

The Effect of Modification on Structure and Dynamic Mechanical Behavior During the Processing of Acrylic Fiber to Stabilized Fiber

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Synopsis

Polyacrylonitrile (PAN) fibers pretreated with potassium permanganate have reduced the time required for stabilization, and also improved mechanical properties of the resultant carbon fibers. In this study, the effect of modification on the stabilization process and the dynamic mechanical properties of PAN fibers have been examined. The beta peak appeared at about 125°C on the loss tangent curves caused by molecular motion in the PAN fiber. Appearing at about 254°C, the alpha peak is attributed to chemical reactions and molecular motion in the formation of the crystalline phase of stabilized fibers. The alpha peak of the modified PAN fiber had lower absorption and had a smaller peak in the temperature range of 212–239°C. This indicated that potassium permanganate acts as a catalyst to lower the reaction temperature by about 20°C of the initial cyclization reaction. The dynamic storage modulus analysis indicated that modified PAN fibers have a lower initial transition temperature and that formation of the ladder polymer is gradual and steady.

INTRODUCTION

Pyrolysis of PAN fibers, the stabilization process, is necessary to obtain high-quality carbon fibers. The low temperature treatment (200–300°C) led to the formation of the ladder polymer, due to additional polymerization of the nitrile side groups. Important changes in the physical characteristics of fiber during stabilization, such as the viscoelastic properties, which relate to molecular motion in the fiber, have only recently been discussed. Gupta et al.^{1–3} reported that the thermal treatment of polyacrylonitrile (PAN) in air produced remarkable changes in its dielectric relaxation in the glass transition region. Other researchers also reported two transition peaks occurring in the treatment of PAN at temperatures of approximately 80–100°C and 140–160°C.^{4–6} Andrews and Kimmel⁴ proposed the concept of a heterobonded solid-state structure to explain these transitions and suggested that transition at the lower temperature was the result of chain mobility caused by weakening of the van der Waals forces, while the transition at the higher temperature resulted from intermolecular dipole–dipole dissociation of the nitrile groups in more localized sections of the chain. Okajima et al.⁷ reported that the lower

temperature transition, beta (2) peak, could be attributed to molecular motion in the amorphous phase and the higher temperature transition, beta (1) peak, to motion in the crystalline region. Ferguson and Ray⁸ found that the loss tangent curves for the PAN fibers were characterized by a strong peak at 110°C (beta) and 280°C (alpha), and suggested that the alpha peak was attributed to cyclization of the acrylonitrile units in the polymers which were enhanced by the acid comonomers.

In this paper, the dynamic viscoelasticity study, combined with analyses of thermal properties, chemical reactions, and mechanical properties during thermal treatment, is reported to provide a better understanding how the modification of PAN fiber can reduce the stabilization time and make high-quality carbon fiber having better tensile strength.⁹

EXPERIMENTAL

A special grade polyacrylonitrile (PAN) fiber tows, Courtelle fiber (Courtaulds Ltd., U.K.), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in our work. Each single tow of this fiber, designated sample A, contained 6000 filaments of 1.1 denier. PAN fibers were modified with hot potassium permanganate solution at 85°C for 2 min under a fixed length method. The color changed from clear white to brown after the modification. These fibers were designated sample B. Other PAN fibers were treated with heated water under the same conditions, and designated sample C. Both samples were washed with distilled water and dried to a constant weight in an oven. The manganese content in the prepared carbon fibers was determined by atomic emission spectroscopy, and was found to have increased about 60 times over its original content.⁹

Temperature dependents of dynamic modulus E' , loss modulus E'' , and $\tan \delta$ were measured by using a Rheovibron DDV-IIC (manufactured by Toyo-Boldwin Co., Ltd., Japan) under the following conditions: frequency f was 35 Hz and the heating rate was 2°C/min. The step temperature of each record point was 3°C. For elevating the measured temperature, the heater was modified to increase the temperature range from 250 to 350°C. Because the processing of PAN fiber to stabilized fiber is an exothermic reaction, the heating rate was controlled with a digital PID program controller with a built-in microprocessor to maintain a constantly increasing temperature rate.

