Studies of the Preparation, Structure, and Properties of an Acrylic Chelating Fiber Containing Amidoxime Groups

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SYNOPSIS

Polyacrylonitrile fiber was treated with hydroxylamine to form a chelating fiber containing the amidoxime group with high adsorption capacity to the Au^{3+} ion (up to 626 mg/g, when the nitrile group conversion reaches 53.7%), reasonable mechanical properties, and good thermal stability; the relationship among reaction conditions, fiber structures, and properties were investigated. The amidoxime group content rapidly increases to a steady value with increasing reaction time or $HONH_2 \cdot HCl$ concentration, the fiber strength drops linearly with increasing reaction time, when the reaction takes place at the temperature where the morphology and order structure begins to be destroyed, and the amidoxime group content increases significantly, while fiber strength decreases remarkably. It is suggested that, to prepare a chelating fiber with high adsorption capacity and reasonable mechanical property, the reaction could be carried out at temperatures from 70 to 75°C, time of about 30 min, and concentration around 75 g/L. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since fibrous chelating agent possesses a higher selective adsorption capacity and is used more conveniently in various forms than is spheric chelating resin, more and more attention has been focused on the preparation of chelating fiber.

Chelating fiber with the amidoxime group was one of the extensively studied chelating fibers. Vernon and Shah[1] and S. Katoh et al.[2] prepared a chelating fiber containing the amidoxime group and used it to recover uranium from sea water. Recently, we[3,4] prepared a kind of nonwoven fabric with the amidoxime group by grafting acrylonitrile onto PVA nonwoven fabric followed by the amidoximation of the PAN branch and found that this kind of chelating nonwoven fabric presents a high adsorption capacity for the ions of mercury, copper, platinum, silver, and gold besides uranium, which is of great advantage to both the recovery of precious metal and the treatment of waste water.

So far as manufacturing is concerned, there still remained two problems: One was the high cost due to the complicated preparation process; the other was the difficulty in keeping the mechanical property of the fiber during preparation. In the present work, a simple process to prepare a chelating fiber containing the amidoxime group using commercial polyacrylonitrile fiber as raw material is reported; the relationship between reaction conditions, fiber structure, and properties is investigated; and a suggestion is proposed to control amidoximation reaction in order to prepare a chelating fiber with high adsorption capacity and reasonable mechanical property.

EXPERIMENTAL

Raw Materials and Amidoximation Process

PAN staples with length of 38.4 mm and fineness of 1.92 dTex was supplied by Maoming Chemical Industry and Textile Chief Factory, Guangdon Province, People's Republic of China. Hydroxylamine hydrochloride and sodium carbonate were all analytical reagents.

Hydroxylamine hydrochloride ($HONH_3^+Cl^-$) and sodium carbonate, with a weight ratio of 2 : 1.5, were added into a 250 mL flask, to which 40 mL of deion-

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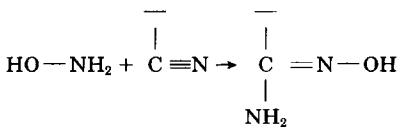
ized water and 1 g of PAN staples were added. After being treated at a steady temperature for several minutes, the staples were taken out and washed with deionized water and later dried under vacuum.

The schema formula for the reaction of hydroxylamine with the nitrile group in the PAN fiber is shown as follows:



Schema formula for the amidoximation reaction

(In the following discussion, the nitrile group is referred to as the CN group and the amidoxime group is referred to as the AO group.)

Conversion of Nitrile Group in PAN

The conversion of the nitrile group in PAN was calculated as follows:

$$Cn = \frac{W_1 - W_0}{W_0} \cdot \frac{M_0}{M_1} \times 100 \qquad (1)$$

where Cn is the conversion of nitrile group in PAN (%); W_1 is the weight of staples after reaction (in grams); M_1 is the molecular weight of H_2NOH (33); M_0 is the molecular weight of chain unit $CH_2CH(CN)$ (53); and W_0 is the weight of PAN staples before reaction (g).

