



Surface characterization of pan-ba
by K Battleson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Carbon-epoxy materials are finding increased structural uses in areas such as aerospace, aeronautical, and sporting goods applications because they can be produced with desirable strength-to-weight properties. Historically, the limiting factor to the strength of those composites has been the integrity of the fiber-resin interface bond. Recently, surface analysis methods have been introduced to study this fiber/matrix interface.

In this study, SIMS, XPS, and AFM were used to characterize both untreated and electrochemically treated PAN-based carbon fibers. Hexcel Corp. provided the fibers studied and included poor quality fibers from lots with mechanical properties that failed to meet the product specification as well as fibers from good quality lots. It was hypothesized that the poor mechanical performance observed in some of the fiber lots was the result of either chemical or topographic abnormalities in the fibers. It was proposed that these abnormalities could be detected by the surface sensitive techniques mentioned.

Multivariate statistical techniques were used to explore relationships between the SIMS spectra and the mechanical test results. Principal components analysis (PCA) and discriminant analysis with cross validation were used to analyze the SIMS spectra of both treated and untreated fibers. Statistically significant differences in the surface chemistry of "good" and "poor" quality fibers were identified in both treated and untreated fibers. The PCA and discriminant loadings assisted in identifying the chemistry of changes in both inorganic and organic functionalities on the poor quality fibers. These changes include an increase of oxygen on poor property untreated fiber spectra, an increase of unsaturated hydrocarbon fragments on good property untreated fiber spectra, and differences in the amount of aluminum, PDMS, magnesium, calcium, and potassium. Treated fibers primarily differed in magnesium and calcium concentrations, as well. The resulting analysis also includes that there was an increase in nitrogen containing fragments on the spectra of poor property fibers.

Preliminary Atomic Force Microscopy analysis found differences in topography correlating to the mechanical properties; however, more work would be needed to determine whether variations are statistically significant.

SURFACE CHARACTERIZATION OF PAN-BASED CARBON FIBERS

USING XPS, SIMS, AND AFM

by

Kris Anne Battleson

A thesis submitted in partial fulfillment
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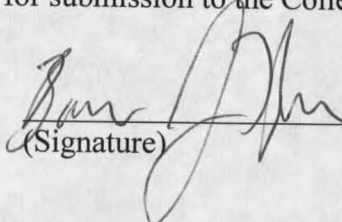
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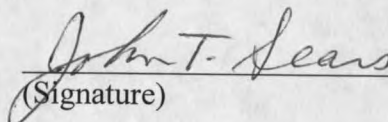
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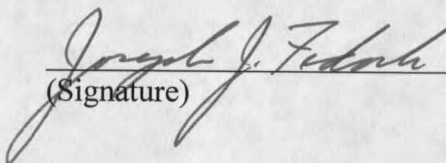
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TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT.....	xii
1. INTRODUCTION.....	1
Problem in This Area.....	1
Motivation for Research	2
Research Objectives.....	3
2. BACKGROUND	4
Analytical Methods.....	4
X-ray Photoelectron Spectroscopy.....	4
Theory and Principles of the Technique	4
Previous Work on Carbon Fiber Surfaces	10
Secondary Ion Mass Spectrometry	14
Theory and Principles of the Technique	14
Previous Work on Carbon Fiber Surfaces	17
Atomic Force Microscopy	18
Theory and Principles of the Technique	19
Previous Work on Carbon Fiber Surfaces	21
Numerical Methods.....	21
Principal Components Analysis.....	21
Theory and Principles of the Technique	22
Previous Work on Carbon Fiber Surfaces	25
Discriminant Function Analysis	26
Theory and Principles of the Technique	26
Cross Validation.....	27
Theory and Principles of the Technique	27
3. EXPERIMENTAL METHODS AND MATERIALS	28
Analytical Methods.....	28
SIMS Analysis	28
XPS Analysis	31
AFM Analysis	32
Numerical Methods.....	32
4. RESULTS.....	33
Untreated Fiber Spools	33