The mechanical properties of the fibers were determined using the Instron Universal Testing Machine with a crosshead speed of 0.5 mm/min, load cell of 10 g, and 2 cm of testing gauge. In each specimen at least 25 filaments were tested and their average value is reported here.

A Rigaku X-ray diffractometer, using Ni-filtered Cu K_α radiation, was used to measure the crystalline related properties of the sample. The step-scan method was used to determine the d spacing and crystal size $L(hkl)$, the step interval was set at 0.02°. The preferred orientation of the fibers $O(hkl)$ was determined by an X-ray diffractometer combined with a fiber specimen attachment. The precursors were located at around 17° (2θ) [the (100) plane of PAN fiber which is thought to have a hexagonal structure], and the 360° azimuthal circle was used to permit the fiber axis to be rotated 360° about the

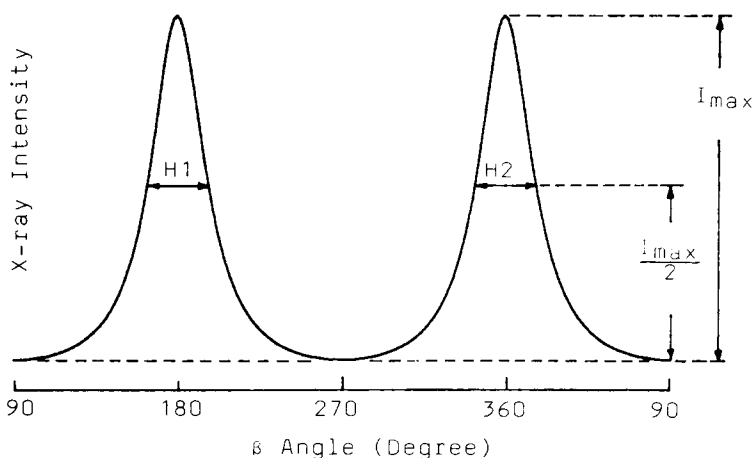


Fig. 1. Orientation distribution from fiber specimen.

vertical. $L(hkl)$ and $O(hkl)$ were calculated by using eqs. (1) and (2), respectively:

$$L(hkl) \text{ (in nm unit)} = K\lambda/B \cos \theta \quad (1)$$

$$O(hkl) \text{ (in \%)} = [(360 - H)/360] \times 100 \quad (2)$$

in which $\lambda = 0.154$ nm, K is the apparatus constant ($= 1.0$), and B is the half-value width in the radian of the X-ray diffraction intensity (I) vs. 2θ curve, and H is the half-value width in degrees of the curve of (I) vs. azimuthal angle (in Fig. 1). Preferred orientation, $O(hkl)$, 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.

The "aromatization index" (AI) value, described by Uchida et al.,¹⁰ was calculated from the following equation:

$$AI = I_a / (I_p + I_a) \quad (3)$$

in which I_a is the diffraction intensity of the aromatic structure (ladder polymer) at $2\theta = 25^\circ$ and I_p is the diffraction intensity of the PAN crystal at $2\theta = 17^\circ$.

RESULTS AND DISCUSSION

Fiber Properties Below 200°C

Plots of loss tangent as a function of temperature curves shown in Figure 2 are distinguished by two defined peaks at around 125°C (beta) and about 254°C (alpha). The beta peak was attributed to molecular motion. The alpha peak from 200 to 280°C was believed to be due to some type of chemical reaction such as cyclization, crosslinking, or degradation, during the stabilization process. For samples A and C, the beta peak observed at around 150°C,