Content of Amidoxime Group in the Fiber

The content of amidoxime group in the fiber was calculated as follows:

$$CA = \frac{W_1 - W_0}{M_1 W_1} \qquad (2)$$

where CA is the content of amidoxime group in the fiber (mol/g).

Elemental Analysis

After the fiber was dried in vacuum, the contents of carbon, hydrogen, and nitrogen in the fiber were analyzed by a Perkin-Elmer 240 C elemental analyzer.

Infrared Absorption Spectrum

The sample was cut into fine pieces and dried in vacuum, then pressed into a pellet with KBr. The infrared absorption spectrum of the sample was obtained in a Nicolet "5DX" FTIR spectrometer.

Wide-Angle X-ray Diffraction

The fiber sample was cut into tiny pieces and then measured with a Rigaku D/max-III A X-ray diffractrometer using Ni-filtered CuKα radiation generated at 40 kV and 30 mA. The diffraction spectrum with diffraction angle from 6° to 36° was obtained.

Scanning Electron Micrographs

The fiber was sprayed with gold, then observed and photographed by a Hitachi-450 scanning electron microscope.

Concentration of Au^{3+} in $AuCl_3$ Solution

The concentration of the Au^{3+} in $AuCl_3$ solution was determined by an ICAP-9000 inductive coupling plasma emission spectrometer (ICP).

Adsorption Capacity

A few chelating fibers were dried in vacuum until constant weight, then put into a conical flask. The $AuCl_3$ solution was transferred into the flask with a pipet. The flask was vibrated at 25°C with a vibrator until the concentration of the Au^{3+} ion in $AuCl_3$ solution detected by the ICP did not decrease at all. The adsorption capacity was calculated as follows:

$$A = \frac{V(C_1 - C_2)}{W} \qquad (3)$$

where A is the adsorption capacity of the chelating fiber (mg/g); W, the weight of the chelating fiber used (g); V, the voluum of the $AuCl_3$ solution used (L); and C_1 and C_2, the concentrations of Au^{3+} ion before and after the adsorption test, respectively (ppm).

Mechanical Property

The mechanical property of the fiber was tested by a YG-001A fiber strength electronic tester (Taican Textile Instrument Co.).

Differential Scanning Calorimetry

The fiber was measured by a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Co.) in air with heating rate of 20°C/min.

Table I Results of Elemental Analysis

Sample	Elemental Content (%)			Elemental Mol Ratio
	N	C	H	N : C : H
PAN precursor	24.83	65.90	5.64	0.96 : 3.00 : 3.02
Amidoximated PAN[a]	27.15	39.90	7.34	1.74 : 3.00 : 6.62

[a] Nitrile group conversion is 98.4%.

Dynamic Mechanical Property

The fiber was measured by a DDV-II Rheovibron (Toyo Instrument Co.) at frequency of 110 Hz and heating rate of 3°C/min.

RESULTS AND DISCUSSION

Structural Analysis for the Molecular Chain of Amidoximated PAN Fiber

To identify whether the nitrile group in PAN fiber is converted into amidoxime group or not after reaction, the chain structure of the amidoximated PAN fiber was analyzed. Table I presents the results of elemental analysis of the fibers before and after amidoximation, respectively. For PAN precursor, the experimental data of the N : C : H ratio is about 1 : 3 : 3, which is similar to the data calculated according to the formula of PAN chain unit $CH_2C(CN)H$; for the amidoximated PAN fiber with a nitrile group conversion of 98.4%, simultaneously, the experimental data of N : C : H ratio approaches 2 : 3 : 6, which is similar to the data calculated from the formula of the structural unit $CH_2C[H_2NCNOH]H$. Figure 1 presents the IR spectra of the fibers. With the increase of nitrile group conversion, the absorption peak at 2240 cm^{-1} that identifies the nitrile groups weakens, while the peak at 1600 cm^{-1} corresponding to the stretch vibration of bond C=N broadens and strengthens. Also, a new absorption peak at 921 cm^{-1} corresponding to the stretch vibration of bond N—O (Ref. 5) appears, compared with the IR spectrum of PAN precursor fiber. Accordingly, it is certain that many amidoxime groups exist in an amidoximated PAN fiber.

