Preparation and Characterization of High Efficiency Ion-Exchange Crosslinked Acrylic Fibers

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ABSTRACT: Commercial acrylic fiber samples were first pretreated with hydrazine under various concentrations to give crosslinked structure. Then, the crosslinked fiber samples with different degree of crosslinking were treated with hydroxylamine hydrochloride to develop ion-exchange fibers. These fibers contain amidoxime, amine, amide, and hydrazide groups simultaneously. The effects of reaction conditions on physical properties, thermal characteristics, surface morphology, ion adsorption quantity, and reusability were investigated. The results show that by increasing the reaction time, temperature, and concentration of hydroxylamine hydrochloride, the content of amidoxime groups in all samples were increased, but with noncrosslinked fibers noticeable drop in the mechanical properties were observed, while in crosslinked sample prepared under optimum conditions of reaction, good ion adsorption capacity with keeping mechanical properties was achieved. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2202–2209, 2006

Key words: ion-exchangers; fibers; functionalization of polymers; crosslinking; adsorption

INTRODUCTION

Among the well-known methods for the removal or reduction of ions from solutions , such as filtration, chromatography, evaporation, precipitation and etc., ion-exchange method is high efficient, simple, and economical, specially, for diluted solutions.[1] However, among different types of ion-exchangers, fibrous ion-exchangers have attracted great interest in recent years.[2] This can be related to their structure and characteristics, like high specific surface, small cross section, uniformity in diameter (in macroscopic scale),[3] long length of fiber to diameter that preventing packing of the ion material to the surface of ion-exchangers,[4] good mechanical strength, and convenient applications in different forms (filaments, staple, clothes, and nonwoven materials) and with different density of packing in accordance with technological requirements.[2] Moreover, they can be used in the purification of water and air from chemically active pollutants like acids, bases, acid anhydrides, and also they can be applied for protection of respiratory organs from aggressive gases and vapors.[5]

In the literature, various methods and technologies for producing fibrous ion-exchangers have been described. The main methods can be expressed as follows: Addition of ion-exchange materials in solution or molten polymers,[6] coating of fiber surface with ion-exchange materials,[7] use of common commercial fiber and introducing functional groups on its structure that can remain the properties of the fiber and meanwhile can produce various types of anions, cations, amphoteric ion-exchangers.[8]

Fibrous ion-exchangers containing functional groups may be based on different polymeric fibers. However, more success in producing ion-exchange fibers from polyacrylonitrile fibers or its copolymers having suitable functional groups has been reported.[8]

In the present work, a new efficient process to prepare ion-exchange crosslinked fibers contain simultaneously amidoxime, amine, amide, and hydrazide groups using commercial polyacrylonitrile fibers as raw material has been described. Then, the effects of treatment conditions on physical properties, thermal characteristics, surface morphology, ion adsorption quantity, and ion desorption were investigated.

EXPERIMENTAL

Raw materials and reagents

Commercial acrylic fibers supplied from Iran polyacryl with 3.3 dtex as fibrous raw material were used. All chemicals consisting of hydrazine hydrate (80%), hydroxylamine hydrochloride, calcium carbonate, ferrous and copper sulfate, dimethyl formamide (DMF)