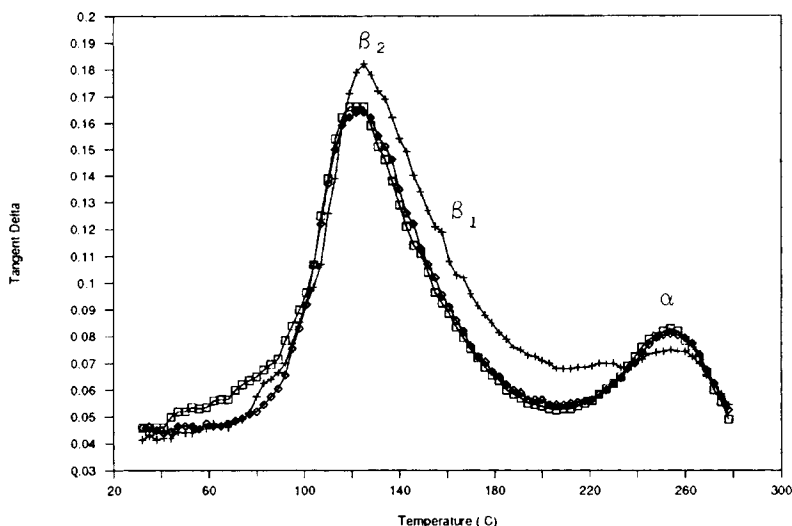


Fig. 2. Temperature dependence of loss tangent for PAN fibers: (\square) sample A; (+) sample B; (\diamond) sample C.

and for sample B at around 160°C, has a shoulder absorption. Ferguson and Ray⁸ suggested that the beta absorption consists of two different absorption models: beta (1) (150–160°C) and beta (2) (125°C). Kenyon and Rayford¹¹ found that the peak temperatures of tangent delta can be evaluated by separating the absorption.

Ferguson and Ray⁸ assumed that the beta (1) peak in homopolymer PAN or in copolymer PAN was due to the ordered regions and that the beta (2) peak rose in intensity as acrylic acid comonomer increased in concentration, indicating that there was more molecular motion in the disordered regions. Okajima et al.⁷ gave the same report. Minami¹² suggested that the beta (1) peak should be attributed to the molecular motion in the amorphous phase, and the beta (2) peak to the molecular motion in the crystalline phase of PAN.

In our analysis of these phenomena, sample A is heated from room temperature to 280°C in a Rheovibron and then allowed to cool down to room temperature. This same process is then repeated, again using the pretreated sample A. The loss tangent curves for the pretreated sample A are shown in Figure 3. We found that the intensity of beta peak absorption in the pretreated sample A is weaker and broader than that of sample A, and the beta (1) peak has disappeared. The original beta peaks were replaced by a series of new peaks, about five in number. Information in the literature of this subject appears insufficient to explain these new peaks.

There were two different chemical structures evident in sample A after the first Rheovibron analysis. One was original PAN structure, AN unit; and the other was the ladder polymer, which is converted from AN unit. Each structure has two phases, the ordered region and the amorphous phase.¹³ The evidences, obtained with X-ray diffractometer analysis, are discussed later (see Figs. 9 and 10). After the heat treatment, the majority of AN units in the PAN are converted into ladder polymer. The acid constituent of PAN fibers

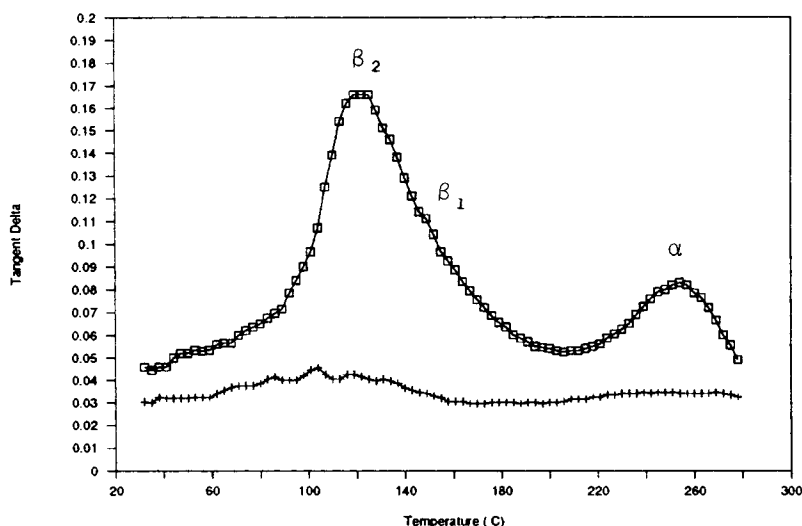
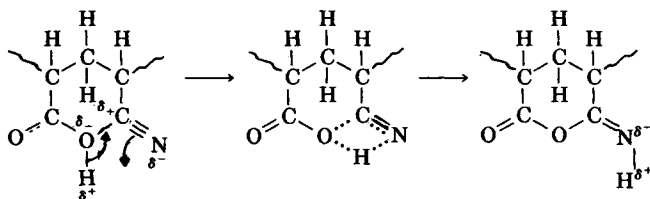