Effect of Reaction Condition on the Content of the Amidoxime Group in the Fiber

The effects of the reaction conditions such as temperature, time, and concentration on the content of the amidoxime group in the fiber were investigated. Figure 2 presents the effect of the concentration of hydroxylamine hydrochloride ($HONH_2 \cdot HCl$) on the content of the amidoxime group. The content of the amidoxime group increases with the increase of $HONH_2 \cdot HCl$ concentration because the molecular diffusion of $HONH_2$ from the solution into the fiber is accelerated by increasing the $HONH_2$ concentration. When the concentration is higher than

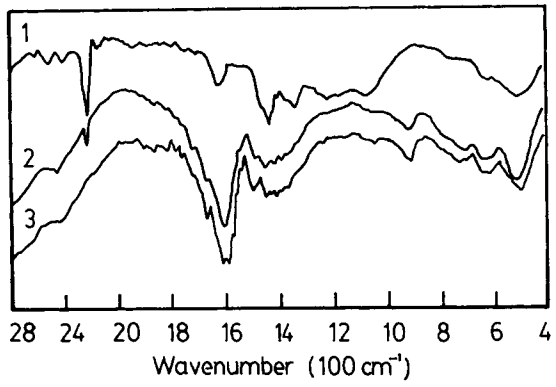


Figure 1 IR spectra of fibers with various nitrile group conversions: (1) 0%; (2) 53.7%; (3) 98.4%.

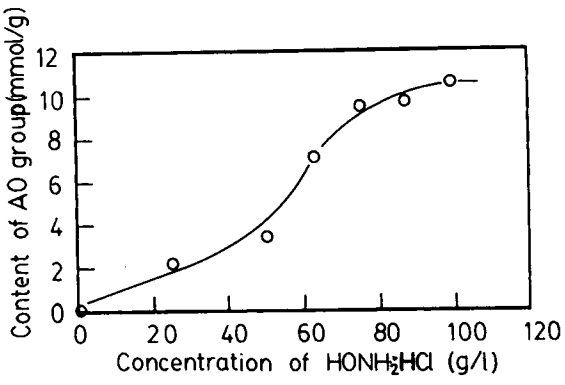


Figure 2 Effect of hydroxylamine hydrochloride concentration on the content of amidoxime group: temperature, 80°C; time, 30 min.

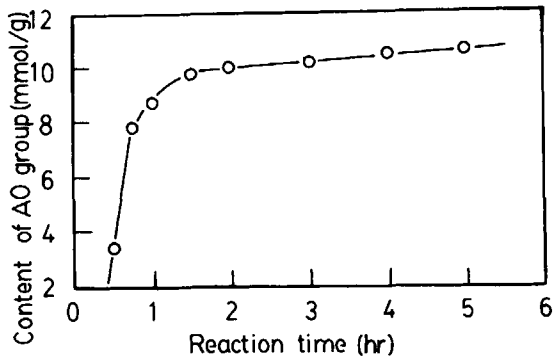


Figure 3 Effect of reaction time on the content of amidoxime group: temperature, 80°C; concentration, 100 g/L.

75 g/L, the content of the amidoxime group increases slowly and tends to a steady value with increasing concentration because the diffusion rate tends to a constant value in this case. Therefore, it is suitable for the concentration to be selected near 75 g/L. Figure 3 shows the relationship between reaction time and the content of the amidoxime group. The content of the amidoxime group sharply increases linearly with time at the beginning period of reaction, then tends to a steady value after 2 h, so it is not necessary to prolong reaction time. Figure 4 shows the relationship between the content of the amidoxime group and the time at various temperatures. In spite of different temperature, the amidoxime group content increases linearly with reaction time in the discussed period. Since both the molecular diffusion of $HONH_2$ and the amidoximation reaction are accelerated when the reaction temperature rises, the increasing rate of amidoxime group content with time indicated by the slope of the line shown in the figure rises with the increase of temperature.

