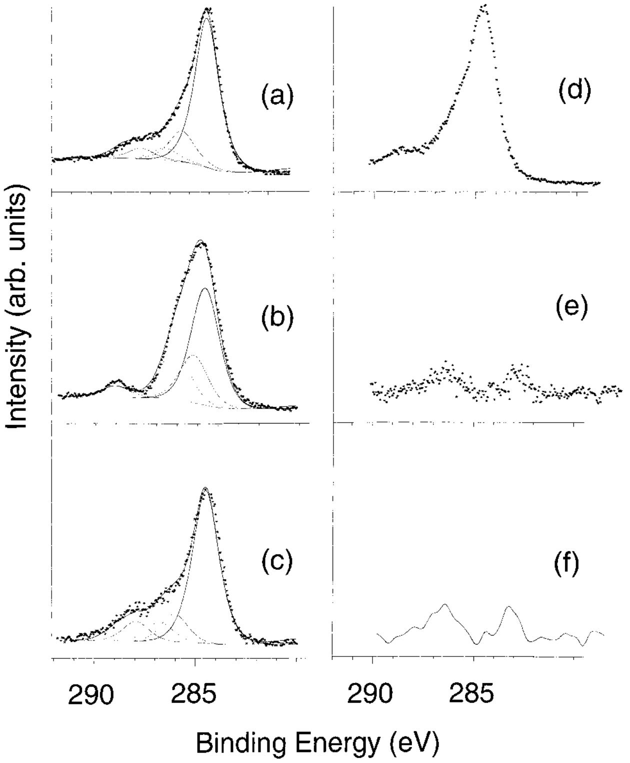

Figure 7. C1s spectrum for (a) as received IM7 fibers; (b) K3B powder; (c) fibers in part a dip-coated with K3B solution; (d) addition of parts a and b; (e) difference of parts d and c; (f) smoothed version of part e. The intensity scales for parts d, e, and f are the same.

seen in Figures 1a and Figure 6b). The spectrum for the fiber coated with a thin layer of K3B is represented in Figures 8c, and the spectrum in Figure 8d is a

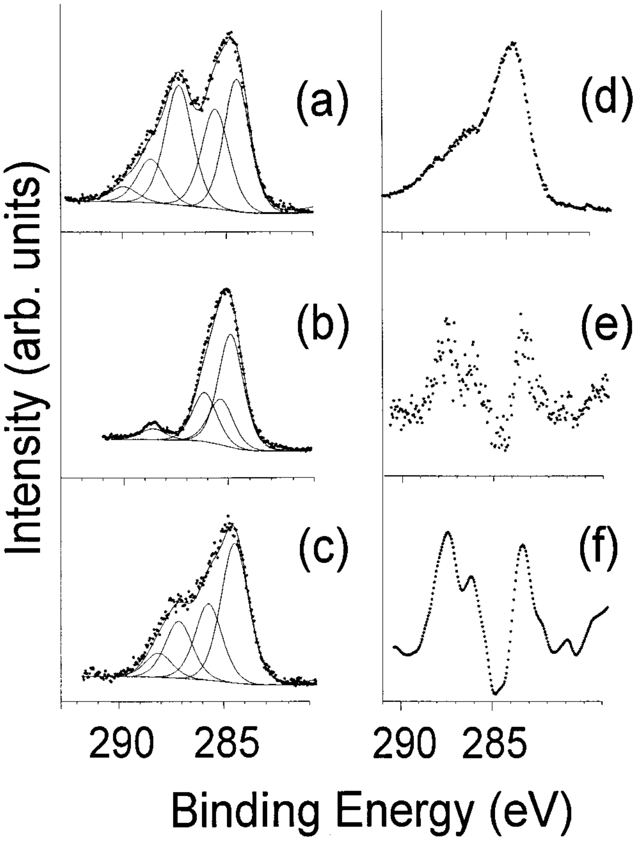

Figure 8. Curve-fitted C1s spectrum for (a) detreated IM7 fibers oxidized at 0.5 A in 1 M HNO_3 for 40 s; (b) K3B powder; (c) IM7 fibers, as in part a, dip-coated with K3B solution; (d) addition of parts a and b; (e) difference of parts d and c; (f) smoothed version of part e. The intensity scales for parts d, e, and f are the same.