TABLE OF CONTENTS- Continued

	Page
Secondary Ion Mass Spectrometry	34
Atomic Force Microscopy	42
Treated Fiber Spools	48
Secondary Ion Mass Spectrometry	48
X-ray Photoelectron Spectroscopy.....	58
Atomic Force Microscopy	60
Variable Treated Fibers.....	65
Secondary Ion Mass Spectrometry	65
X-ray Photoelectron Spectroscopy.....	69
5. CONCLUSION.....	72
Untreated Fibers.....	72
Treated Fibers	72
Variable Treated Fibers.....	73
Future Work and Recommendations	73
REFERENCES CITED.....	75
APPENDICES.....	78
Appendix A- Fiber Sample Identification.....	79
Appendix B- Fiber Sample SIMS Spectra.....	86
Appendix C- Complete Peak Area Matrices.....	153
Appendix D- MATLAB™ Programs.....	232
Appendix E- Fragmentation Pieces Listed by Atomic Mass.....	236

LIST OF TABLES

Table	Page
1. Information obtained by x-ray photoelectron spectroscopy from Ratner and Castner	5
2. Common binding energy assignments for the carbon 1s peak from Ratner and Castner	9
3. Common binding energy assignments for the oxygen 1s peak from Ratner and Castner	9
4. Advantages and disadvantages of contact mode AFM from <i>Digital Instruments Scanning Probe Microscopy Training Notebook</i>	20
5. Advantages of principal components analysis from Malinowski	22
6. Fiber lot mechanical property descriptions.....	29
7. Atomic concentrations for D1374-6A and D1424-6C	60
8. Atomic concentrations for D1239-3C variable treated fibers	71
9. Calculated F values and confidence levels	71

LIST OF FIGURES

Figure	Page
1. Schematic of x-ray photoelectron spectroscopy	7
2. Schematic of a carbon atom undergoing the photoelectron process	8
3. High resolution carbon 1s peak of untreated carbon fiber by Sherwood et al.....	12
4. High resolution carbon 1s peak of surface treated carbon fiber by Sherwood et al.	13
5. Schematic of secondary ion mass spectrometry	15
6. Schematic showing the components of contact mode atomic force microscopy.....	19
7. Graphical representation of principal components analysis	24
8. An illustration of the discriminant function for a two-dimensional case	26
9. Loading #1 shows a variance in aluminum concentration ($m/z = 27$) in the untreated fiber group	35
10. Loading #2 shows a variance in PDMS concentration ($m/z = 28, 73, 147$) in the untreated fiber group.....	35
11. Loading #3 shows a variance in magnesium concentration ($m/z = 24$), potassium concentration ($m/z = 39$), calcium concentration ($m/z = 40$), and PDMS concentration ($m/z = 28, 73, 147$) in the untreated fiber group	36
12. Discriminant analysis with cross validation correctly identified differences between good and poor property untreated fibers.....	37
13. Discriminant loadings show the differences in good and poor untreated fibers can be attributed to organic components	38
14. Loading #1 shows a variance in PDMS concentration ($m/z = 73, 147$) in the untreated fiber group.....	39

15. Discriminant analysis with cross validation correctly identified differences between good and poor property untreated fibers using organic components	40
16. Discriminant loadings show the differences in good and poor untreated fibers	40
17. Discriminant analysis with cross validation correctly identified differences between good and poor property untreated fibers using organic components in the absence of PDMS	41
18. Discriminant loadings show organic differences between good and poor property untreated fibers can be attributed to organic components other than PDMS	42
19. Surface contour plot of R128-04 (good property) fiber	44
20. Surface contour plot of R128-08 (poor property) fiber	44
21. Horizontal section plot of R128-04 (good property) fiber	45
22. Horizontal section plot of R128-08 (poor property) fiber	45
23. Vertical section plot of R128-04 (good property) fiber	46
24. Vertical section plot of R128-08 (poor property) fiber.....	46
25. Scanning electron microscope image of R128-04 (good property) fiber	47
26. Scanning electron microscope image of R128-08 (poor property) fiber	47
27. Loading #1 shows a variance in magnesium concentration ($m/z = 24$) and calcium concentration ($m/z = 40$) in the treated fiber group	49
28. Loading #2 shows a variance in aluminum concentration ($m/z = 27$) in the treated fiber group	49
29. Loading #3 shows a variance in PDMS concentration ($m/z = 28, 73, 147$) in the treated fiber group.....	50
30. Loading #4 shows a variance in PDMS concentration ($m/z = 28, 73, 147$) and potassium concentration ($m/z = 39$) in the treated fiber group	50

