Thermal Stabilization of Polyacrylonitrile Fibers

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Synopsis

Polyacrylonitrile (PAN) fibers pretreated with potassium permanganate have reduced the activation energy of cyclization and the oxidation time, and also improved the properties of the resultant carbon fibers. The activation energy of cyclization is reduced to 24 ± 1 kcal/mol from 30 ± 3 kcal/mol and the tensile strength of the carbon fibers increases by about 20–40%. The method of measuring the "aromatization index" (AI) value is modified and is recommended in checking the oxidation process. All fully stabilized PAN fibers have almost the same AI value. However, the oxidation time is decreased by 30 min when oxidation temperature is raised by 10°C.

INTRODUCTION

Polyacrylonitrile (PAN) fiber has been used as the precursor for making high-performance carbon fibers. An important step in preparing carbon fiber from the PAN fiber is to heat the precursor from 200 to 300°C in the air. Morita et al.[1] and Raskovic and Marinkovic[2] stated that treating PAN fiber by sulfur dioxide gas instead of air oxidation, is a better method of stabilizing fiber structure, and results in more economical production of high-performance carbon fibers.

It has been established that heat treatment of PAN fiber under a tension load improves fiber quality.[3,4] However, recent trends in developing high-performance carbon fibers from PAN is through chemical modification of the precursor with certain additives before oxidation. Mathur et al.[5] and Bahl et al.[6] have pretreated PAN fiber with CuCl to make high-performance carbon fibers. Our previous study[7] presented the preliminary results of the process taking place during the pretreatment of PAN fibers with potassium permanganate. This study offers further details of our investigations, the microstructure, physical, and mechanical properties of the oxidized fibers.

EXPERIMENTAL

A special grade acrylic fiber, Courtelle fiber (Courtaulds Limited, Coventry, UK), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in our work. Each single tow of the fiber contains 6000 strands of 1.1 denier monofilament. A fiber-wound frame was pretreated by immersing it in a 7% potassium permanganate solution at 85°C for a few minutes, then washed with distilled water and dried to a constant weight in an oven. The color changed from clear white to brown after pretreatment. The manganese content in the prepared carbon fibers was determined by atomic emission spectrometer analysis and found to be 25 ppm for the untreated, and 1630

ppm for the treated PAN fibers. The content of manganese in the fiber after pretreatment had increased about 60 times over its original content.

Oxidized PAN fibers and the pretreated precursor were heat-treated in a constant temperature zone furnace under constant load (0.1 g/denier) at 230, 250, and 270°C from 1 to 10 h, respectively, in a purified air atmosphere. The oxidized fiber tows were carbonized to 1300°C in a ceramic reaction tube under oxygen-free Ar atmosphere. A heating rate of 250°C/h was carried out up to 1000°C, then continued at 60°C/h until reaching 1300°C, then the specimens were cooled down immediately.

Mechanical properties of PAN and stabilized fibers were measured by Instron 1122 tensile-testing machine at crosshead speed of 0.5 mm/min with testing length of 2 cm and load cell of 10 g. In each case, at least 25 sample filaments were tested, and the average value is reported. The diameters of all fibers were measured under an Olympus BHT microscope with closed circuit television camera, and the average of 30 filaments was taken in each experiment.

A Rigaku X-ray diffractometer with CuK_α radiation as the source was used to study the wide-angle diffraction pattern, and the step-scan method was used to determine the d spacing and stacking size (Lc), the step interval was 0.02° and the Lc was measured by a fiber specimen attachment.

A LKB Ultramicrotome was used in preparing the samples for microscope investigation. The oxidized fibers were mounted in thermosetting polyester, and sectioned to 1 μm thick. A two-zone morphology of oxidized fibers was observed under an Olympus BHT microscope.