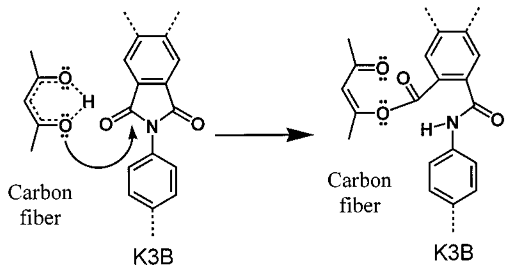

Figure 9. Schematic representation of mechanism for reaction of carbon fiber surface with K3B.

synthetic spectrum obtained by the 1:1 addition of the spectra in Figures 8a and Figure 8b. There is a chemical interaction at the interface between the fiber and the resin if the spectrum of the coated fiber is significantly different from the spectrum obtained by the addition of the spectrum for the uncoated fiber and unreacted resin. It is clear that the addition spectrum in Figure 8d is significantly different from the spectrum of the coated fiber (Figure 8c). This can be seen when the two spectra are subtracted, to give the difference spectrum seen in Figure 8e. If in fact the addition spectrum and the experimental spectrum had been the same, the difference spectrum would be simply a flat line. The fact that the spectrum in Figure 8e has a definite shape, and the failure to “fit” the addition spectrum with the experimental data is conclusive evidence for the presence of chemical interaction at the interface. In fact, the spectrum in Figure 8e can be used as a model for the interface. The spectrum is subjected to a 15-point quadratic/cubic smooth to allow features in the difference spectrum to be clearly discerned, and this is shown in Figure 8f. The negative peak seen at 285 eV represents the difference between the two main C1s peaks in Figure 8d and 8c. The peak produced on subtraction is negative, because there is a small difference in the full width at half-maximum (fwhm) of the main graphitic peak in the two spectra. Positive peaks are observed at shifts of 2.0 and 4.0 eV, respectively, from the negative peak and can be assigned specific functional groups, based on the data given in Table 1. These correspond to the keto−enol bridge (2.0 eV) and the ester (4.0 eV) groups, respectively. This, combined with our proposed structure for the resin molecule enables the proposal of a mechanism for the interaction at the interface, given in Figure 9. Additionally, the fact that this interaction is significantly different from the interaction of the commercially treated IM7 fibers with K3B can be seen from the differences in the relative percentages and peak widths seen in Table 2. The relative fwhm of the N1s peak of the reacted polymer with carbon fiber, the N1s peak of the K3B and the N1s peak of the PAN-based IM7 fiber is 1.00:0.77:0.65, respectively.

Interaction of IM7 Fibers with PMI. As indicated earlier, there are distinct structural similarities between K3B and the molecule PMI. Therefore, this compound, when used as the matrix phase, should interact with the IM7 fibers. The fibers are detreated and electrochemically oxidized as described earlier and then dip-coated with a layer of PMI, prepared as a 1% solution in NMP. The fibers are then dried for 24 h to allow the solvent to be completely driven off. Figure 10c shows the spectrum for the IM7 fiber coated with the PMI. This can be compared to the addition spectrum in Figure 10d, generated by the addition of the spectrum for the oxidized fiber in Figure 9a with the experimental spectrum of the PMI powder in Figure 10b. It can be seen that the experimental spectrum for the coated fiber and the 1:1 addition spectrum are different, and this difference is amplified by the difference spectrum shown in Figure 10d. The fact that this difference spectrum is not a flat line but has a distinct shape, with prominent features at separations of 2.0 and 5.0 eV, indicates that some *chemical interaction has taken place between the fiber and the matrix phase.* This indicates that we have formed a reactive surface on the fibers by surface treatment, and both PMI and K3B react with the surface, indicating the importance of surface treatment to induce chemical reaction with functionalities that are relevant to practical matrix systems. We believe that the surface reaction with PMI is similar, but not identical, to that which we have proposed for K3B.

The Role of the Solvent in Fiber−Matrix Interaction. Although the fiber sample is thoroughly dried following the dip-coating procedure, there is a possibility that some NMP solvent may remain on the surface. Further, taking into account the structural similarity of the solvent and K3B, it is possible that the solvent may play a part in the interaction of K3B with the surface of the oxidized fiber. Solvent interactions of this type could be potentially detrimental because they could cause significant complications during the manufacture of the ultimate composite. To investigate any possible solvent interaction we performed the sequence of experiments described above with the solvent alone. To obtain a spectrum of NMP alone we recorded the spectrum of solid NMP. NMP is a volatile liquid and cannot thus be directly examined by XPS. The solid spectrum was obtained by cooling NMP to liquid nitrogen temperature using a specially cooled probe. We used this spectrum as our standard for the NMP spectrum.