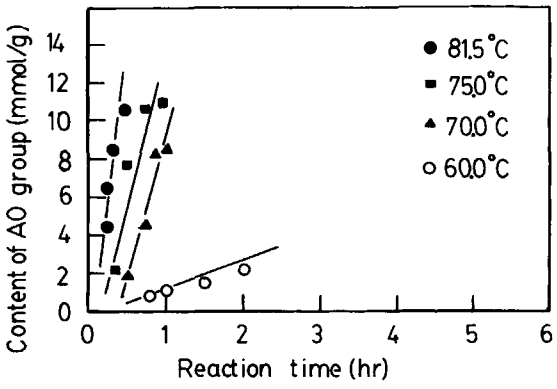


Figure 4 Effect of reaction time on the content of amidoxime group at various temperatures; concentration: 100 g/L.

Table II Comparison of Nitrile Group Conversions (Amidoxime Group Contents) of PAN Films (Fiber) with Different Supermolecular Structures (Reaction Temperature: 80°C; reaction time: 1 h; concentration of $HONH_2 \cdot HCl$: 65 g/L)

Sample	Nitrile Group Conversion (%)	Amidoxime Group Content (mmol/g)
As-coagulated film	98.4	11.5
Air-dried film	93.8	11.2
Heat-treated film[a]	50.0	7.2
Drawn steam-set fiber	38.1	5.8

[a] Temperature: 120°C; time: 2.5 h.

Relationship between Fiber Morphology and Amidoximation Reaction

The morphology of raw fiber may influence the penetration of $HONH_2$ from solution into the fiber. To investigate the effect of morphology on the amidox-

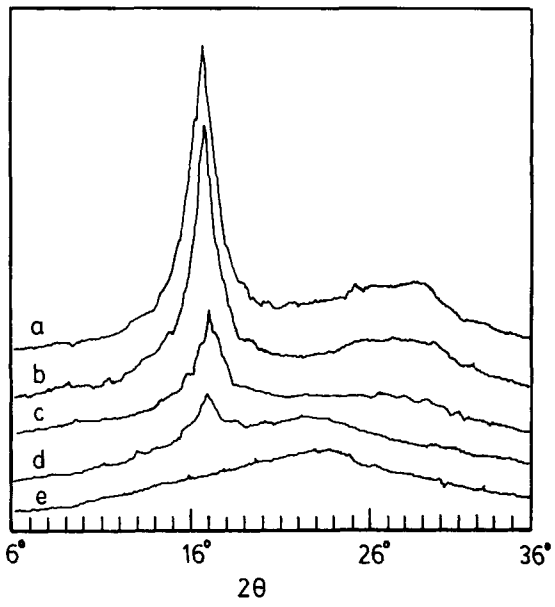


Figure 5 WAXD diagrams of the fibers amidoximated at various temperatures: (a) before reaction; (b) 65°C; (c) 70°C; (d) 75°C; (e) 80°C.

imation, the morphology of PAN film (or fiber) was modulated by controlling the formation conditions and the films (or fibers) with different morphological structures were amidoximated under the same condition. Table II shows the comparison of the content of the amidoxime group among those films (fibers). The as-coagulated film, from the DMSO solution with a dope concentration of 15%, is highly swollen and the molecule of $HONH_2$ is easily penetrated into the film and completely reacts with the nitrile groups, so the content of amidoxime group is the highest among the discussed samples. The air-dried as-coagulated film is deswollen, and although the molecular chains pack more compactly, there are still numerous microvoids throughout the film,[6,7] which is of advantage to the penetration of $HONH_2$ from solution into the film; therefore, the amidoximated film still possesses a relatively high amidoxime group content. When the as-coagulated film is heated at 120°C for 2.5 h, the microvoids decrease