The semiquantitative analysis of oxygen content of the fiber was determined by using an automated ARL-SEMQ electron microprobe (EXPA) with the following operating conditions: accelerating potential 15 kV, beam diameter 2–5 μm, specimen current 0.1 μA, counting interval 10 s, Au-coating thickness 140 Å. Type I PAN-based carbon fibers (Grafil, HM-S) and boron nitride were used as standards. The hydrogen content of the oxidized fibers was approximately 2.20%, based on the Clarke model of the stabilized fibers.[9]

A Mettler TA 3000 thermal analyzer with a DSC 20 module was used to study the reaction kinetics of the samples. The sample weight was 3.5 mg and the heating rate was 10°C/min, heated to 450°C under an air atmosphere.

RESULTS AND DISCUSSION

Effect of Pretreatment on the Structure of the Precursor

During the last few years, X-ray diffractometer has been used to examine the structure of polyacrylonitrile fibers but no conclusion has been reached on the crystal structure of this polymer.[10-12] Bahl et al.[13] have concluded that the PAN fibers have either orthorhombic or hexagonal structure that depends on the spinning conditions and the composition. An orthorhombic unit-cell has been proposed to account for the observed reflections obtained by mounting the specimen at 16.5° and showing the (004) reflection.[12] Bohn et al.[14] and Warner et al.[15] have proposed models for the morphological structure of PAN fibers and indicated that the existence of ordered regions was due to the formation of lamellar-like structure. In this work the precursor is found to

have similar structure. Warner et al.[15] have calculated the length of the rods of the lamellar to be 80 Å and the diameter averaging about 6.0 Å. Bahl et al.[6] repeated the same work and obtained the same value. The value obtained by Jain and Abhiraman[18] was 47 Å, and the value measured by us was 44.3 Å. When pretreated with potassium permanganate it became 40.2 Å, a decrease of about 10%.

To study the changes taking place in the microstructure of PAN fibers on pretreatment, the wide-angle reflection technique is used to record the intense (100) peak caused by the PAN crystal lattice near 17° (2θ angle). The Scherrer formula used for these calculations is:[16]

$$L = \frac{K\lambda}{B\cos\theta}$$

in which B is the line breadth (radians in 2θ), K is 0.9 (a constant), λ is 1.542 Å, $\cos\theta$ is determined by the position of the observed line, and L is the average crystallite size. Crystallinity of the fiber is determined by using Sotton's method.[17] The preferred orientation of PAN fibers is studied by the fiber specimen attachment, the precursors are located at 2θ, around 17°, and at this position the 360° azimuthal circle permits the fiber axis to be rotated 360° about the vertical. The formula used in these calculations is:

$$H(\%) = \frac{360 - \Sigma X_i}{360} \times 100$$

where X_i is the half width of the intensity distribution at 17°, (2θ angle). Preferred orientation, H, has a value of 0, if the specimen is completely unoriented. If the crystallites are all arranged perfectly parallel to one another it is equal to 100.

As shown in Table I, the structure parameters of PAN fibers have changed during pretreatment. According to our measurement on the length of two sample rods—one unpretreated PAN fiber, the other pretreated, the size of the one pretreated with $KMnO_4$ decreases 10%; and the degree of crystallinity decreases 1% after pretreatment. Because of the decrease of crystalline degree and the decrement of crystalline size, a partial increment in the amorphous region is expected. Consequently, the rate of diffusion of oxygen in the fiber becomes easier in the pretreated sample than in the unpretreated PAN fiber.