31. Loading #5 shows a variance in potassium concentration ($m/z = 39$), chromium concentration ($m/z = 52$), and iron concentration ($m/z = 56$) in the treated fiber group.....	51
32. Variations in score #1 (magnesium and calcium intensity) and score #5 (potassium, chromium, and iron intensity) are present in the treated fiber lots	52
33. Discriminant analysis with cross validation correctly identified differences between good and poor property treated fibers	53
34. Discriminant loadings show the differences in good and poor treated fibers can be attributed to primarily inorganic elements	53
35. Loading #1 shows a variance in PDMS concentration ($m/z = 73, 147$) in the treated fiber group.....	54
36. Loading #2 shows a variance in PDMS concentration ($m/z = 73, 147$) in the treated fiber group	55
37. Discriminant analysis with cross validation correctly identified differences between good and poor property treated fibers using organic components	55
38. Discriminant loadings show the differences in good and poor treated fibers	56
39. Relative magnesium and calcium intensities for treated fibers show that good fibers have higher cation concentration	57
40. Treated D1374-6A (good) fibers with calcium and magnesium overlay show an uneven distribution of cations.....	58
41. XPS survey spectra of D1374-6A, 1500 ft. good property fiber	59
42. XPS survey spectra of D1424-6C poor property fiber.....	59
43. Surface contour plot of D1374-6A, 1500 ft. (good property) fiber	61
44. Surface contour plot of D1424-6C (poor property) fiber.....	61
45. Horizontal section plot of D1374-6A, 1500 ft. (good property) fiber	62

46. Horizontal section plot of D1424-6C (poor property) fiber.....	62
47. Vertical section plot of D1374-6A, 1500 ft. (good property) fiber	63
48. Vertical section plot of D1424-6C (poor property) fiber	63
49. Scanning electron microscopy image of D1374-6A (good property) fiber	64
50. Scanning electron microscopy image of D1424-6C (poor property) fiber	64
51. Loading #1 shows a variance in aluminum concentration ($m/z = 27$) in the variable treated group	65
52. Loading #2 shows a variance in elemental silicon concentration ($m/z = 28$) and dialkylphthalate concentration ($m/z = 149$) in the variable treated group	66
53. Loading #3 shows a variance in potassium concentration ($m/z = 39$) and PDMS ($m/z = 28, 73, 147$) in the variable treated group	66
54. Discriminant analysis with cross validation correctly identified differences between untreated and treated fibers	67
55. Discriminant loadings show differences in untreated and treated fibers can be attributed to organic components	68
56. Discriminant analysis with cross validation correctly identified differences between regular and high treated fibers	68
57. XPS survey spectra of untreated D1239-3C fiber	69
58. XPS survey spectra of regular treated D1239-3C fiber	70
59. XPS survey spectra of high treated D1239-3C fiber	70

ABSTRACT

Carbon-epoxy materials are finding increased structural uses in areas such as aerospace, aeronautical, and sporting goods applications because they can be produced with desirable strength-to-weight properties. Historically, the limiting factor to the strength of those composites has been the integrity of the fiber-resin interface bond. Recently, surface analysis methods have been introduced to study this fiber/matrix interface.

In this study, SIMS, XPS, and AFM were used to characterize both untreated and electrochemically treated PAN-based carbon fibers. Hexcel Corp. provided the fibers studied and included poor quality fibers from lots with mechanical properties that failed to meet the product specification as well as fibers from good quality lots. It was hypothesized that the poor mechanical performance observed in some of the fiber lots was the result of either chemical or topographic abnormalities in the fibers. It was proposed that these abnormalities could be detected by the surface sensitive techniques mentioned.