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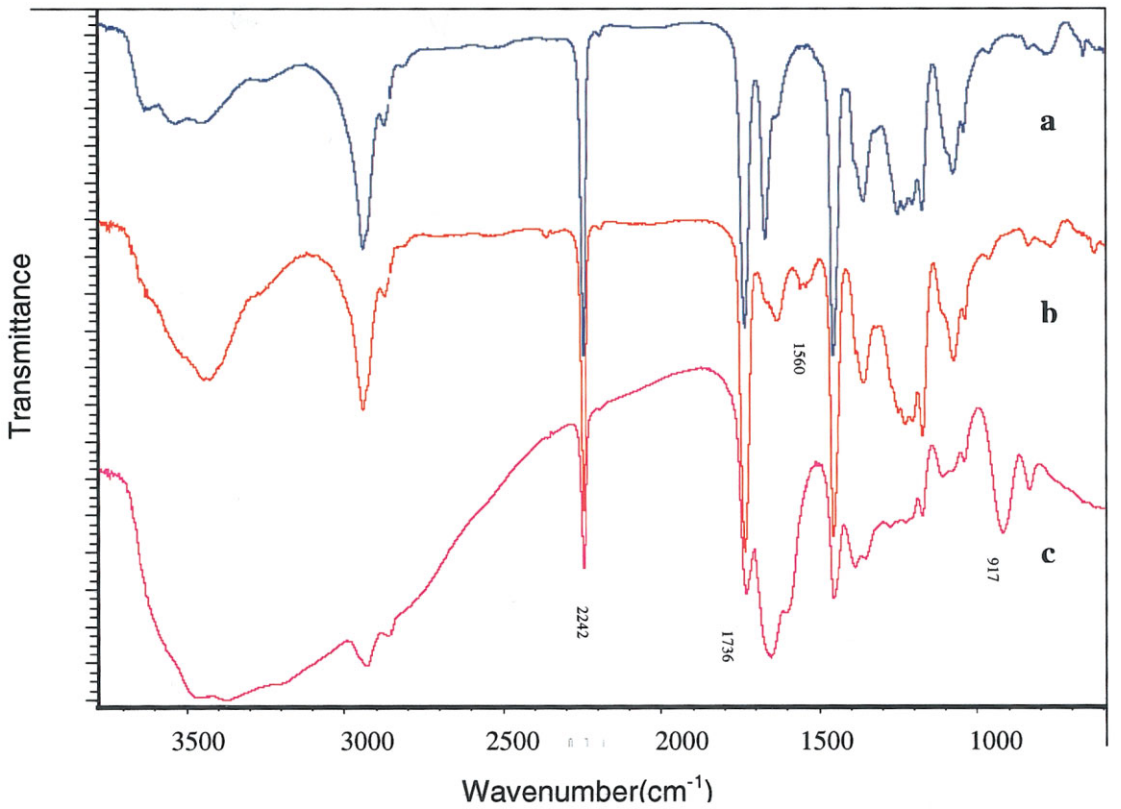


Figure 1 FTIR spectra of raw acrylic fiber (a), the crosslinked fiber (b), and the crosslinked amidoximated fiber (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

used in this work, were laboratory reagents grade and supplied from Merck (Germany).

Treatment procedures

Treatment with hydrazine

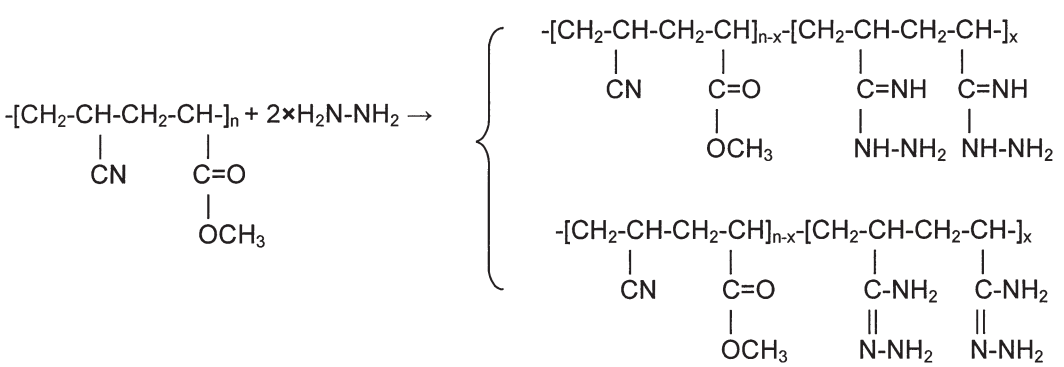
Crosslinking treatment of acrylic fiber samples with hydrazine was carried out according to the previous work,[9] in which 1 g of acrylic fibers were treated with 50 mL of hydrazine hydrate (L : G 50 : 1) in boiling water, under different concentration, for 80 min.

Treatment with hydroxylamine hydrochloride

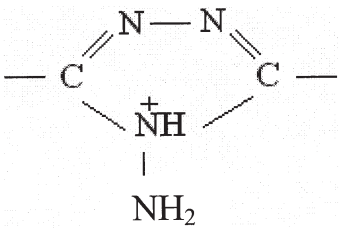
Crosslinked and noncrosslinked samples are treated with hydroxylamine hydrochloride and calcium carbonate (2 : 1.5) under various reaction conditions using distilled water with (L : G 50 : 1). The content of amidoxime group in the fiber is calculated as follows:

$$AO = (W_1 - W_0)M_0/(M_1W_0) \quad (1)$$

where AO is the content of amidoxime group in the fiber (%), W_1 is the weight of dry fiber after reaction



Scheme 1 Formula for the interaction mechanism of hydrazine with nitrile group in acrylic fiber.