TABLE I
Structural Parameters of PAN Fibers

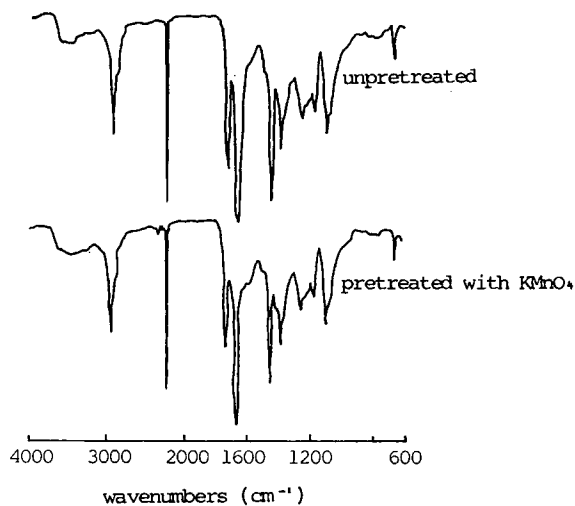|	Unpretreated	$KMnO_4$ pretreated
d (Å)	5.00 ± 0.01	5.40 ± 0.04
Crystal size (Å)	44.3	40.2
Crystal degree (%)	58	57
Orientation (%)	82.6	80.0

Fig. 1.   Infrared spectrum of Courtelle film.

Infrared and Thermal Studies of PAN Fibers

Many workers have used infrared (IR) spectra to establish the chemical reaction taking place in PAN fibers or films on thermal treatment.[19-21] Coleman and co-workers[8,22,23] have studied in detail the thermal degradation of polyacrylonitrile copolymers with Fourier transform infrared (FTIR). In this study, PAN films were prepared by Shindo's method to obtain a better resolution under IR analysis.[31] The spectrum of PAN fibers contains prominent peaks at 2930 and 2240 cm^{-1} due to stretch vibration of the methylene (CH$_2$) and the nitrile (C≡N) groups. When PAN fiber is treated with potassium permanganate, the spectrum gives rise to a new peak at 2340 cm^{-1} (due to —C=N conjugation) and shows a shoulder at 1600 cm^{-1} (due to C=C and C=N) (Fig. 1). The shoulder at 1600 cm^{-1} and new peak at 2340 cm^{-1} for the pretreated PAN fiber implies that potassium permanganate acts as a catalyst. The manganese atom attracts the C≡N groups of the AN units to initiate the cyclization reaction, consequently enabling the cyclization reaction to occur at a lower temperature.

The degradation of PAN during oxidation is always associated with a large exotherm. The exothermic behavior and the activation energy (Ea) of cyclization of PAN fibers have been studied by differential thermogravimetric analysis (DTA) and the differential scanning calorimetry (DSC).[6,24,30] In our work the complete test procedure was done by using the DSC unit connected with a TC-10 microprocessor which printed out the Ea values on the attached printer-plotter. Figure 2 shows DSC studies for the pretreated and the original PAN fibers. The activation energy of cyclization is 30 ± 3 kcal/mol for PAN fiber and is larger than 24 ± 1 kcal/mol for the pretreated PAN fiber. A smaller value of Ea suggests that the cyclization reaction can be initiated at a lower temperature, this was proven by our present study. The cyclization temperature of the untreated PAN fiber occurs at 160°C and for the pretreated PAN fiber at 140°C (Fig. 2). The time required for the completion of oxidization of the pretreated PAN fiber can be reduced (Table II).
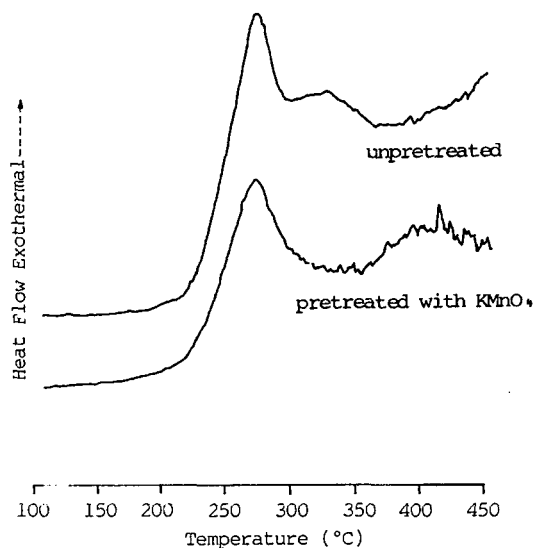
Fig. 2.   DSC curves of Courtelle fiber (heating rate: 10°C/min, in air).