Multivariate statistical techniques were used to explore relationships between the SIMS spectra and the mechanical test results. Principal components analysis (PCA) and discriminant analysis with cross validation were used to analyze the SIMS spectra of both treated and untreated fibers. Statistically significant differences in the surface chemistry of "good" and "poor" quality fibers were identified in both treated and untreated fibers. The PCA and discriminant loadings assisted in identifying the chemistry of changes in both inorganic and organic functionalities on the poor quality fibers. These changes include an increase of oxygen on poor property untreated fiber spectra, an increase of unsaturated hydrocarbon fragments on good property untreated fiber spectra, and differences in the amount of aluminum, PDMS, magnesium, calcium, and potassium. Treated fibers primarily differed in magnesium and calcium concentrations, as well. The resulting analysis also includes that there was an increase in nitrogen containing fragments on the spectra of poor property fibers.

Preliminary Atomic Force Microscopy analysis found differences in topography correlating to the mechanical properties; however, more work would be needed to determine whether variations are statistically significant.

CHAPTER 1

INTRODUCTION

Carbon and graphite materials are among the lightest refractory materials known [1, 2]. They have low density, low thermal expansion, high thermal and electrical conductivity, and are considered attractive for high-temperature applications because they maintain strength and stiffness above 2500K [2]. Because carbon fibers can be produced with desirable strength-to-weight properties, they are finding increased structural uses in areas such as aerospace, aeronautical, and sporting goods applications.

Carbon fibers are usually produced commercially with either a textile precursor such as polyacrylonitrile (PAN) or a pitch precursor [3]. The carbon fibers are woven together and used to reinforce various matrix materials including epoxy and cyanate ester resins. This reinforcement allows for improved impact strength and fracture toughness for the composite material by slowing down cracks that would otherwise propagate through the matrix and weaken the material [1, 2].

Problem in This Area

Historically, the strength of the fiber-resin interface bond has been found to be the limiting factor to the mechanical properties of carbon-epoxy materials [4]. Without maximum adhesion between the fiber and the matrix material, poor interlaminar shear

strength, a lack of delamination resistance, and low tensile strength all result in rendering the composite structure useless [1, 5, 6]. To optimize this adhesion between the fiber and the matrix material, the surface properties of the fiber are often electrochemically oxidized through the application of surface treatments [1, 2, 4-12]. This results in heightened dispersive interactions (London Forces), nondispersive interactions based on acid-base groups, covalent chemical bonds, and physical interactions, which all result in an increase in mechanical properties [6].

Motivation for Research

The strength of composite structures has historically been predicted through the mechanical testing of particular matrix/fiber reinforcement combinations. These tests include, but are not limited to, tensile testing, compression testing, shear testing, fatigue testing, or a combination thereof.

It is known that many of the measured mechanical properties of composites are governed by the quality of the adhesion between the fiber and the matrix. Without suitable interfacial interaction, proper load sharing between the fibers does not take place, resulting in a weaker material [3]. Recently, surface analysis techniques have been introduced to quantify the integrity of this fiber/matrix interface and compared to current mechanical methods. It is believed that the results obtained by mechanical tests are a function of surface characteristics and can be correlated to surface analysis techniques such as x-ray photoelectron spectroscopy, secondary ion mass spectrometry, and atomic force microscopy.

Research Objectives

The goal of this project was to explore the feasibility of using surface analysis to predict strength of carbon composite materials. Specifically, the ability of secondary ion mass spectrometry to identify differences between fibers with poor mechanical properties and good mechanical properties was explored. This objective was completed using the following procedures:

- Surface analysis methods were used to analyze poor property fibers that failed to meet product specification as well as fibers from good quality lots.
- Differences among the fiber groups and relationships between the acquired spectra and mechanical results were explored by using multivariate techniques.
- The statistical significance of differences between the poor property fibers and the good property fibers was determined.

CHAPTER 2

BACKGROUND

Analytical Methods

Carbon fibers are a challenge to study using surface sensitive techniques. Most spectroscopies are used with appropriate experimental protocol but traditional methods usually provide only the bulk information, 1000 Å or more, into the material. With chemical functionality studies, the information sought after is in the range of 1 Å to 100 Å so limited analysis techniques are available with specific advantages and disadvantages to each [1].

