

ESCA Characterization of Polyacrylonitrile-Based Carbon Fiber Precursors During Its Stabilization Process

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SYNOPSIS

Oxidation process control plays a key role in influencing the development of carbon fiber properties. The characterization of oxidized fibers is difficult because of their poor solubility in organic solvents and strong absorbance. X-ray photoelectron spectroscopy (XPS) has been used in the surface characterization of carbon fiber precursors during the oxidation or stabilization process. The changes in surface elemental composition and functionalities of carbon and oxygen have been identified. Quantitative changes have been noticed in surface functional groups as the oxidation process proceeds. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Carbon fiber composites have emerged as one of the important structural materials that fulfill the need of aerospace, military, sport goods, biomedical, and other engineering applications.¹ Despite its high-tech applications, the chemistry of carbonization as well as the evolution of carbon fiber structure and properties have not been fully understood. The determination of the chemical composition of oxidized precursor fibers and carbon fibers have not received much attention because (a) stabilized fiber is insoluble in any kind of organic solvent and (b) the carbon fiber shows intense absorbance.

Manufacturing of carbon fiber is carried out by a controlled thermal oxidation process followed by carbonization, which strips pendant atoms from the carbon-carbon backbone of the precursor, until only the bare backbone remains. Polyacrylonitrile (PAN) copolymers are precursors of choice because they can be converted to carbon fiber with minimum weight loss, while retaining molecular orientation during the entire pyrolysis process. This is made possible by the unique oxidative chemistry of the stabilization of PAN copolymers. Stabilization is the most critical step in carbon fiber production in the sense that the conditions of stabilization affect the quality of the resulting carbon fibers. During sta-

bilization, oxygen plays an important role, yet it is not clearly known how the added oxygen is incorporated into the fiber. It may be present in a number of different structures, but the percentage of each functional group is unknown. Morphological changes (i.e., cyclization and graphitization) and changes in elemental composition occur in the carbon fiber surface toward the fiber interior, until the interior is fully transformed and the required fiber density is attained. ESCA, being a surface-sensitive analytical tool, can give meaningful information regarding (a) identification of the fiber at different stages (oxidation, carbonization, graphitization) of carbon fiber production from its surface elemental data and (b) monitoring of various oxygen-containing surface functional groups in stabilized fibers that facilitate further condensation of ring systems.

ESCA has also been used with barium labeling to quantify surface chemical groups² responsible for adhesion, reaction of epoxy resin with carbon fibers, structure of the stabilized fiber, degree of surface graphitization, etc. The twofold objectives of the present study are (1) to study the chemistry of oxidation of carbon fiber precursors and its possible effect on fiber quality and (2) to improve the fundamental knowledge of stabilization.

EXPERIMENTAL

A Vacuum Generators ESCALAB MK II spectrometer with MgK α radiation source (1253.6 eV) was

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used for recording spectra of fiber samples. The X-ray anode was operated at 10 kV and 10 mA and the vacuum in the analysis chamber was maintained at better than 10^{-9} mbar during analysis. Fiber samples were boiled in distilled water for 1–2 h to remove any surface contamination due to the process. These were then dried before being used for the XPS study. These fibers were placed on double-side adhesive tape mounted on a sample holder. To eliminate the possibility of hydrocarbon contamination from the pump oil on the surface of the fiber, liquid nitrogen traps were filled at least 8 h before introducing the sample and this was continued until the analysis of the sample was completed. Degassing in fiber samples was not observed and, hence, these fiber samples after introducing them through the fast entry lock could be maintained at better than 10^{-7} mbar within minutes of entering. The spectrometer was calibrated using Cu(2p3/2) and Ag(3d5/2) photoelectron lines at 932.7 and 368.3 eV, respectively. The low binding energy C(1S) peak at 285 eV from neutral carbon was used as the internal reference in the photoelectron line measurements.

Photoelectron spectra were collected and analyzed using an Apple IIe computer system interfaced to the spectrometer, which permitted signal averaging on repeated scans to improve the signal-to-noise ratio. The data stored as a series of data files on floppy disks were analyzed on a second Apple-IIe computer. Reported values of binding energies are accurate to ± 0.1 eV and are the average of at least three different runs.