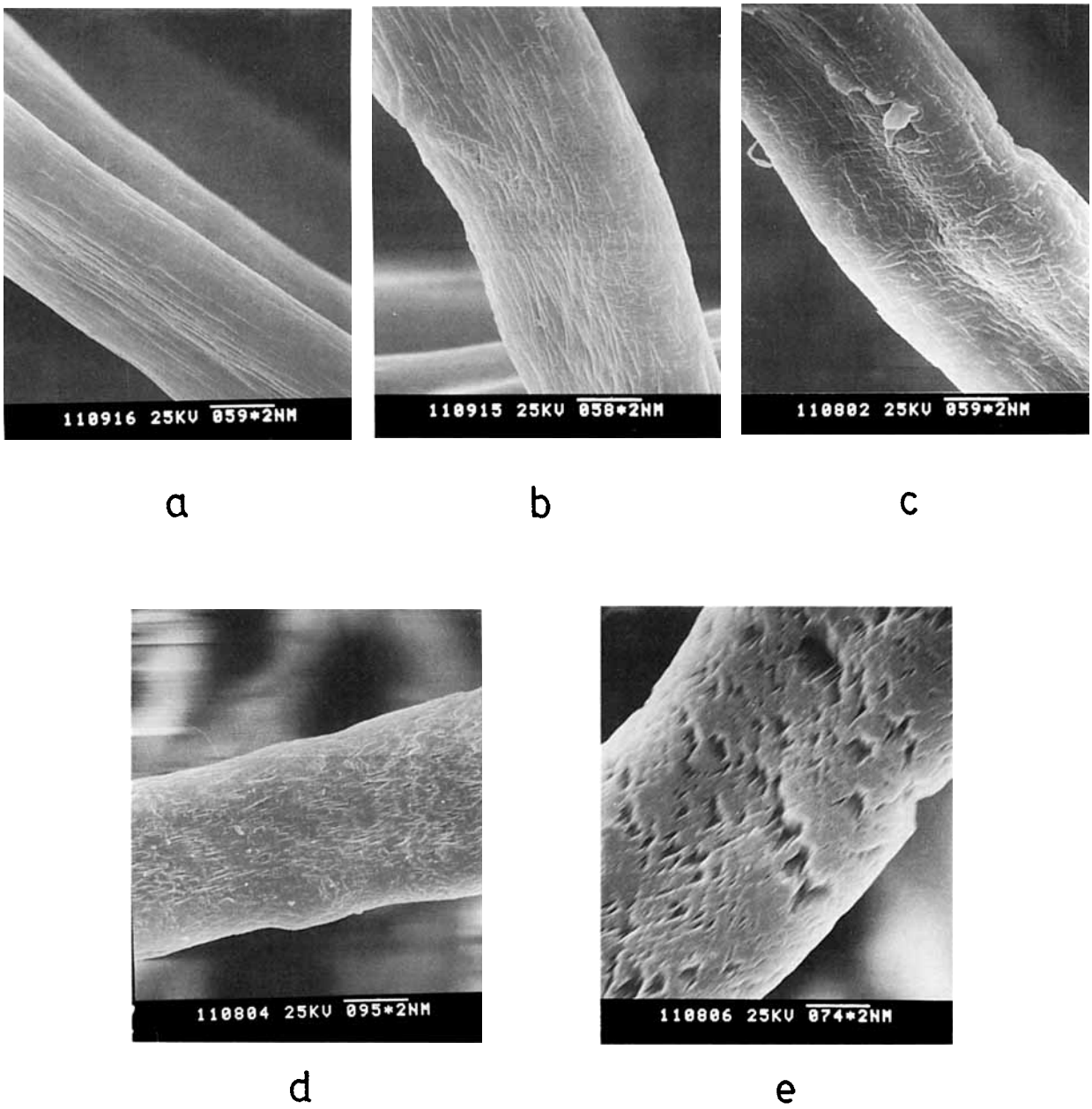


Figure 6 Scanning electron microscope photographs of the fibers amidoximated at various temperatures: (a) before reaction; (b) 65°C; (c) 70°C; (d) 75°C; (e) 80°C.