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is the most widely used of the contemporary surface characterization methods [13]. A large amount of information is acquired from each spectrum (Table 1) and the technique is flexible enough to be used on a large variety of sample types.

Theory and Principles of the Technique. Each atom on the surface of a material (except for hydrogen) consists of valence electrons that are involved in chemical bonding

along with core electrons. These core electrons possess a unique binding energy which is characteristic of the type of atom to which it is bound. By analyzing the binding energies of the electrons and the peak areas, quantitative elemental surface analysis is possible [14].

Table 1. Information obtained by x-ray photoelectron spectroscopy from Ratner and Castner[16].

In the outermost 10 nm of a surface, XPS can provide:

- Identification of all elements (except H and He) present at concentrations greater than 0.1 atomic percent
 - Semiquantitative determination of the approximate elemental surface composition (error < $\pm 10\%$)
 - Information about the molecular environment (oxidation state, bonding atoms, etc.)
 - Information about aromatic or unsaturated structures from shake-up ($\pi^* \rightarrow \pi$) transitions
 - Identification of organic groups using derivatization reactions
 - Nondestructive elemental depth profiles 10 nm into the sample and surface heterogeneity assessment using (1) angular-dependent XPS studies and (2) photoelectrons with differing escape depths
 - Destructive elemental depth profiles several hundred nanometers into the sample using ion etching (for organics)
 - Lateral variations in surface composition (spatial resolution of 8 μm to 150 μm , depending upon the instrument)
 - "Fingerprinting" of materials using valence band spectra and identification of bonding orbitals
 - Studies on hydrated (frozen) surfaces
-

Because the electrons can only travel a short distance through the sample without undergoing inelastic collisions resulting in a drastic loss of energy, XPS is considered to be highly surface sensitive. Usually only the upper 50 Å to 100 Å of the sample is analyzed using this technique [13].

Surface analysis by x-ray photoelectron spectroscopy begins by placing the sample in an ultra-high vacuum environment ($\sim 10^{-10}$ torr) and then irradiating the material with a source of low-energy x-rays. If the frequency of the excitation x-rays are greater than the binding energy for each element, photoemission will occur. Schematics of the x-ray photoelectron process are seen in Figures 1 and 2 [13].

The resulting photoelectrons are emitted from the surface having a kinetic energy (E_k) measured by a hemispheric analyzer. Using the known x-ray energy ($h\nu$), the binding energy (E_b) is calculated using the Einstein relation seen in Equation 1 [13, 15, 16] where ϕ is the work function of the spectrometer.

$$E_b = h\nu - E_k - \phi \quad (1)$$

The photoelectrons are then separated according to energy, counted, and related to the atomic and molecular environment from which they were ejected. A spectrum of the number of emitted electrons versus binding energy is obtained.