TABLE II
The Aromatization Index (AI) of Fully Stabilized PAN Fibers
Under Different Oxidations

KMnO$_4$ pretreated	Sample number	Oxidation temp. (C)	Oxidation time (h)	AI (%)
No	A	230	7	72.2
No	B	240	6.5	72.4
No	C	250	6	72.3
No	D	260	5.5	72.3
No	E	270	5	72.2
Yes	F	230	5	67.1
Yes	G	270	3	67.5

X-Ray Diffractometer Studies and Cross-Section Examination of Oxidized Fibers

X-ray diffractometer studies on PAN fibers showed two equatorial diffraction peaks at Bragg angles $2\theta = 17°$ and $29°$. When PAN fiber is heated in air during thermal treatment, a new peak appears at $2\theta \approx 25°$ corresponding to the sheetlike structure of the ladder polymer. As oxidation proceeds, the intensity of the new peak increases and that of the old peak decreases.

Uchida et al.[25] have attributed the new reflection to the sheetlike structure of aromatized ladder polymer, and has introduced an "aromatization index," AI:

$$AI = \frac{I(A)}{I(A) + I(P)}$$

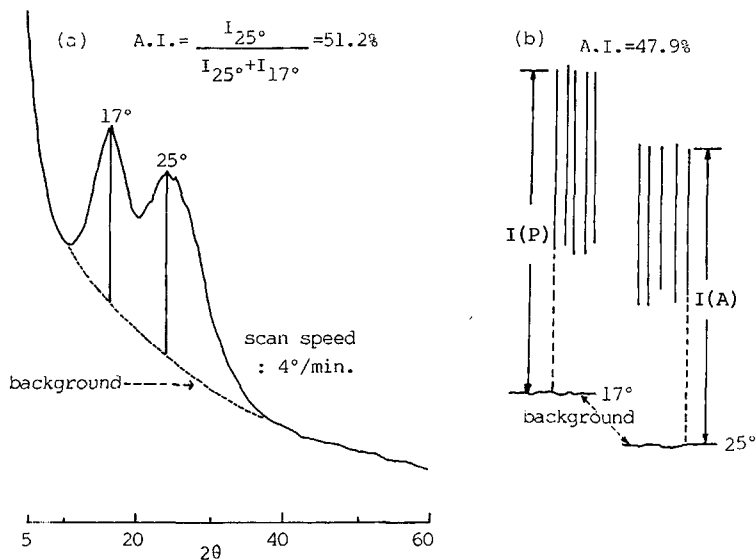where $I(A)$ is the intensity of the diffraction produced by the aromatized

Fig. 3.   Two testing methods of aromatization index values, PAN fibers heated in air at 230°C for 30 min: (a) method of Uchida et al.,[25] (b) our method, using fiber specimen attachment.

structures at $2\theta = 25°$, and $I(P)$ is the intensity at $2\theta = 17°$. In this work, a careful measurement of the AI value was made to estimate the amount of ladder polymer.

In Figure 3 the fiber specimen attachment is used to measure the AI value as follows: First, step-scan method was used to determine the maximum peak intensities at 2θ angles from 16 to 18° and from 24 to 26°. Next, the sample was removed from the attachment and the background intensities of air near 25° and 17° (two major peaks of the sample) was determined. After that the sample was put back in place; then the fiber stage was rotated until the highest intensities were observed. Finally, the difference in intensity from the highest of each peak to the relative background was measured. The procedure was repeated five times for each measurement. The advantages of using this method are improved accuracy and avoidance of 2θ shift of the sample during scanning. The measured AI values truly reflect the degree of stabilization of the sample, and it is recommended as an exact index in estimating the amount of ladder polymer in the sample.

