X-Ray Photoelectron Spectroscopy Investigation into Thermal Degradation and Stabilization of Polyacrylonitrile Fibers

Gangping Wu,[1] Chunxiang Lu,[1] Xueping Wu,[1] Shouchun Zhang,[1] Fu He,[1] and Licheng Ling[1,2]

[1]Key Laboratory of Carbon Materials, Chinese Academy of Sciences State Key Laboratory of Coal Conversion, Institute of Coal Conversion, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China
[2]East China University of Science and Technology, Shanghai 200237, People's Republic of China

ABSTRACT: Polyacrylonitrile copolymer fibers have been heated in air to different maximum heat treatment temperatures (MHTT) from 190 to 270°C. The functionalities of C, O, and N in the precursors were determined by X-ray photoelectron spectroscopy. The intensity of the C1s spectra line 286.8ev, which is identified as C-O and C = N functionalities, was found to initially increase and suddenly decrease above 230°C. Additionally, the significant broadening of the N1s spectra line was also observed at the same MHTT. It is suggested that some oxygen was incorporated into the six-member heterocyclic structures that formed by cyclization of nitrile groups and transformed into pyrrole-type structures by the elimination of carbon monoxide. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1705–1709, 2004

Key words: polyacrylonitrile; stabilization; pyrolysis; crosslinking; ESCA/XPS

INTRODUCTION

Thermal degradation and stabilization of polyacrylonitrile(PAN) has been the subject of extensive research since the 1960s. Most activities were centered on the physical and chemical changes; physical changes include color, crystallinity, entropy, density, and tensile strength, while chemical changes include nitrile polymerization, chain scission, evolution of volatile gases (NH_3, CH_4, CO, CO_2, H_2O, and so on), and formation of carbonyl, carboxyl, and peroxide groups. Various reaction mechanisms have been proposed in the literature to account for the changes occurring in the stabilization process[1] since 1950 when Houtz postulated the formation of a conjugated, fully heteroaromatic cyclic structure. However, none of the hypotheses has been proved by experimental evidence. One of the most important reasons is that the reactions are quite complicated in the presence of oxygen. How the added oxygen is incorporated into chain and (or) cyclized structures is not clearly understood. Previous workers suggested that it was due to reactions in the presence of oxygen leading to nitrone,[2] ketone,[3] epoxide,[3] lactone,[4] lactam,[4] and other structures.[5] But these are not decisive enough to allow us to fully understand the chemistry involved in the stabilization process.

X-ray photoelectron spectroscopy (XPS) was expected to be a powerful tool for detailed information about tanglesome samples like thermal stabilized PAN precursors, because it is a kind of surface-sensitive analytical tool, which can give meaningful information on various oxygen-containing surface functional groups in treated fibers quantifiably. In addition, it can be used to monitor elemental changes in the surface (except H) during stabilization.

In this article, we present an XPS analysis of thermally degraded PAN fibers and the role of oxygen on the formation and evolution of ladder-like structures.

EXPERIMENTAL

Precursor and stabilization

The precursor fibers, which contained 1% itaconic acid, were fabricated in the carbon fiber line of our laboratories. Their properties were shown in Table I. The fibers were supplied on a reel as a continuous tow, and they were manually untwisted before use in the experiments.

Stabilization was carried out in a batch process using the constant tension modes. The fibers were free to shrink or stretch with a constant stress of 0.045 g/de-

TABLE I
Properties of Polyacrylonitrile Fibers

Filaments in a bundle	Tensile strength (GPa)	Elastic modulus (GPa)	Elongation (%)	Diameter (μm)	Shrinkage in boiling water (%)
3K	0.47	5.67	15.99	12.06	5.1

nier, and stabilization was carried out in continuous air at a heating rate of 1°C /min, with an air flow of 0.3 m^3/h. The final maximum heat treatment temperature (MHTT) varied from 190 to 270°C. Fiber collection was carried out through heating the fiber from ambient temperature to the desired MHTT and rapid quenching in air. Then the samples were preserved in a desiccator for XPS measurements.