Oxidation Conditions

The fiber precursor was oxidized at a temperature of 225°C, keeping an air flow of 70 m/min. Four fiber samples (a–d) were collected, corresponding to oxidation intervals of (a) 35, (b) 40, (c) 45, and (d) 50 min and were examined by ESCA.

RESULTS AND DISCUSSION

Figure 1 shows XPS survey scans of pure polyacrylonitrile (PAN) and PAN-based carbon fiber (CF) precursors, heated for gradually increasing times during its stabilization/oxidation process, and also of finished CF. All these fibers show the presence of C, N, and O elements, which are identified by C(1S), N(1S), and O(1S) photoelectron lines. A quantitative analysis of surface spectroscopic data of samples (a–d) indicates a variation in nitrogen at 6.0–

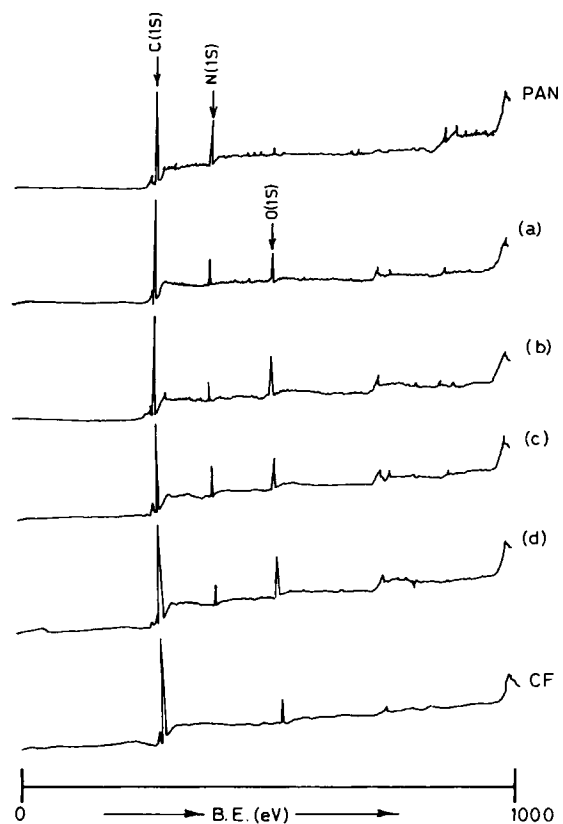


Figure 1 XPS survey spectra of PAN, CF precursors oxidized to (a) 35, (b) 40, (c) 45, and (d) 50 min and finished CF with epoxy resin.

9.0 and oxygen at 9.0–13.0 atomic percent, respectively. Survey spectra shown in Figure 1 have been normalized for C(1S) and, hence, peak heights of C, N, and O qualitatively give us an idea about the changes in the surface atomic concentration on these fibers during the oxidation process. It has been observed that surface concentration of oxygen on the fiber surface increases and nitrogen initially decreases and subsequently increases with the duration of heat treatment and again decreases. The heated precursor at stage (d) has ~ 6 atomic percent nitrogen and ~ 13 atomic percent oxygen. This trend in nitrogen and oxygen concentration indicates that, during the stabilization process, oxygen enters into the surface structure of precursor fibers up to the extent of $\sim 13\%$ and nitrogen evolution occurs on the surface.

Literature information³ on this subject has shown that prolonged heat treatment under an oxygen atmosphere leads to dehydrogenation with concomitant aromatization of the ring structure. During dehydrogenation and cyclization, HCN is evolved at an initial temperature⁴ and NH_3 is assumed to be

formed from imino end groups of a cyclized sequence with the aromatization of rings.⁵ Burlant and Parsons⁶ demonstrated the evolution of HCN and NH₃ at 270°C in vacuum by infrared spectroscopy.