Fig. 3. Temperature dependence of loss tangent for PAN and pretreated PAN fibers: (□) sample A; (+) pretreated sample A.

acts as an initiator for ladder polymer by the following mechanism as shown by Grassie and Hay:¹⁴



Such transformation will be (a) initially from AN units in the amorphous phase, and/or (b) due to interrupted AN sequences in the ordered phase, and/or (c) caused by AN units at the boundaries of the ordered phase. Since ladder polymer is stable to heat, maintaining its solid structure, even if it is heated to 300°C, molecular motion of the ladder polymer is limited for the alpha peak in the pretreated sample A. We contend that the alpha peak for pretreated sample A is also attributed to the chemical reaction occurring in the AN units that remain in the pretreated fiber. And we wonder whether it is also due to the molecular motion of the transformed ladder polymer, repacking from the amorphous to the ordered phase.

In Figure 2, the beta (1) peak at 146°C, for the samples A, and C, shifted upwards about 12° when sample A was modified with potassium permanganate. Figure 4 shows the temperature dependence of the dynamic storage modulus (E'). The storage modulus fell sharply in the temperature range in which the beta (1) and beta (2) loss peaks occurred. The existence of the dynamic storage modulus was due to molecular motion before 160°C.

The mechanical properties of three kinds of PAN fibers, original PAN, sample B which was modified with potassium permanganate, and sample C which was pretreated with hot water, respectively, are shown in Table I.

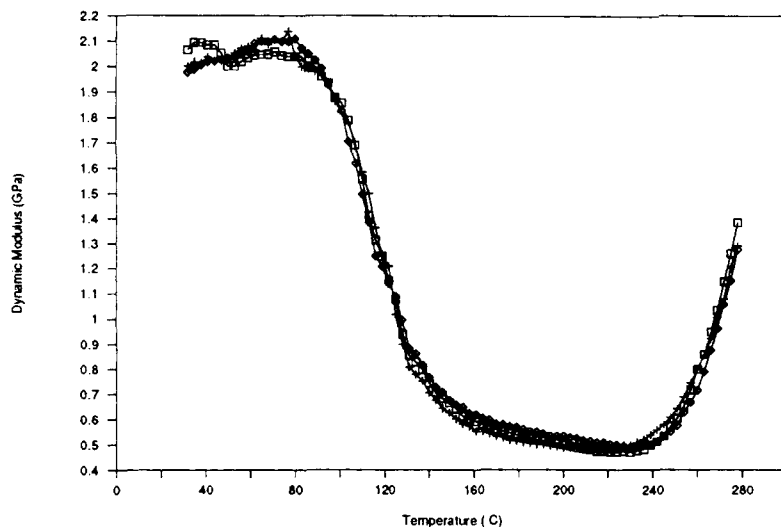


Fig. 4. Effect of temperature on E' for PAN fibers: (\square) sample A; (+) sample B; (\diamond) sample C.

According to the Scherrer formula,¹⁵ the crystal size, $L(100)$, and preferred orientation, $O(100)$, are shown in Table II. After PAN fiber was modified with potassium permanganate solution, the color of the fiber changed from white to tan. It is difficult to explain what chemical reaction occurred during the pretreatment process. However, the Mn content of the modified PAN fibers was 1630 ppm as compared to 25 ppm for the original PAN fibers,⁹ representing an increase of sixtyfold.

The infrared 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 ($\text{C}\equiv\text{N}$) groups. Sample B, modified with potassium permanganate solution, gives new peaks at 2340 cm^{-1} (due to $-\text{C}=\text{N}$ conjugation) and a shoulder appears at 1600 cm^{-1} (due to $\text{C}=\text{C}$ and $\text{C}=\text{N}$)⁹ (in Fig. 5). No new peaks are found for sample C. The shoulder at 1600 cm^{-1} for sample B implies that potassium permanganate acts as a catalyst, attacking AN units to initiate the cyclization. Some AN units participate in the initial cyclization reaction for sample B. Because the crystal size of sample B is less than that of sample A, the number of intermolecular bonded nitrile groups is decreased in sample B, and it has lower dipole moment than sample A, owing to the greater number of free nitrile groups occurring during the modification process.