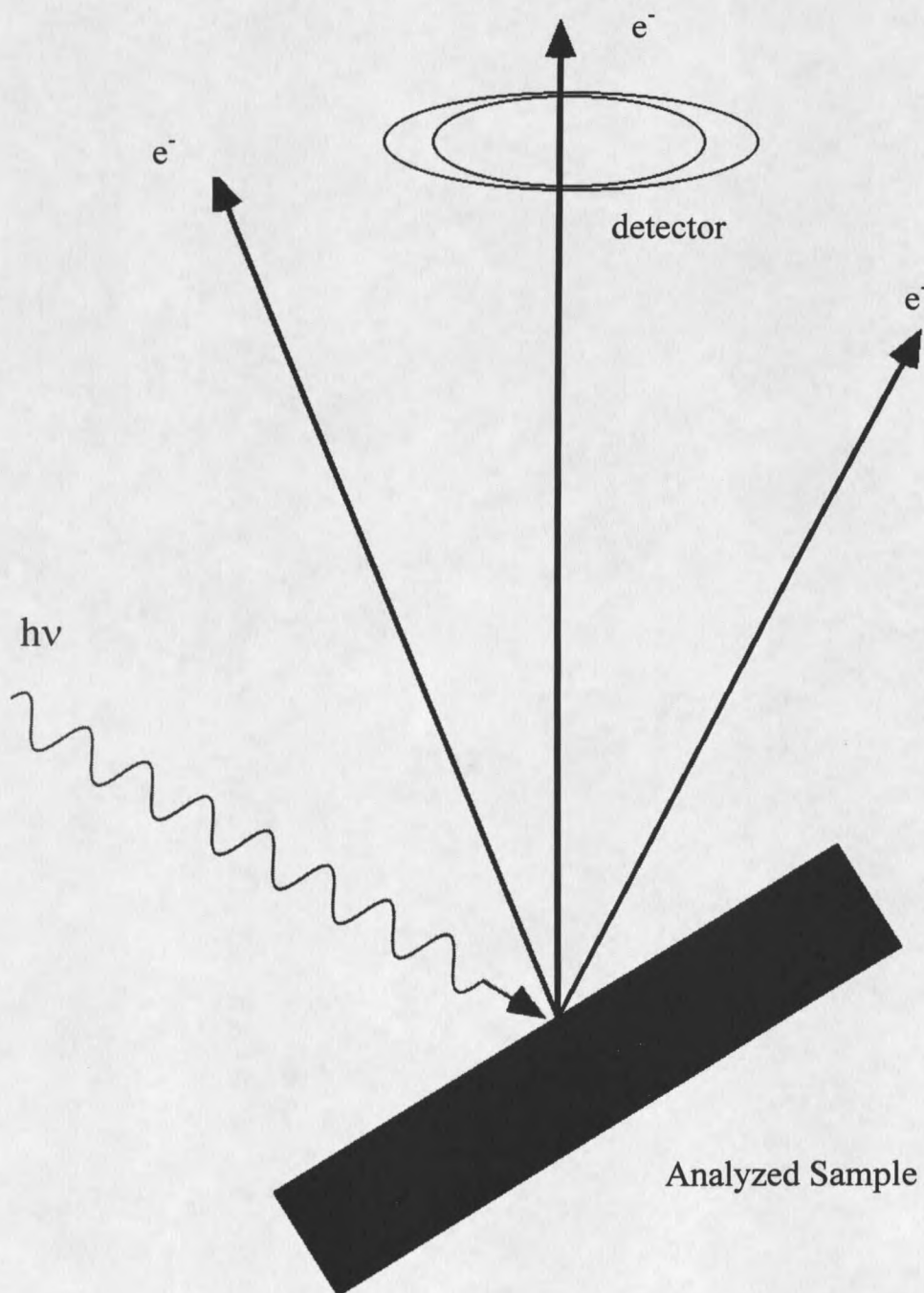


Figure 1. Schematic of x-ray photoelectron spectroscopy.