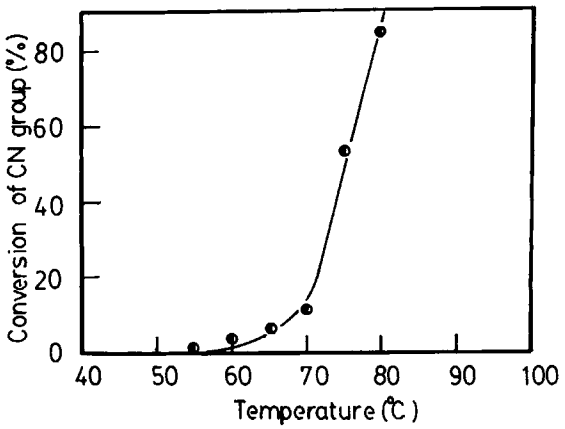


Figure 7 Effect of temperature on nitrile group conversion: time, 30 min; concentration, 100 g/L.

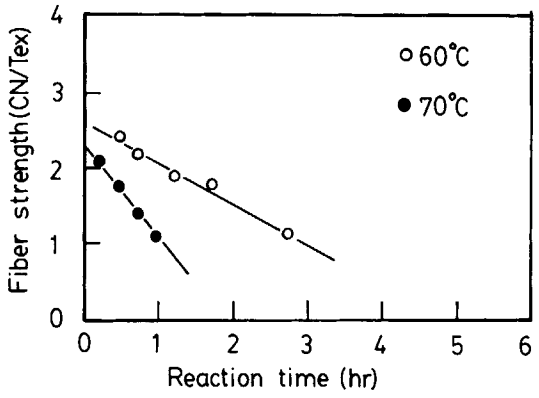


Figure 8 Effect of reaction time on the strength of fiber: concentration: 100 g/L.

remarkably,[8,9] while the crystallinity increases greatly. As a result, the amidoximated film has relatively low amidoxime group content. For the PAN fiber, the packing compactness of chains is further improved due to the hot-drawing and steam-set process; consequently, the amidoximated fiber has the lowest amidoxime group content among the discussed samples.

As is well known, the penetration of the chemical agent, e.g., $HONH_2$ in the present discussion, into the fiber probably causes the destruction of the fiber morphology. To discuss the changes in morphology and its effects on the amidoximation reaction, PAN fiber was amidoximated at various temperatures, the morphology of the amidoximated fiber was analyzed, and the nitrile group conversion was correspondingly measured. Figure 5 shows the WAXD spectra of the fibers. In the spectrum of the amidoximated PAN fiber, there are two diffraction peaks at 16° and 29°, respectively, which is similar to the diffraction spectrum of PAN fiber. Therefore, the amidoximation process does not change the crystal deformation of the PAN fiber. It is also obvious from the figure that the heights of both diffraction peaks hardly change until the reaction temperature reaches 70°C, then fall quickly. The fiber amidoximated at 80°C hardly presents a diffraction peak, indicating the entire destruction of the crystalline region. Figure 6 shows the morphology of the fiber amidoximated at various temperatures. When reaction temperature is below 70°C, no obvious change in fiber morphology is observed. When the reaction temperature is up to 70°C where the crystalline region begins to be destroyed, as shown in Figure 5, there exists a scaly structure on the surface of the amidoximated fiber; when the temperature is 80°C, a large number of great cracks appear on the surface.

From the above, both the crystalline region and the morphology of the fiber begins to be destroyed remarkably at reaction temperature around 70°C, which is of advantage to the further diffusion of $HONH_2$ into the fiber. Corresponding to Figures 5 and 6, Figure 7 presents the effect of temperature on the nitrile group conversion. It is clear that there exists a steep rise of conversion near 70°C, which is attributed to the destruction of crystalline region and appearance of cracks.

Table III Adsorption Capacity of Au^{3+} onto Amidoximated PAN Fiber

Sample	Nitrile Group Conversion (%)	Amidoxime Group Content (mmol/g)	Adsorption Capacity for Au^{3+} [a] (mg/g)
1	10.6	1.9	107.5
2	28.4	4.5	338.3
3	53.7	7.6	626.7

[a] Temperature is 25°C; original concentration of Au^{3+} is 400 ppm.