TABLE I
Mechanical Properties of PAN Fibers

Sample	Pretreatment solution	Young's modulus (GPa)	Broken modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
A	None	10.62	3.97	0.66	17
B	KMnO_4	7.92	3.34	0.60	18
C	Hot water	7.75	2.67	0.54	20

TABLE II
Structural Parameters of PAN Fibers

Sample	Modified solution	<i>d</i> Spacing (nm)	Crystal size (nm)	Preferred orientation (%)
A	None	0.50	4.43	82.6
B	KMnO ₄	0.54	4.02	80.7
C	Hot water	0.50	4.48	82.7

In Table II, the Bragg spacing of samples A and C remains almost unchanged, indicating that original PAN fiber during heated water treatment produces variations in crystal size and the preferred orientation, without changing the 0.5 nm lateral repeat distance. Sample B has larger Bragg spacing, smaller crystal size, and poorer preferred orientation than samples A and C. A chemical reaction occurred in original PAN fiber during the modification process and led to sample B having larger Bragg spacing. The larger Bragg spacing implies that the crystalline lattice of sample B contains interrupted AN sequences in the crystalline phase or is the result of doping by the manganic compound after the modification process. Also, imperfections in the crystalline lattice, either at the boundaries of the crystallites or inside the crystalline phase, may give rise to redistribution of Bragg spacing,¹⁶ which decreased the crystal size and caused poorer orientation. The lower amount of intermolecular nitrile group bonding in the ordered region, and the higher free nitrile groups in the amorphous phase for sample B increased the segmental mobility. Hence the loss tangent curve for sample B has higher intensity and broader half-width than that of samples A and C at beta peak position.

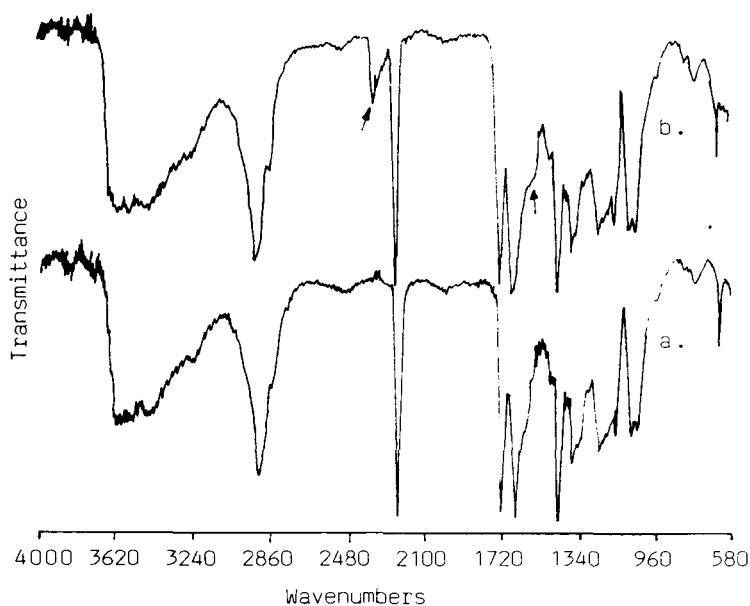


Fig. 5. Infrared spectra of PAN film: (a) Courttelle film; (b) modified with potassium permanganate.

TABLE III
Color Change for PAN Films²¹

	Temperature (°C)						
	25	160	190	210	230	250	260
Sample A	White	Buff	Deep yellow	Cocoa	Brown	Sorrel	Black
Sample B	Tan	Tan	Tan	Brown	Sorrel	Black	Black

Fiber Properties Beyond 200°C

The dynamic viscoelastic properties in the temperature range from about 200 to 280°C are believed to be due to some types of chemical reactions such as cyclization, crosslinking, dehydrogenation, and degradation.¹⁷⁻²⁰ Houtz¹⁷ tested thermal stability in low temperature ranges and found that the color of fibers changed from white to brown at about 200°C. This coloration change is the result of chemical reactions in which adjacent nitrile side groups react with each other to produce a sequence of conjugated C=N bonds running parallel to the main chain backbone. It produces a section of ladder polymer chain. We have studied the coloration reaction of PAN film during the thermal process and analyzed it under an IR. A series of color changes during the stabilization process are shown in Table III.