E-120 fibers whose chemical behavior is similar to that of the detreated IM7 fibers[22] were electrochemically oxidized as indicated earlier and then dip-coated with a thin layer of solvent at 80 °C for 30 min and dried at the same temperature for approximately 24 h so that any unreacted solvent will be driven off. We report the E-120 results because these fibers were obtained in an untreated and unsized form from the manufacturer and did not require detreatment. Further, the surface chemistry of the E120 fibers after electrochemical oxidation (Figure 11a) and the IM7 fibers after electrochemical oxidation (Figure 10a) are similar. Figure 11 shows the experimental spectrum for solid NMP discussed above. The spectrum for the solvent-coated fiber is shown in Figure 11c. As in the case of the interaction with K3B, a 1:1 addition spectrum (Figure 11d) is generated for comparison. The remarkable similarity between the spectra seen in Figure 11d and Figure 11c indicates that there is little if any interaction between the solvent and the oxidized fibers. The difference spectrum shown in Figure 11e is obtained by subtracting the spectrum in Figure 11d from the one in Figure 11c. This spectrum is significantly different from the difference spectrum seen for K3B interaction in Figure 8e. The difference spectrum is essentially a flat line with little chemical feature, indicating that the solvent is

Table 2. Relative Peak Areas and Chemical Shifts from C1s Curve Fitting

	main peak			peak 2			peak 3			peak 4			peak 5		
sample	BE (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)	CS (eV)	area (%)	fwhm (eV)
IM7-as recd	284.6	67.0	0.8	1.7	12.0	0.9	2.4	8.0	0.9	3.8	8.0	0.9	4.8	5.0	0.9
K3B resin	284.6	52.0	1.6	0.9[a]	21.0	1.6	1.4[b]	22.0	1.6	4.2	5.0	1.6			
IM7-K3B	284.6	68.0	0.8	1.4	15.0	0.9	2.3	6.0	0.9	3.6	5.0	0.9	4.5	5.0	0.9
IM7-D/0.5A	284.6	31.0	0.7	1.0[c]	25.0	0.9	2.8	30.0	0.9	4.2	11.0	0.9	5.6	4.0	0.9
IM7-D/K3B	284.6	54.0	0.9	1.5	16.0	1.1	2.7	19.0	1.1	3.8	11.0	1.1			
IM7-D/NMP	284.6	61.0	0.8	1.7	13.0	0.9	2.1	15.0	0.9	3.4	7.0	0.9	4.4	4.0	0.9
E120-U/0.5A	284.6	39.0	0.8	0.9[c]	13.0	0.9	2.5	41.0	0.9	4.3	6.0	0.9	5.6	1.0	0.9
E120-U/NMP	284.6	66.0	0.8	1.3	14.0	0.9	2.5	11.0	0.9	4.1	9.0	0.9			

[a] For K3B, peak 2 represents intensity due to −C−N− functional groups. [b] For K3B, peak 3 represents intensity from −C−OH functional groups. [c] For oxidized E120 and IM7 fibers, peak 2 represents intensity from the β-carbon atoms.