Table IV Effect of Reaction Temperature on the Mechanical Property of the Fiber (Concentration: 100 g/L; Time: 30 Min)

Temperature (°C)	Strength (CN/dTex)	Elongation at Break (%)	Yield Stress (CN/dTex)	Initial Modulus (CN/dTex)
55	2.21	22.2	0.97	31.9
65	2.21	24.8	0.96	29.9
70	2.01	24.6	0.97	29.2
75	1.25	34.7	0.81	15.4

Property of Amidoxime Group Containing Chelating Fiber

Adsorption Property for Gold

Table III shows the Au^{3+} adsorption capacities of chelating fibers containing amidoxime groups. With the increase of nitrile group conversion (or amidoxime group content), the adsorption capacity increases. When the nitrile group conversion reaches 53.7% (amidoxime group content is 7.6 mmol/g), the adsorption capacity reaches 626 mg/g. Since the amidoxime group content increases with the rise of reaction temperature, the chelating fiber prepared at high temperature may possesses high adsorption capacity.

Mechanical Property

Table IV indicates the effect of reaction temperature on the mechanical properties of amidoximated fibers corresponding to Figures 5 and 6. The properties of the fiber do not become inferior until reaction temperature reaches about 70°C; when the reaction temperature is 75°C, the mechanical properties of the amidoximated fiber drop remarkably due to the destruction of the paracrystalline region and the appearance cracks on the fiber surface. Figure 8 presents the effect of reaction time on the fiber strength. The fiber strength decreases linearly with the prolongation of time, and the decreasing rate of strength with time increases with the rise of temperature.

In general, the rise in temperature and prolongation of time is of a disadvantage in retaining mechanical properties. To prepare a chelating fiber with high adsorption and mechanical properties, the reaction temperature and time should be carefully selected. Table V shows the strength of the fiber with nitrile group conversion in the range of 10–13%. Although the nitrile group conversions of the fibers are similar, the mechanical properties are different due to the different reaction conditions. The values of both force at break (in the unit of CN) and elongation at break of the fiber amidoximated at high temperature for shore time are greater than those of the fiber amidoximated at relatively low temperature for a relatively long time. Since fiber fineness increases with reaction temperature because of the remarkable increases in both the fiber shrinkage and the fiber weight, the fiber strengths (in CN/dTex) are similar in spite of temperature and time. Therefore, so far as manufacture efficiency is concerned, it is reasonable for the amidoximation reaction to be carried out at relatively high temperature for a short time (about 30 min). Since fiber structure is remarkably destroyed near 80°C, causing the significant falling in mechanical property, it is suggested that the reaction temperature should be selected in the range of 70–75°C.

Table V Effect of Reaction Condition on the Mechanical Property

Condition (Temp./Time)	Nitrile Group Conversion (%)	Fiber Shrinkage during Reaction (%)	Fiber Fineness (dTex)	Force at Break (CN)	Elongation at Break (%)	Strength (CN/dTex)
60°C/2 h	11.5	2.9	2.09	3.78	17.7	1.87
70°C/30 min	10.6	6.8	2.16	4.41	24.6	2.04
75°C/20 min	11.9	20.6	2.46	4.03	24.8	1.64
79°C/30 min	12.6	25.4	2.57	4.52	32.0	1.76

Thermal Property

Figure 9 shows the relationship between temperature and loss tangent of the fiber. The amidoximated PAN fiber presents a slightly lower transition temperature than does PAN fiber, which indicates that since the nitrile groups in the chain of PAN are partly converted into amidoxime groups the dipole–dipole interaction between molecular segments weakens.