The color variation indicates that chemical reactions did occur during the stabilization process. In sample A, the acidic constituent in PAN fiber acts as an initiator for the conversion to ladder polymer, and the ladder polymer is formed rapidly at 230°C.^{20, 22} The temperature at which the fiber color turns brown is about 230°C for sample A and 210°C for sample B. It seems that potassium permanganate acts as a catalyst in the formation of ladder structure and reduces the temperature of cyclization by about 20°C.

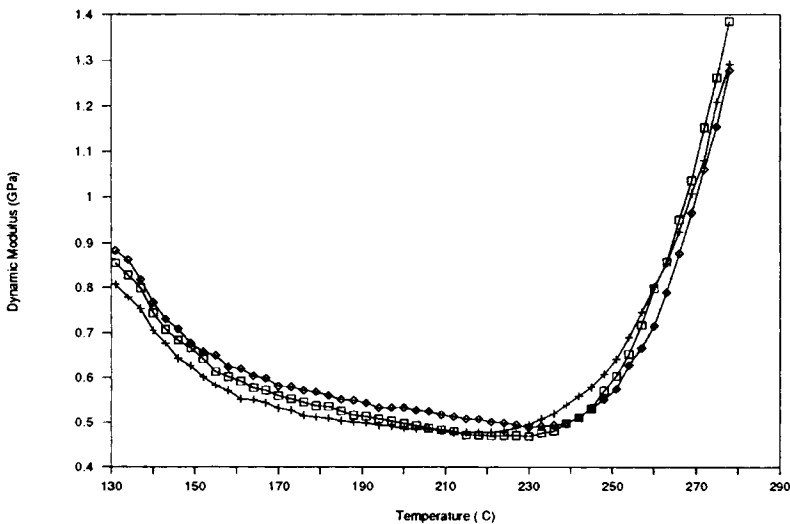


Fig. 6. Storage modulus (E') as function of temperature: (\square) sample A; (+) sample B; (\diamond) sample C.

TABLE IV
AI Values for Stabilized Fibers

	Sample no.		
	Sample A	Sample B	Sample C
AI(%)	54.5	50.4	52.7

The dynamic storage modulus (E') curves (Figs. 4 and 6) for all three samples decrease as the temperature rises. However, at 218°C for sample B, the dynamic storage modulus curve B begins to rise, followed by sample A at 224°C and sample C at 230°C. This indicates that the ladder polymer can be formed at a lower temperature for sample B. However, ladder polymer for sample B was formed rapidly at first, and then slower after 263°C than that of sample A during the stabilization process. From Figure 6, the E' curves for sample A have a higher value than those of samples B and C after 263°C.

The "aromatization index" (AI) values have provided a useful method for estimating the progress of the oligomerization of the nitrile groups and the subsequent oxidation and dehydrogenation processes.^{9,10} Sample A has the highest value, indicating that sample A has more ladder polymer in its stabilized fibers. The rate of cyclization reaction of sample A also increases more rapidly after 263°C and causes it to have the highest dynamic modulus (E') (see Table IV).

The loss tangent curve of sample B has a small broad peak occurring in the temperature range from 212 to 239°C (see Fig. 7), and the color of sample B film turned brown at about 210°C (see Table III). This indicates that the temperature during oxygen takeup to the backbone of the ladder polymer chain is about 210°C. That is the reason why PAN fiber modified with potassium permanganate solution can reduce the stabilization time.