XPS measurements

A PHI-5300 XPS (Perkin-Elmer) system spectrometer with Mg Kα(1253.6 ev) as the radiation source was used to record spectra of fiber samples. The X-ray anode was operated at 12.5 kv and 20 mA. The residual vacuum in the analysis chamber remained at about 1.333 × 10^{-6} Pa during analysis. Before measurements, fiber samples were washed in distilled water in flux to eliminate surface contamination. Then the samples were dried and mounted on a sample holder using double-sided adhesive. A constant pass energy of 89.50 ev was used. The measured spectra data were collected with the analyzer in fixed transmission mode and normal to the plane of the sample. All measured peaks were calibrated with reference to the major C-C/C-H 1s peak at 285.0 ev. Surface compositions were calculated using the areas of the respective photoelectron peaks after subtraction of a Shirley-type background. The photoelectron peak broadening due to X-ray line shape effects was removed from the high-energy resolution carbon 1s spectra using in-

house software on a professional microcomputer PE-7500.

RESULTS AND DISCUSSION

Figure 1 shows XPS broad scans of PAN fibers heated in air for different MHTTs during stabilization. The elements C, N, O, and Si (except H) are present in all samples. The elemental analytical data are listed in Table II. This indicates that external oxygen concentration increased during stabilization/oxidation. This is expected by the incorporation of oxygen into fiber structures. It is interesting to note that external nitrogen concentrations initially increased with increasing MHTT and, above 230°C, suddenly decreased (from 3.69 to 0.91 between 230 and 250°C); then after further oxidization up to 270°C, the element N started to concentrated in the surface. This trend differs from the observation by Ashish Bhardwaj et al.[6] Their observation was an initial decrease and then an increase. In addition, Table II indicates a variation of oxygen at 21.24–25.64 and nitrogen at 0.91–3.69 atomic % in our study, while Ashish Bhardwaj et al. reported 9.0–13.0 and 6.0–9.0, respectively. All differences may be due to the stabilization conditions and the used PAN precursors (copolymers in our study but pure polymer used by Ashish Bhardwaj et al.). Gupta et al.[7] reported that cyclization reactions occur initially in an amorphous region in low temperatures for copolymer PAN fibers and then the reactions develop to the crystalline region at high temperatures; but for pure polymer fibers, the reactions proceed nearly simultaneously. This is because the amorphous structures in copolymer PAN are less dense than that in pure copolymer, due to the presence of comonomers in the amorphous phase. A similar phenomenon was also observed in our laboratory, and the major "melting" of the crystalline region was validated to be around 230°C. Thus,
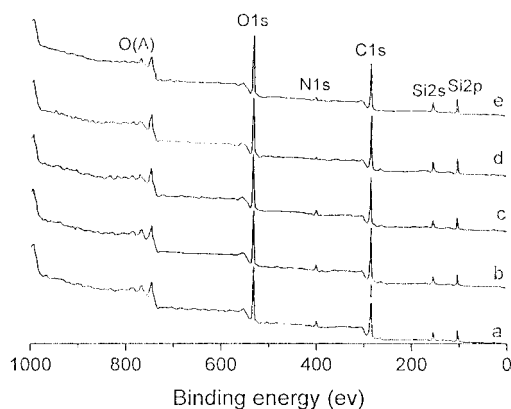

Figure 1 XPS spectra of PAN fibers at different MHTTs. (a) 190°C, (b) 210°C, (c) 230°C, (d) 250°C, (e) 270°C.