Scheme 2 Formula for crosslinking mechanism of hydrazine with nitrile groups in two adjacent molecule chain.[4]

(g), W_0 is the weight of dry fiber before reaction (g), M_0 is the molecular weight of chain unit CH_2CHCN(53), and M_1 is the molecular weight of H_2NOH(33).[10]

Adsorption and desorption processes of metal ions

To measure the quantity of ions adsorbed by the modified fibers, first, two metal salt solutions, ferrous and copper sulfate, at the concentration of 0.1*M* were prepared. Then, 10 mL of each metal solutions were added to 100 mg of dry modified fibers at the room temperature (25°C) and left them for 30 min to reach to equilibrium state.[8] The quantity of ions adsorbed by modified fibers, using atomic absorption spectrometer (AAS), was calculated as follows:

$$Q = V(C_1 - C_2)/W \quad (2)$$

where Q is the adsorbed ion quantity by the samples (mg/g dry), C_1 is the initial ion concentration in the metal solution (mg/L), C_2 is the ion concentration after adsorption period (mg/L), V is the volume of ion solution (L), and W is the dry weight of the applied samples (g).

To study the reusability of the modified samples, 100 mg of the fibers containing adsorbed ions were added to 20 mL of 0.1*M* nitric acid solution at the room temperature for 60 min,[5] and then, again, these ion-desorbed fibers were immersed in metal solutions and left to reach its equilibrium state, according to described process. The quantity of ion adsorbed by these fibers was calculated by formula (2).

Characterization and measurement procedures

Ftir absorption spectrum

The samples were cut into fine pieces, then pressed into a pellet with KBr. The FTIR spectrums of the samples were obtained by Spectrometer Nicolet NEXUS 670.

Scheme 3 Formula for the amidoximation reaction in acrylic fiber.[10,15]

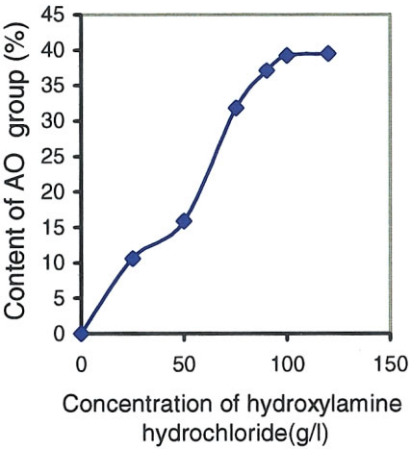


Figure 2 Effect of hydroxylamine hydrochloride concentration on the content of AO group (%): temp. 70°C; time 30 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mechanical properties

The mechanical properties of the samples were tested by Vibromat and Fafegraph from Textechno (Germany). In all samples, elongation rate of 20 mm/min and sample length of 20 mm were selected.[11]

Atomic absorption spectrometry

To determine ion adsorption quantity from salt solutions, aquatic solution of metal salts after adsorption were determined by the atomic absorption spectrometer 939 AA Spectrometer made by UNICAM.

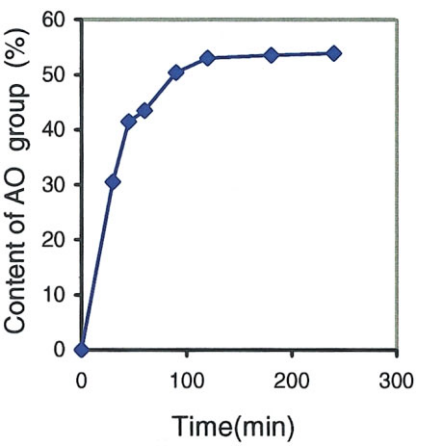


Figure 3 Effect of reaction time on the content of AO group (%): temp.70°C; conc. 80 g/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

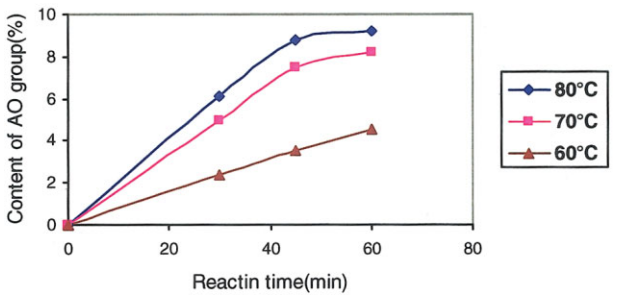


Figure 4 Relationship between the content of the amidoxime groups and reaction time at various temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scanning electron microscopy

To investigate fiber surface characteristics, micrographs of the surface fibers before and after the reaction were obtained by SEM PHILIPS XL30.