To identify functionalities of carbon during the oxidation/stabilization process and correlation of these functionalities with the surface elements, deconvolution of C(1S) photoelectron lines was attempted. This deconvolution was carried out for two fibers oxidized to different extents in order to look for the quantitative changes occurring during the stabilization process. Figure 2 (i) shows a high-resolution C(1S) spectrum of highly oxidized CF precursor. The line shape of this photoelectron line clearly shows the presence of more than one carbon species on the fiber surface. To estimate the peak position of different carbon functionalities,^{7,8} the second derivative of the line envelope was deduced. The C(1S) line envelope with its second derivative spectrum is shown in Figure 2, which clearly shows the presence of three lines at 285.0 ± 0.1 , 286.7 ± 0.1 , and 289.3 ± 0.1 eV binding energy values. The 285.0 eV line position corresponds to C—C and C—H groupings, whereas that at 286.7 eV (shifted by 1.7 eV) can be attributed to C=N—C, COOH, and C—O—C groups and that at 289.3 eV (shifted by 4.3 eV) can be attributed to the C=O group.⁹⁻¹¹ To corroborate carbon and oxygen functionalities in fibers oxidized to different extents, O(1S) photoelectron lines of these fibers were also examined. These lines showed broadening, indicative of more

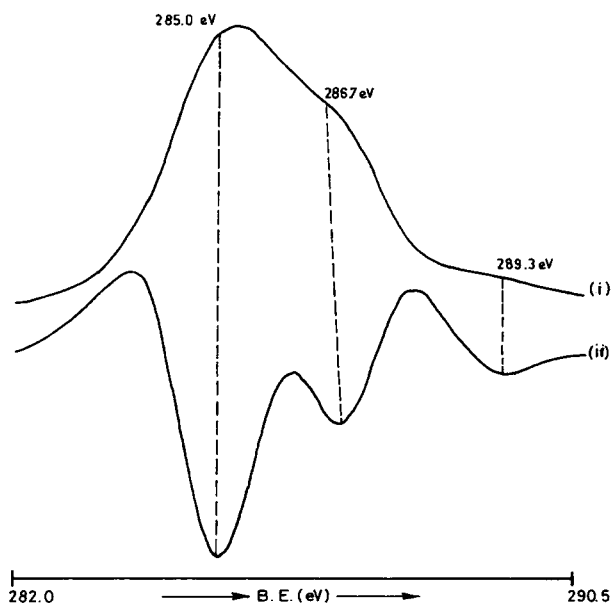


Figure 2 C(1S) photoelectron spectrum and its second derivative for fiber shown in Figure 1(c).

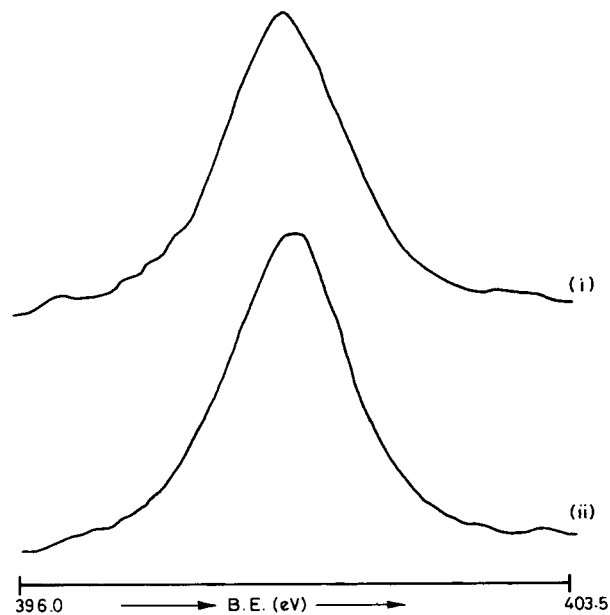


Figure 3 N(1S) photoelectron spectra of CF precursors oxidized to (i) 45 and (ii) 50 min.

than one oxygen state. A second derivative process [similar to that for C(1S)] was followed to find the line position of two functional groups. Line positions and separation of peak maxima indicate that C—O and C=O functional linkages are present.^{12,13}

Line positions of these two O(1S) also agree with the value derived from molecular orbital calculations