TABLE II
Atomic Concentration Data Obtained from XPS for PAN Fibers at Different MHTTs

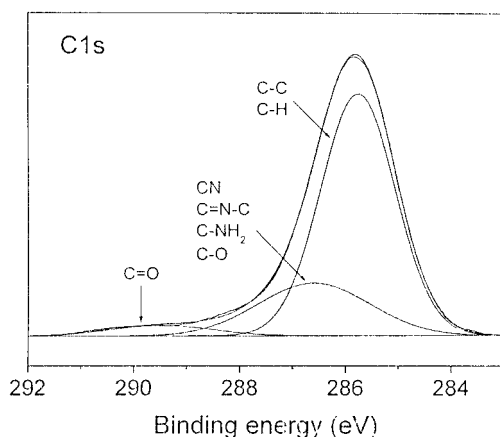| Element	Atomic concentration (%)				
	190°C	210°C	230°C	250°C	270°C
C1s	76.08	76.24	74.35	74.41	72.68
O1s	21.24	20.30	21.96	24.68	25.64
N1s	2.68	3.46	3.69	0.91	1.68

Figure 2 Curve deconvolutions of C1s photoelectron spectrum with their assignments for fibers heated to 230°C.

we can propose that when cyclization proceeds in the amorphous region (before 230°C), the N element in bulk can migrate to the surface, which accounts for the increase of external N concentration; then after crystalline melting, a large amount of cyclization reactions occur, which results in mass loss of nitrogen in the form of HCN and NH_3. This evolution was reported by previous authors,[8] and is suggested to be formed from imino end groups of a cyclized structure. In addition, the consolidated structures also made migration from bulk to fiber surface difficult for N elements.

The C1s spectra from narrow XPS scanning were deconvoluted with software XPS PEAK (80% Gaussian and 20% Lorentzian) (Figure 2). The major peak (285.0 ± 0.1 ev) of the C1s band corresponds to C-C and C-H groups in both aromatic and aliphatic structures. The component at around 286.8 ev (shifted about 1.8 ev) can be assigned to C-O, $C = N$-C, $C \equiv N$, and C-N bonds. The peak at high binding energy of 289.1 ev (shifted 4.1 ev) can be assigned to carbonyl and carboxyl groups. It is worth noting that all C1s peaks showed a long "tail" at high binding energy position and the 286.8 ev peaks can only be deconvoluted with asymmetric shape. This indicates that the functionalities in the surface are quite pronounced, and every peak corresponds to more than one carbon species. According to previous reports,[6] only C-O and $C = O$ functionalities are present in O1s spectra lines. The N1s spectra lines were quite complex and cannot be simply deconvoluted. This will be further discussed below.

Deconvolution of C1s data for the fibers heated to different MHTTs is shown in Table III. The data clearly show some important trend of development as heat treatment continues. It is expected that relative concentration of the functionalities (C-O and $C = N$) has a initial increasing trend and a corresponding decrease for C-C and C-H groups before 230°C. But when the PAN fibers were heated to 230°C, the relative amount of C-O and $C = N$ groups started to

TABLE III
Fitting Results of C1s Peaks of PAN Fibers Oxidized to Different MHTTs

HTT	C–C/C–H	C–O/C=N	C=O
190°C			
Position (ev)	285.0	286.8	289.1
Full width at half maximum (ev)	1.8	2.0	1.8
Area	23440	6211	1316
Relative concentration (%)	75.69	20.06	4.25
210°C			
Position (ev)	285.0	286.9	289.1
Full width at half maximum (ev)	1.9	2.0	1.8
Area	22083	6576	955
Relative concentration (%)	74.57	22.21	3.22
230°C			
Position (ev)	285.0	286.8	289.1
Full width at half maximum (ev)	1.9	1.9	1.8
Area	22415	5556	766
Relative concentration (%)	78.00	19.33	2.67
250°C			
Position (ev)	285.0	287.9	290.0
Full width at half maximum (ev)	1.8	1.8	1.8
Area	24663	2133	876
Relative concentration (%)	89.13	7.71	3.17
270°C			
Position (ev)	285.0	287.1	289.0
Full width at half maximum (ev)	1.8	1.9	1.9
Area	24663	2325	729
Relative concentration (%)	88.98	8.39	2.63