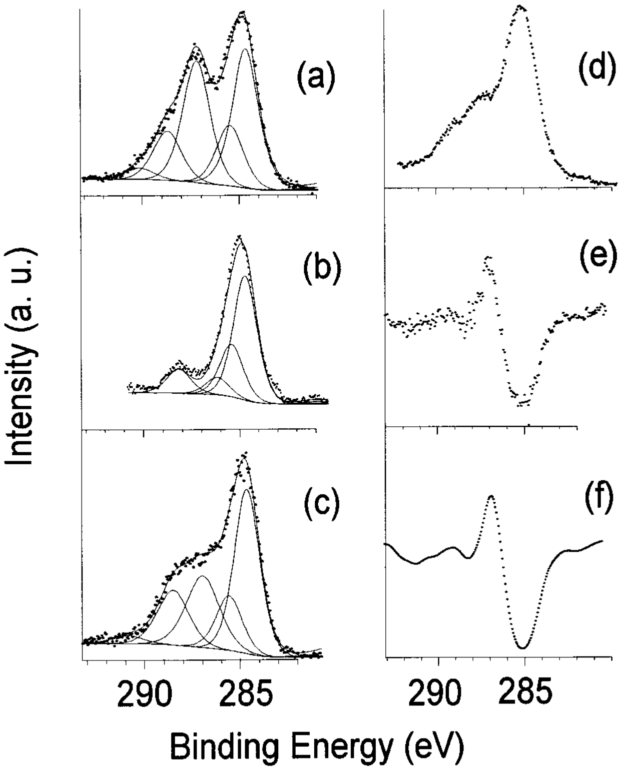

Figure 10. Curve-fitted C1s spectrum for (a) detreated IM7 fibers oxidized at 0.5 A in 1 M HNO_3 for 30 s; (b) PMI powder; (c) IM7 fibers, as in part a, dip-coated with PMI solution; (d) addition of parts a and b; (e) difference of parts d and c; (f) smoothed version of part e. The intensity scales for parts d, e, and f are the same.

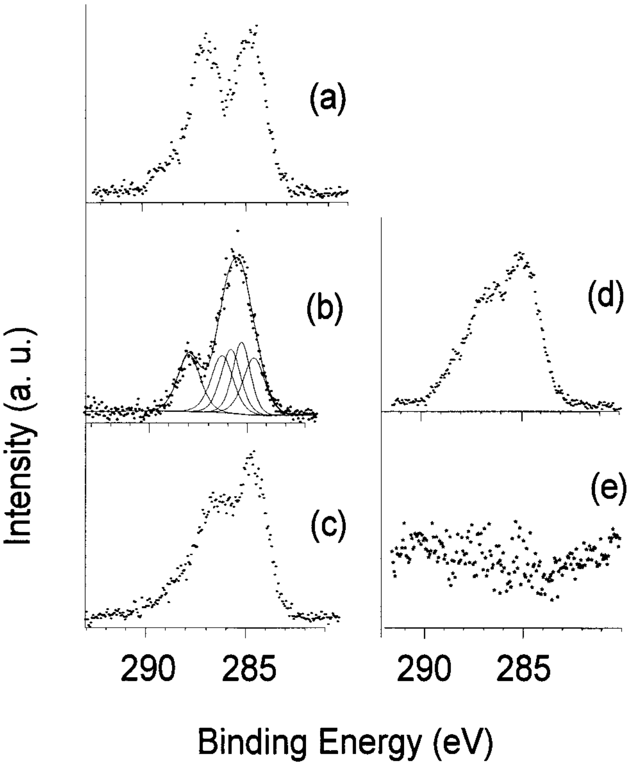

Figure 11. C1s spectra for (a) untreated E120 oxidized at 0.5 A in 1 M HNO_3 for 30 s; (b) solid NMP collected with the frozen liquid maintained at 77 K; (c) fibers, as in part a, dip-coated with NMP solution; (d) addition of parts a and b; and (e) difference of parts d and c. The intensity scales for parts d and e are the same.

simply adhering to the surface of the oxidized fiber and/or little chemical reaction has taken place between them. To further reinforce this fact, a similar study was conducted using the IM7 fiber system. The fibers were electrochemically oxidized in nitric acid, as described for the E-120 fibers and then dip-coated with the solvent in the manner indicated above. The spectra obtained (not shown) are very similar to the spectra obtained for E-120 (Figure 11) again showing that little interaction takes place between the fibers and the solvent alone. This provides further support that the detreatment process for the IM7 fibers does indeed remove the surface functionality introduced by the manufacturer's surface treatment. Based on these observations, it is possible to conclude that the fibers interact only with the matrix phase and that the solvent plays no significant chemical role in the interaction.

Conclusions

The interface between a carbon fiber and a thin layer of resin material coated on it can be effectively studied using core and valence band XPS. The data presented here indicates that while commercially surface-treated carbon fibers do not chemically interact with K3B, a definite chemical interaction takes place between detreated IM7 fibers that were subsequently electrochemically surface treated. The solid-state NMP XPS spectrum is seen to compare well with the calculated C1s region, and this spectrum formed a useful standard for studies that showed that there was not NMP chemical interaction with oxidized fiber surfaces. Ab initio calculations were effectively used to determine whether the estimated structure of the polyimide resin was reasonable and also to confirm the resemblance of selected model compounds to the resin itself. The determination of the interaction between the fiber and the matrix is a significant step in composite manufacture and testing.

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