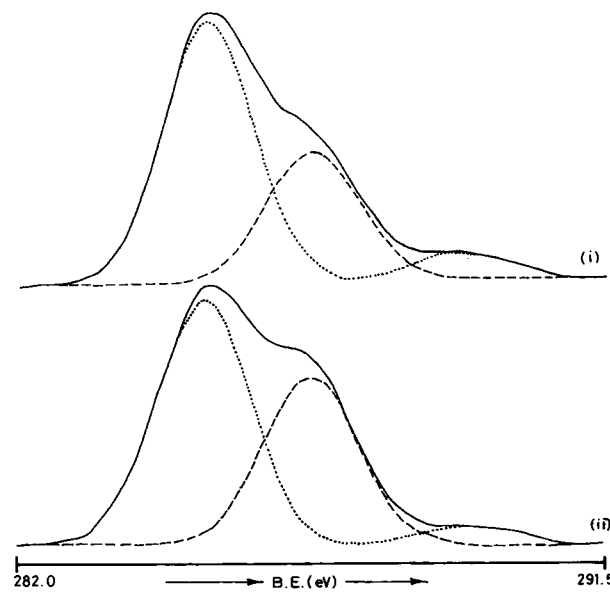


Figure 4 C(1S) photoelectron spectra of CF precursors oxidized to (i) 45 and (ii) 50 min.

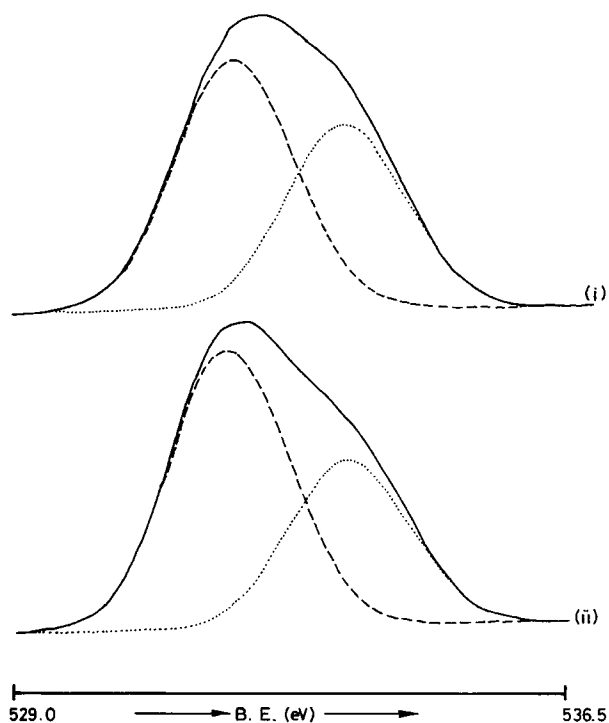


Figure 5 O(1S) photoelectron spectra of CF precursors oxidized to (i) 45 and (ii) 50 min.

by Schwartz and Switalski.¹⁴ The N(1S) spectrum indicates a line around 399.6 eV (Fig. 3). Hence, from the derivative spectrum and deconvolution of XPS line envelopes of C(1S) and O(1S) photoelectron lines, it can be concluded that the carbon functionalities on the surface of oxidized fiber precursors are as below:

Group	Probable origin
C—H, C—C	Aromatic and aliphatic
C=N—C	Cyclized rings
C—O—C	Inter- or intramolecular cross-links
C=O	Pendant group attached to the cyclized ring that can participate in cross-linking to give C—O—C groups

Deconvolution of C(1S) and O(1S) data has been attempted for two precursor fibers oxidized to different extents and is shown in Figures 4 and 5. The change in functional group concentration as a result of a different extent of oxidation is clearly evident from these figures. Line positions of different functional groups present on the fiber surface are given in Table I.