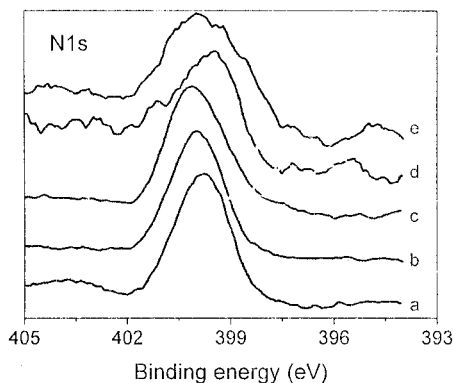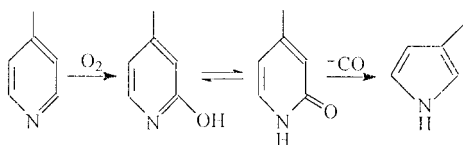**Figure 3** N1s spectra lines for PAN fibers heated to different MHTTs. (a) 190°C, (b) 210°C, (c) 230°C, (d) 250°C, (e) 270°C.

Figure 4 Variation of released amount of CO for PAN fibers heated to 320°C at 1°C /min.

reduce. The sudden decrease from 230 to 250°C was observed (from 19.33 to 7.71%). The results indicate that at high temperatures the C = N and (or) C-O functional groups reduce in number. Figure 3 shows that there exists a significant broadening of N1s spectra lines at 250 and 270°C, especially at the high binding energy region. This can be attributed to the molecular structures that give the nitrogen atoms various chemical environments with the process proceeding. Zhu et al. assigned a peak above 400 ev to pyridone from their XANES studies of carbonaceous materials.[9] Schmiers et al. also investigated the pyroyisis of polymeric *N*-heterocyclic compounds using the XPS technique.[10] According to their observation, high binding energy (above 400 ev) can be mostly assigned to pyridone, pyridine-*N*-oxide, and pyrrole structures. Pyridine-*N*-oxide, pyridone, and pyrrole structures are related to partially gassified carbons. The reactions are shown in Scheme 1.

The reaction was verified by Brent et al.[11] The broadening spectra line for binding energy above 400 ev indicates that there may exist similar *N*-heterocyclic oxide, because oxygen was taken up into six-member *N*-heterocyclic structures of PAN fibers. The conversion of pyridine-like structures into pyrrole-like structures resulted in reduced amounts of C-O and C = N functionalities, which explains the decreased concentration of spectra line of 286.8 ev with the proceeding of pyrolysis for PAN fibers. To prove the presence of the above mechanism, we performed thermogravimetric/mass spectrometric (TG/MS) analysis, which
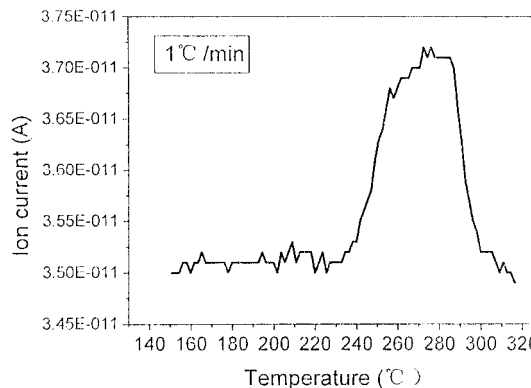
is shown in Figure 4. The results indicate that carbon monoxide was released over the region of 230–280°C. Although the origin of carbon monoxide is not well understood, it gives us further support that the above-assumed mechanism may exist. Then we can propose that, at low temperatures (lower than 230°C), oxygen is incorporated into fiber structures by oxidizing the weak methylene groups and firmly binding the molecular chains together, as suggested by Ashish Bhardwaj et al. Then at high temperatures (above 230°C in our study), some oxygen has been "linked" to the heterocyclic structures that are formed by cyclization of the nitrile groups and transformed into pyrrole structures by the elimination of carbon monoxide. The expulsion carbon has generally been believed to introduce defects for final carbon fibers and results in poor mechanical properties. However, there remains some doubt about whether the conversion of pyridine to pyrrole structure largely occurs or only on a small scale. We tried to clarify this by FT-IR analysis, but the overlapping adsorption bands make it ambiguous. This is really a pity and we will discuss it in a future paper.