Figure 4 presents the plots of the AI value versus the thermal treatment time for the fibers at 230 and 270°C. When the oxidation is carried out at higher temperature, the larger AI value is obtained and more ladder polymers are formed during the higher temperature treatment. In the first hour of thermal treatment (at 230°C), the AI value of the oxidized fiber developed from original PAN fiber is lower than that of the oxidized fiber developed from the pretreated one, and after 1 h of heat treatment, the AI value of the former is higher than that of the latter. We speculate that for the pretreated PAN fiber, the cyclization reaction takes place on the surface of the oxidized fiber. The ladder polymer is formed immediately on the surface of the fiber with higher density, which acts as a filter to impede the inward diffusion of oxygen from the exterior. This might contribute to the lower AI values for the pretreated PAN fibers in the process.
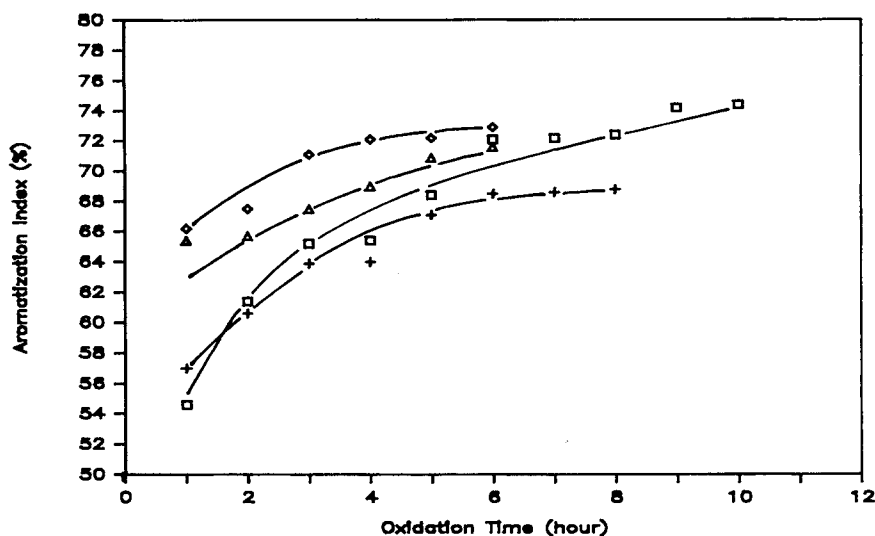
Fig. 4. Aromatization index as a function of oxidized time: (□) original PAN fiber heated at 230°C; (+) modified PAN fiber heated at 230°C; (◇) original PAN fiber heated at 270°C; (△) modified PAN fiber heated at 270°C.

Examination of the fiber cross-sections shows that when thermal treated in air up to 6 h at 230°C, unpretreated PAN fiber is characterized by a two-zone morphology. At the 7th hour, the fiber is brown across the cross section (Fig. 5). No sheath-core structure is visible in the oxidized fiber, indicating that its composition is similar to that of a stabilized material.[26,27] When thermal treated at 250°C, the fiber develops a brown color after 6 h, and at 270°C, brown color appears along a cross-section after 5 h. When the pretreated PAN fiber is heat-treated under the same temperatures to give the same morphology, the required time is decreased by 2 h; that is at 230, 250, and 270°C, the required time periods are 5, 4, and 3 h, respectively.

The fully stabilized PAN fibers always have the same AI values when the oxidation temperature increased by 10°C the required time decreases by half an hour, as shown in Table II. Thus when oxidation was carried out on the same fiber and if the same degree of chemical reaction of the oxidation occurs in the fiber, all samples will give the same AI value, irrespective of change in temperature and time of heat treatment. In other words, for oxidized fibers having the same AI values, the microstructure of these fibers will be of almost the same type.