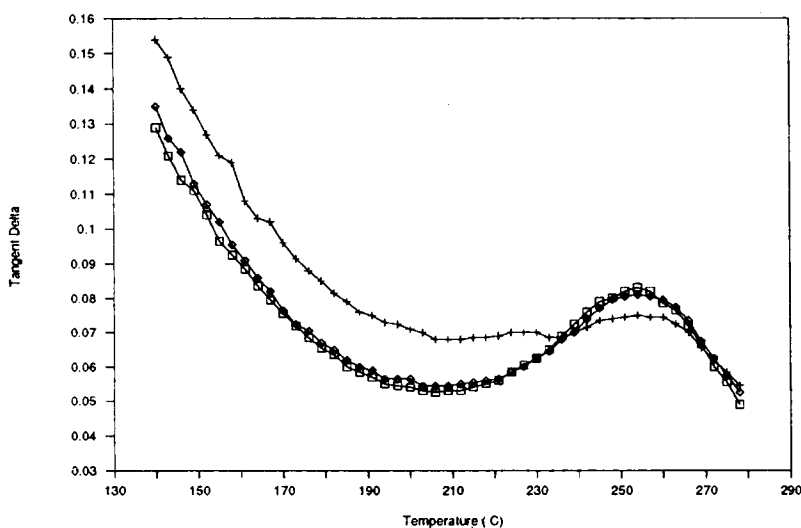


Fig. 7. Temperature dependence of loss tangent for PAN fibers: (□) sample A; (+) sample B; (◇) sample C.

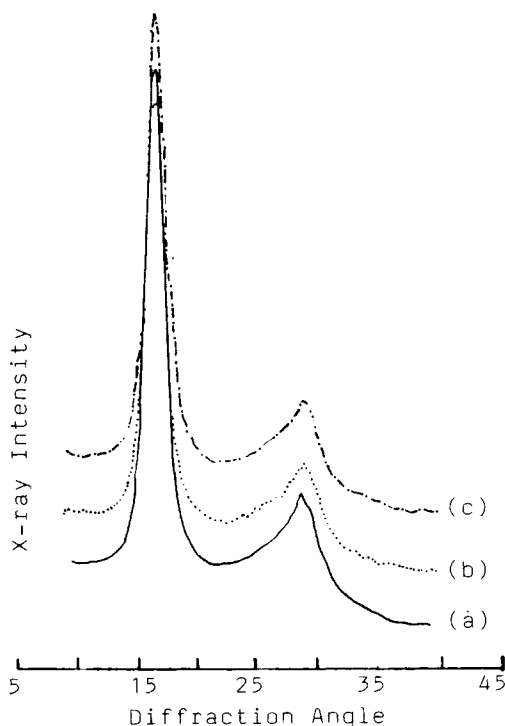


Fig. 8. Wide-angle X-ray diffraction patterns of PAN fibers: (a) sample A; (b) sample B; (c) sample C.

X-Ray Diffractometer Studies

Diffraction patterns of samples A, B, and C are shown in Figure 8. The first diffraction maxima at $d = 0.50$ nm ($2\theta = 17^\circ$) corresponds to (100) planes of the pseudo-hexagonal cell or (200) reflections of the orthorhombic structure.²³ The off-equatorial diffraction maxima at $d = 0.31$ nm ($2\theta = 29^\circ$) could be attributed to the (101) of the pseudo-hexagonal cell or the (201) reflection of the orthorhombic structure.²³

The samples were studied using a wide-angle X-ray diffractometer after Rheovibron analysis (see Fig. 9). The original PAN structures ($2\theta = 17^\circ$) still remained in stabilized fibers, and the ladder polymer structures ($2\theta = 25^\circ$) were formed. The wide-angle X-ray diffraction photograph of sample B is shown in Figure 10(a). The wide-angle X-ray diffraction photograph of sample B which had been studied by Rheovibron analysis is shown in Figure 10(b). The first diffraction arc remains, but the equatorial arc length and the line broadening both increase, looking like a loop. The increase in the equatorial arc lengths for this sample shows a random distribution in molecular orientation along the fiber axis. The increased line broadening of the reflections for the first diffraction arc shows a decrease in crystal size. The first reflections connect in a foggy arc to form a ring. The foggy arc shows the existence of a disordered phase in this sample. The original second diffraction maxima at $d = 0.31$ nm ($2\theta = 29^\circ$) disappears, and a new one at $d = 0.36$ nm ($2\theta = 25^\circ$) is formed. The new off-equatorial arc (ladder polymer structure, or turbostratic