CONCLUSIONS

The present investigation of XPS on PAN fibers has shown the following:

1. The major functional groups identified on the surface of oxidized fiber are C-H, C-C, C = N, C ≡ N, C-N, C-O, and C = O, as suggested by various authors.

2. During the oxidation process, nitrogen concentrations increase on the surface of PAN fibers and then all suddenly reduce. It was proposed that when cyclization proceeds in amorphous region (before 230°C), the N element in bulk can migrate to the fiber surface for the less dense amorphous structures, which accounts for the increase of external N concentration; then after crystallline melting (above 230°C), a large amount of

Scheme 1

cyclization reactions occurred, which results in mass loss of nitrogen in the form of HCN and NH_3. At the same time, the consolidated structures also made it difficult for the nitrogen elements to migration from bulk to fiber surface.

3. At low temperatures (lower than 230°C), oxygen is incorporated into to fiber structures by oxidizing the weak methylene groups and firmly binding the molecular chains together. Then at high temperatures (above 230°C), some oxygen was linked to the six-member heterocyclic structures that formed by cyclization of nitrile groups and transformed into pyrrole structures by the elimination of carbon monoxide.

4. Previous authors[12] suggested that the ladder structure consists of 40% acridone ring, 30%naphtyridine ring, 20% hydronaphtyridine ring, and 10% others. The ladder structure is an essential factor for the thermal stabilization and the structure well explains the succeeding carbonization processes of carbon fiber production. However, pyrrole-type structures were found to be more stable in our studies than expected from the reviewed literature. Pyrrole-type structures seem be the dominant form of bonding on the surface of the stabilized fibers. Obviously, the pyrrole-type structures are difficult to convert into graphite sheets during high-temperature carbonization and lead to the formation of flaw sources to initiate failure under stress. Thus it is possible to predict that, in the absence of the conversion of pyridine to pyrrole-type structures, carbon fibers with superior mechanical properties should be possible.

References

1. Bashir, Z. Carbon 1991, 29, 1081.
2. Peebles, L .H. J.; Brandrup, J. Makromol Chem 1966, 98, 189.
3. Standage, A. E.; Matkowsky, R. D. Eur Polym J 1971, 7, 775.
4. Conley, R. T.; Bieron, J. F. J Appl Polym Sci 1963, 7, 1757.
5. Frigge, K.; Büchtemann, A.; Fink, H. P. Acta Polymer 1991, 42, 322.
6. Bhardwaj, A.; Bhardwaj, I. S. J Appl Polym Sci 1994, 51, 201.
7. Gupta, A.; Harrison, I. R. Carbon 1996, 34, 1427.
8. Wang, M. Z.; He, F. The Production, Properties and Applications of Carbon Fibers; Academic Press: Beijing, 1984.
9. Zhu, Q.; Money, S. L.; Russell, A. E.; Thomas, K. M. Langmuir 1997, 13, 2149.
10. Schmiers, H.; Friebel, J.; Streubel, P.; Hesse, R.; Köpsel, R. Carbon 1999, 37, 1965.
11. Brent, D.A.; Hribar, I. D.; Dejongh, D. C. J Org Chem 1970, 35, 137.
12. Takahagi, T.; Shimada, I.; Fukuhara, M.; Morita, K.; Ishitani, A. J.; Polym Sci Polym Chem Ed 1986, 24, 3101.