The oxygen content of the pretreated PAN fibers and the original PAN fiber is shown in Figure 6 as a function of heat treatment time in air at 230°C. The oxygen uptake for both fibers increased linearly with the $min^{1/2}$, the oxygen uptake for the pretreated PAN fibers was much slower, indicating that formation of the ladder polymer was slow and steady. This action could minimize the chance of excessive bond rupture and chain scission of the precursor during thermal treatment. This is possibly one of the reasons that carbon fiber developed from the pretreated PAN fiber will give better mechanical properties than that from the original PAN fiber. The carbon fibers show an increase in tensile strength of about 20–40%.
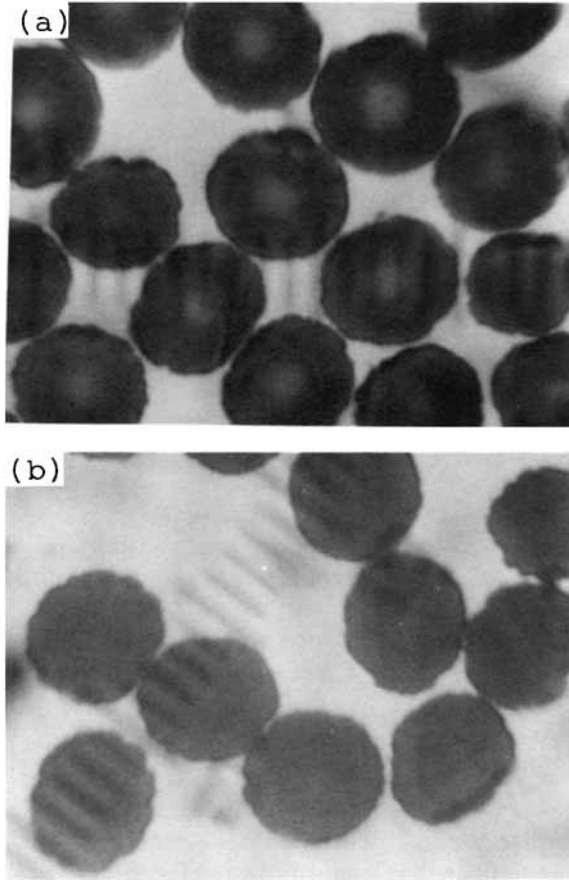
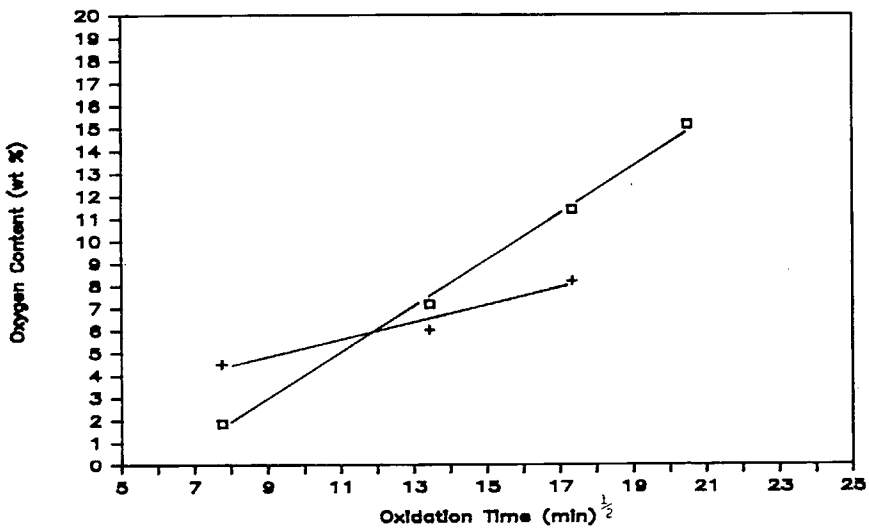Fig. 5.   Cross-sections of original PAN fibers heated at 230°C for (a) 1 h, (b) 7 h.