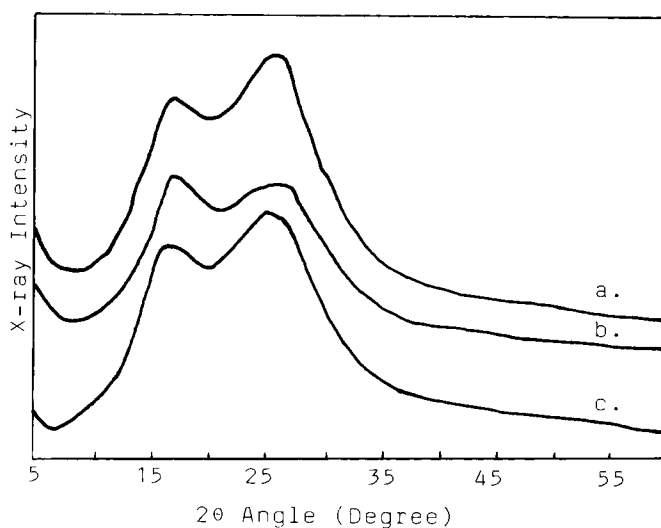


Fig. 9. X-ray diffraction patterns of PAN fibers after dynamic mechanical analysis: (a) sample A; (b) sample B; (c) sample C.

carbon) is like (002) planes of the hexagonal cell for carbon fibers. The new one has a loop shape similar to the first one. Samples A and C have the same behaviors.

Both a flat-plate X-ray diffraction photograph and the diffraction record of the samples indicate that each sample has two structures, each structure having two phases—amorphous and ordered. These result in the presence of a two-chemical structure for stabilized fibers, in which one is original PAN structure and the other one is a new structure attributed to the ladder polymer converted from the AN units. These results suggest that the alpha peak absorption was caused not only by a chemical reaction, but also by

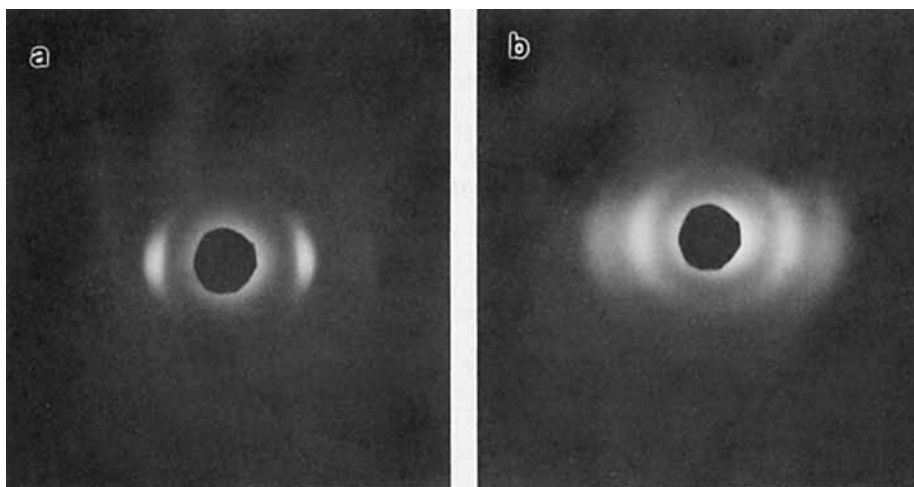


Fig. 10. Wide-angle X-ray diffraction photographs of modified PAN fibers: (a) sample B; (b) after Rheovibron analysis.

molecular motion occurring in the formation of the ordered region of the stabilized fibers.

CONCLUSIONS

1. The alpha peak of the modified PAN fiber (sample B), having an additional smaller peak in the temperature range of 212–239°C, indicates that potassium permanganate acts as a catalyst to initiate the cyclization reaction at a lower temperature.

2. The dynamic storage modulus of fiber samples A, B, and C shows a sharp rise after temperatures 224, 218, and 230°C, respectively. This is additional evidence that the ladder polymer in PAN fibers pretreated with KMnO_4 can be formed at a lower temperature.

3. X-ray diffractometer studies of the microstructure of PAN fibers after thermal treatment shows that the fibers have two chemical structures (the original AN structure and the ladder polymer), and each chemical structure has two phases, the amorphous phase and the ordered phase.

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