Oxidation Process

The peak synthesis routine available on the VGS-1000 data system was used for determination of line intensities of two fibers oxidized to different extents. For synthesis of photoelectron lines, their shape was taken as Gaussian and full-width at half-maxima (fwhm) for C(1S) was fixed at 1.7 ± 0.1 , and for O(1S), at 1.8 ± 0.1 eV.¹¹ Also, the relative line intensities were estimated for these carbon and oxygen functionalities, which are given in Table II. These results indicate that as the fibers approach the final stabilization stage the C=O functional groups that are thermally less stable¹⁵ reduce in number. The higher take-up of oxygen on the surface of fiber to the extent of 9–13% during oxidation arises because oxygen stabilizes the precursor structure by oxidizing the weak methylene groups that tend to reduce scission. The take-up of oxygen is thus associated with good cross-links that firmly bond the molecular chains together. Since the CN groups can be oriented at different angles, several molecular chains can be tied together by oxygen bonding. This oxygen bond is believed by Watt and Johnson¹⁶ to be capable of spanning the distance between the molecular chains more effectively than can CH or CN groups. It is expected that the cross-linking at a very early stages of stabilization would reduce the danger of fiber fusion and also counteract molecular fracture, thus reducing carbon loss and/or improving CF tensile property.

The variation in the concentration of nitrogen on the surface of precursors oxidized progressively to a higher degree (Fig. 1) shows that, initially, nitro-

Table I Line Positions of CF Precursors Oxidized to Different Extents

Sample	Figure Reference	C (1S) (eV)			O (1S) (eV)	
		C—H	C—O—C	C=O	C—O	C=O
(c)	4 (i), 5 (i)	285.0	286.7	289.0	531.9	533.4
(d)	4 (ii), 5 (ii)	285.0	286.7	289.3	531.9	533.5

Table II Concentration of Functional Groups in CF Precursors Oxidized to Different Extents

Sample	Figure Reference	Concentration (%)				
		Carbon			Oxygen	
		C—H	C—O—C C=N—C	C=O	C—O	C=O
(c)	4 (i), 5 (i)	64	31	5	56	44
(d)	4 (ii), 5 (ii)	62	35	3	66	34

gen is liberated from the fiber surface and, hence, its concentration decreases. When the oxidation degree is increased, nitrogen liberated from the bulk increases its surface concentration, which again decreases as oxidation is completed. The skin-core structure difference in the fiber is related to its oxidation condition¹⁷; this heterogeneity was investigated by Bennet and Johnson.¹⁸⁻²⁰

Thus, an increase in the degree of oxidation of a precursor fiber can be inferred as much from the surface N/O concentration as from visible changes in their color from yellow to orange to brown to black. Whereas takeup of oxygen is associated with cross-links that firmly bond the molecular chains together, nitrogen liberation takes place because of the evolution of HCN and NH₃ during the process, and color change is because of the cyclized structure.

CONCLUSIONS

The present study on carbon fiber precursors showed the following:

1. During the oxidation process, oxygen takeup on the surface is associated with oxidizing the weak methylene groups that tend to reduce scission. This takeup of oxygen is also associated with "good" cross-links that firmly bind the molecular chains together.
2. The functional groups identified on the surface of oxidized fiber precursor are C—H, C—C, C=N—C, C—O—C, and C=O. These functional groups are expected during stabilization in cyclized ladder structures, as suggested by various authors.²¹
3. The two different types of oxygen functionalities, C—O and C=O, change quantitatively during oxidation. The C=O groups reduce in number as the oxidation process

proceeds and evolves CO₂ in a later stage of heat treatment (i.e., carbonization). Although the mechanism for the appearance of such groups has been suggested by Peebles,²² it is assumed that an excessive amount of C=O groups in the stabilized fibers produce defects in the fiber during carbonization, by expulsion²³ of CO or CO₂.

4. Initially, nitrogen concentration reduces on the surface because of evolution of nitrogen compounds from the surface regions. At later stages, surface nitrogen concentration increases because of the migration of nitrogen from the bulk to the surface during its evolution and it gradually decreases as evolution of nitrogen compounds at oxidation temperature is complete.
5. ESCA is a sensitive analytical tool for the detection of chemisorbed elements with materials of low surface area such as carbon fiber.

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