Fig. 6.   Oxygen uptake of various oxidized fibers as a function of time at 230°C: (□) original PAN fiber; (+) modified PAN fiber.
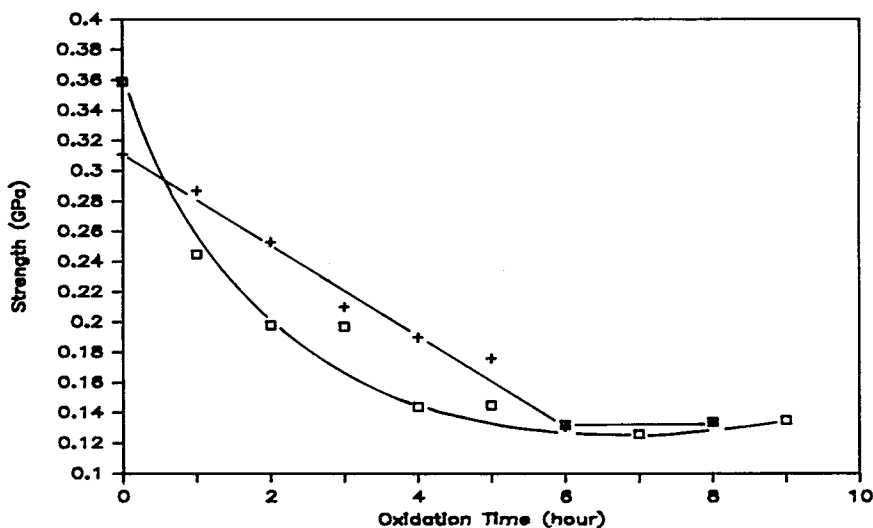
Fig. 7. The tensile strength of oxidized fibers as a function of oxidized time, PAN fibers were heated in air at 230°C: (□) original PAN fiber; (+) modified PAN fiber.

The Strength of Oxidized Fibers

When PAN fiber is heated in the presence of oxygen, C≡N bonds will be converted into C=N bonds, and the cohesive energy between the relative chains will drop appreciably.[28] This accounts for the decrease in strength of the oxidized fibers. The extent of decrease in strength will depend on the percentage conversion of C≡N to C=N.[29] Therefore, the percentage conversion, the amount of ladder polymer, AI value, will be larger at higher temperature than at lower temperature during oxidation and will be larger for PAN fiber than for pretreated PAN fiber. The formation of the ladder polymer in the beginning is rapid and then becomes slow with time during oxidation (Fig. 4). This explains why the decrease in the strength of stabilized fibers should also follow a similar pattern (Fig. 7). In this work, we observed that the strength of oxidized fiber decreased rapidly at initiation and then decreased gradually with time. When fibers were fully stabilized, the strength of fiber increased slowly. After 7 h of heat treatment, the strength of oxidized fiber developed from original PAN fiber increased, suggesting that the intermolecular crosslinking reaction may have occurred. The oxygen content of the original PAN fibers was found to decrease drastically after 7 h of heat treatment at 230°C in the oxidization process. The analysis was made using a Perkin Elmer 240C elemental analyzer. We found that the ratio of oxygen to hydrogen in the fiber is 1:2, indicating that water evaporated during the oxidization process and that heating promotes crosslinking of molecular chains in the fiber. Crosslinking between adjacent molecular chains effectively suppresses chain scission and improves the mechanical properties of the carbon fibers developed from the oxidized fibers.

CONCLUSIONS

1. The activation energy of cyclization is about 30 kcal/mol for PAN fiber and about 24 kcal/mol for the pretreated PAN fibers. This indicates that the cyclization reaction of the pretreated PAN fibers is faster than that of the unpretreated ones.

2. Wide-angle diffraction X-ray analysis shows that the PAN fibers exhibited both higher degree of crystalline order and preferred orientation than those of pretreated PAN fiber.
3. The method for measuring AI value is modified in this work and this index is recommended as a criterion in checking the oxidation process.
4. The fully stabilized PAN fibers show a uniform brownish cross section. The required time to make this fiber from pretreated PAN fiber will be 2 h less than if untreated PAN fiber is used. This is a significant saving of time and energy in the development of carbon fiber.
5. The oxygen content of oxidized fibers is linear with respect to the inverse square of the oxidation time. The oxygen content of the fully stabilized PAN fibers is about 15% by weight.

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