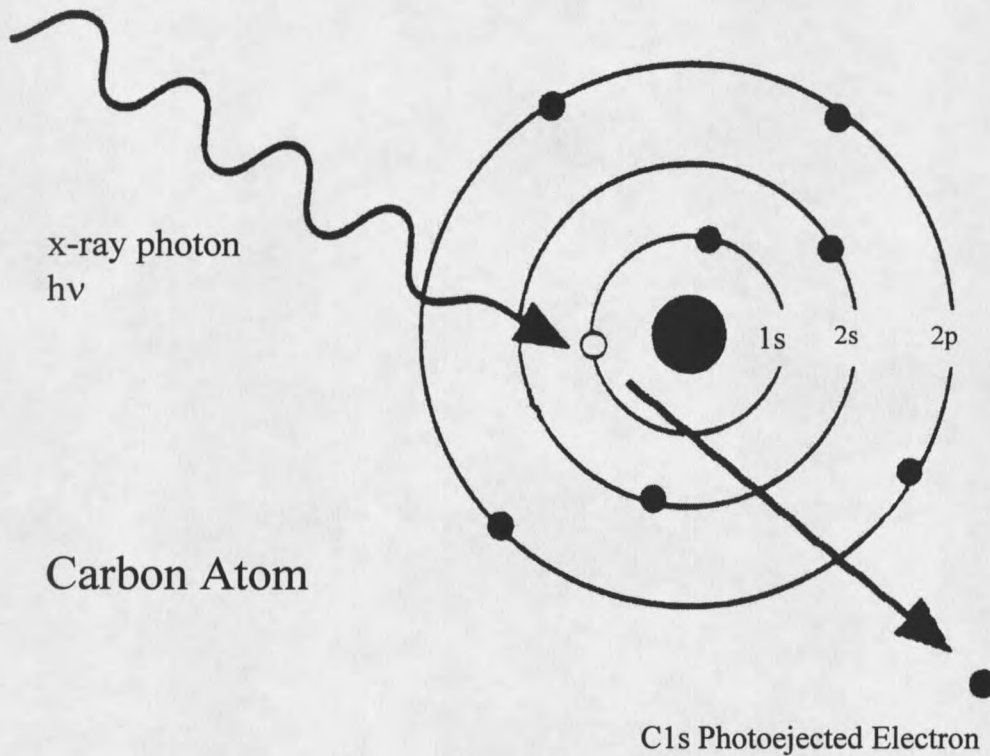


Figure 2. Schematic of a carbon atom undergoing the photoelectron process [13].

Although specific electrons of an atom have certain binding energies, the chemical environment of the atom can create variations in the values. These changes in the energy values, or chemical shifts, represent covalent or ionic bonds between atoms and help deduce the chemical structure of the material surface. Some common binding energy peak assignments for the carbon 1s peak and the oxygen 1s peak are seen in Tables 2 and 3 [13].

Table 2. Common binding energy assignments for the carbon 1s peak from Ratner and Castner [13].

<u>Functional Group</u>		<u>Binding Energy (eV)</u>
Hydrocarbon	$\underline{\text{C}}\text{-H, } \underline{\text{C}}\text{-C}$	285.0
Amine	$\underline{\text{C}}\text{-N}$	286.0
Alcohol, Ether	$\underline{\text{C}}\text{-O-H, } \underline{\text{C}}\text{-O-C}$	286.5
Carbonyl	$\underline{\text{C}}\text{=O}$	288.0
Amide	$\text{N-}\underline{\text{C}}\text{=O}$	288.2
Acid, Ester	$\text{O-}\underline{\text{C}}\text{=O}$	289.0
Urea	$\begin{array}{c} \text{O} \\ \\ \text{N-}\underline{\text{C}}\text{-N} \end{array}$	289.2
Carbamate	$\begin{array}{c} \text{O} \\ \\ \text{O-}\underline{\text{C}}\text{-N} \end{array}$	289.9
Carbonate	$\begin{array}{c} \text{O} \\ \\ \text{O-}\underline{\text{C}}\text{-O} \end{array}$	290.3

The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ± 0.2 eV, but some can be larger.

Table 3. Common binding energy assignments for the oxygen 1s peak from Ratner and Castner [13].

<u>Functional Group</u>		<u>Binding Energy (eV)</u>
Carbonyl	$\text{C=}\underline{\text{O}}, \text{O-}\underline{\text{C}}\text{=O}$	532.2
Alcohol, Ether	$\text{C-}\underline{\text{O}}\text{-H, C-}\underline{\text{O}}\text{-C}$	532.8
Ester	$\text{C-}\underline{\text{O}}\text{-C=O}$	533.7

The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ± 0.2 eV.

Previous Work on Carbon Fiber Surfaces. Surface analysis studies of carbon fibers using x-ray photoelectron spectroscopy were first reported in 1970. The first recorded study of XPS for the study of carbon fibers concentrated on the bulk material of the fiber in order to characterize it in relation to other forms of carbon such as graphite or diamond [9]. However, within a year of x-ray photoelectron spectroscopy's commercial use, it was found that the known increase in the electrochemical oxidation of the fiber due to the surface treatment was seen as an increased carbon-oxygen ratio using analysis techniques. The resulting chemical shifts were also noticed and this began the work in fiber treatment investigations [1, 2, 4, 5, 9, 11].