Figure 10 shows the DSC curves of the fibers. It is clear that there is no peak before the cyclization peak in the curve, which means that the amidoximated PAN chelating fiber is reasonably thermal stable. Besides, it is also obvious from Figure 10 that the amidoximated PAN fiber, in spite of low nitrile group conversion, presents a lower cyclization temperature and a wider cyclization peak than those of PAN fiber. Accordingly, the existence of amidoxime groups in the PAN chain is of advantage to the cyclization of nitrile groups.

CONCLUSIONS

The amidoxime group content increases rapidly to a steady value with the increase of reaction time or $HONH_2 \cdot HCl$ concentration, and the fiber strength drops linearly with the increase of reaction time, so it is not necessary for the reaction to be carried at high hydroxylamine concentration for a long period.

When the reaction takes place at the temperature where the morphology and order structure begins to be destroyed, the amidoxime group content increases significantly, while fiber strength decreases remarkably.

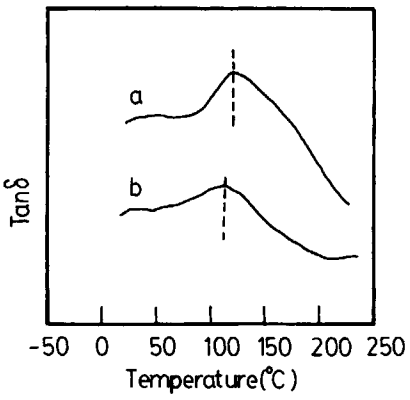


Figure 9 Temperature vs. loss tangent: (a) PAN fiber; (b) amidoximated PAN fiber with nitrile group conversion of 28.4%.

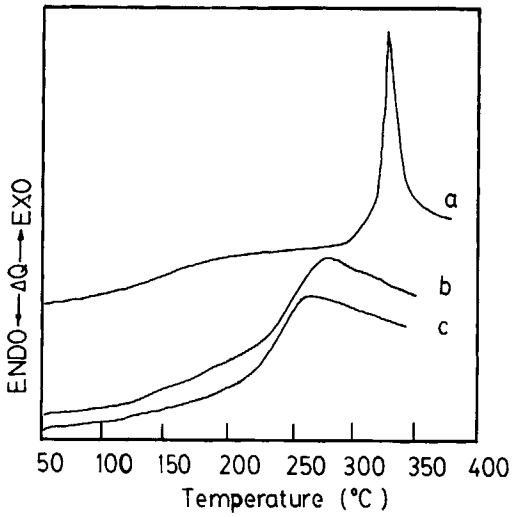


Figure 10 DSC curves of the fibers with various nitrile group conversions: (a) 0%; (b) 5.4%; (c) 28.4%.

To prepare a chelating fiber with high adsorption capacity and reasonable mechanical property, it is suggested that the reaction could be carried out at temperatures from 70 to 75°C, time of about 30 min, and concentration around 75 g/L.

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REFERENCES

1. F. Vernon and T. Shah, *React. Polym.*, **1**, 301 (1983).
2. S. Katoh, K. Sugasaka, K. Sakane, N. Takai, H. Takahashi, Y. Umezawa, and K. Itagiri, *Nippon Kagaku Kaishi*, **9**, 1449 (1982).
3. H. Zeng, Z. Xu, and Y. Lu, in *Symposium of 6th National Conference on Reactive Polymers* (in Chinese), Xian, China, 1990, p. 235.
4. H. Zeng, Z. Xu, and Y. Lu, in *Symposium of 6th National Conference on Reactive Polymers* (in Chinese), Xian, China, 1990, p. 236.
5. G. Socrtes, *Infrared Characteristic Group Frequencies*, Wiley, New York, 1980, p. 103.
6. A. Ziabicki, *Fundamentals of Fiber Formation*, Wiley, New York, 1976, Chap. 4.
7. V. Grobe, G. Mann, and G. Duwe, *Faserforsch. Textiltech.*, **17**, 142 (1966).
8. M. Takahashi, Y. Nukushina, and S. Kosugi, *Textile Res. J.*, **34**, 87 (1964).
9. H. Takeda and Y. Nukushina, *Textile Res. J.*, **34**, 173 (1964).

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