Fiber treatment investigations are usually done using one of two approaches. The first technique involves computer curve fitting programs that can estimate the proportions of carbon and oxygen groups by using the core spectrum (electron binding energies > 30 eV) and the valence band spectrum (electron binding energies < 30 eV). Another approach involves labeling the functional groups with a reagent that contains an element easily detectable by XPS. However, this technique is beyond the focus of this paper and will not be discussed.

The core region of an XPS spectrum is the easiest region to interpret since each type of atom has core electrons (electrons that do not play a significant role in chemical interaction) in a characteristic region, resulting in instantaneous atomic identification. Additional information about the chemical environment and subsequent chemical bonds of the atoms is then provided by core chemical shifts [1, 2]. The resolved carbon 1s and oxygen 1s regions are peak fitted to show overlapping features corresponding to different

chemical functionalities. Each region is fitted to a number of component peaks, each peak corresponding to a different surface functionality.

The valence band region, in contrast to the core region, gives peak features for all of the species present in the same region of the spectrum. This area is able to show differences that are highly sensitive to the type of material present; all the energy levels involved in chemical interaction, specific to the species studied, can be seen. Because core chemical shifts are sometimes unable to distinguish between certain subtle chemical differences, the valence band can play an important role in surface characterization [1, 2]. It must be realized, however, that valence band XPS spectra analysis requires more sophisticated calculation methods and prove that comparisons with model compounds are difficult. The resolution of the valence band spectra is also typically much lower than that of the core spectra.

Various researchers have explored the curve fitting approach with the vast majority concentrating on core spectrum studies. Over 250 papers have addressed the curve fitting area, so, only a brief description of the work that illustrates the type of information that can be provided by XPS will be mentioned here. A complete review of this material can be found in Peter Sherwood's referenced papers [1].

The previous XPS work on untreated fibers showed concentrations of oxygen and nitrogen in addition to the expected carbon in the core spectrum [1, 2, 4, 5, 9, 11, 12]. Simon, Jacobasch, Pleul, and Uhlmann attributed these traces of nitrogen to the manufacturing process and the oxygen peak to surface oxidation reactions. Jacobasch, Grundke, Uhlmann, Simon, and Mäder stated that this same oxygen and nitrogen

polarized the bonds between carbon and the heteroelements and created polar properties of the differently treated surfaces [11].

Previous work by researchers on the high resolved core carbon 1s spectrum of untreated carbon fibers showed the different bonds of carbon where the main component peak (the lowest binding energy peak) corresponded to the carbon fiber and C=C bonds. Other carbon bonds were identified by the higher binding energy features of oxidation: alcohol (C-OH), carbonyl (C=O), and carboxyl (COO) and amino C-N (Figure 3) [1, 2, 4, 11].

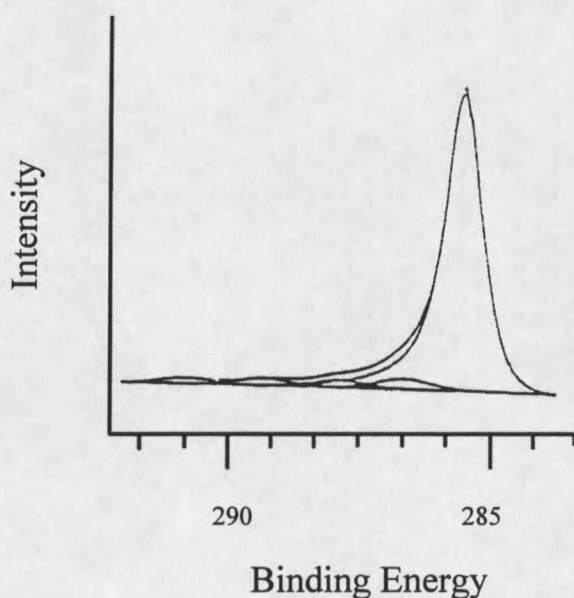


Figure 3. High resolution carbon 1s peak of untreated carbon fiber by Sherwood et al.[1].

A wide shake-up peak was also observed in the carbon 1s core spectrum that indicated conjugated delocalized p_{π} electrons [4]. These component peaks (shake-up peaks) in this range were a result of a charge transfer of π electrons from π orbitals to π