Differential scanning calorimetry

Thermal behavior of the samples was investigated by DSC 2010 TA instrument. The samples were heated from 30 to 400°C at a heating rate of 20°C/min, using nitrogen gas flow of 25 mL/min.

RESULTS AND DISCUSSION

Chemical structure studies

The FTIR spectra of the raw acrylic (RAF), crosslinked (HAF) and crosslinked amidoximated (HAAF) fibers, prepared under optimum condition, are shown in Figure 1(a–c), respectively. The FTIR spectrum of raw acrylic fiber [(Fig. 1(a)] shows the adsorption peaks of stretching vibration at 2242 cm^{-1} (C≡N), 1736 cm^{-1} (C═O) groups,[12,13] confirming that the applied fiber can be a copolymer of acrylonitrile and methyl acrylate.

In the spectrum b of Figure 1 the absorption band at 3400–3500 cm^{-1} was appeared, and the intensity of the peak also increases greatly. This behavior corresponds to the stretching vibration of N—H group. The broad absorption band in the region of 1630–1652 cm^{-1} can be related to stretching vibration of C═N group. The new broad peak at 1560 cm^{-1} is contributed to the overlapping of C—N stretching vibration with N—H bending vibration.[12,13] It is also observed that the intensity of the peaks at 2242 cm^{-1}(C≡N) and 1736 cm^{-1} (C═O) in crosslinked fibers reduces. These data support the argument that the crosslink of hydrazine with acrylic molecular chains leads to the formation of hydrazide group and decrease in the content of nitrile and ester groups.[12,14] In the HAAF sample [(Fig. 1(c)], the absorption peak at 2242 cm^{-1} weakens, while the peak at 1600 cm^{-1} corresponding to the stretch vibration of bond C═N and the absorption peak at 3300–3500 cm^{-1} related to stretching vibration of NH_2 and OH groups in HAAF become broader and stronger in comparison with raw and HAF samples.

As can be seen in the HAAF spectrum sample [(Fig. 1(c)], in comparison with raw acrylic fiber spectrum, a new absorption peak at 917 cm^{-1} corresponding to the stretch vibration of bond N—O appears.

According to the above-mentioned structure analysis and other researcher results,[8,15] it can be assumed that the composition of the treated fiber includes amidrazone, hydrazide, and amidoxime groups.

Consequently, the scheme formula for the reaction of hydrazine with nitrile groups of acrylic fibers can be expressed as Scheme 1:

According to another suggested mechanism, the adjacent molecular chains of polyacrylonitrile fibers can react with hydrazine to form triazoline crosslinked structure, in which the related formula can be presented as Scheme 2:

The formula for the reaction of hydroxylamine with nitrile groups has been presented in Scheme 3.

Relationship between reaction conditions and amidoxime groups

The effects of reaction conditions such as temperature, time, and concentration on the content of the amidoxime groups in the fiber were investigated. Figures 2 and 3 present the effect of concentration of hydrox-

TABLE I
Effect of Hydrazine Concentration on Mechanical Properties of Modified Fiber

Hydrazine conc.(%)	Tenacity (cN/tex)	Elongation at break (%)	Work at rupture (cN × cm)	Initial modulus (cN/tex)	Fiber fineness (dtex)
0	23.82 (2.01)	41.22 (4.25)	3.64 (10.79)	303.51 (2.54)	3.3 (5.17)
2	22.48 (4.46)	38.42 (6.45)	3.53 (10.18)	222.91 (3.64)	3.5 (6.60)
4	22.44 (3.71)	36.63 (1.05)	3.55 (9.34)	232.18 (2.74)	3.5 (4.88)
8	18.51 (10.79)	30.90 (6.15)	3.57 (5.95)	236.70 (3.08)	3.6 (9.21)
16	15.88 (13.49)	28.93 (12.67)	3.42 (2.66)	246.94 (7.98)	3.6 (10.33)

Values in parentheses show coefficient of variation (CV%) of samples.

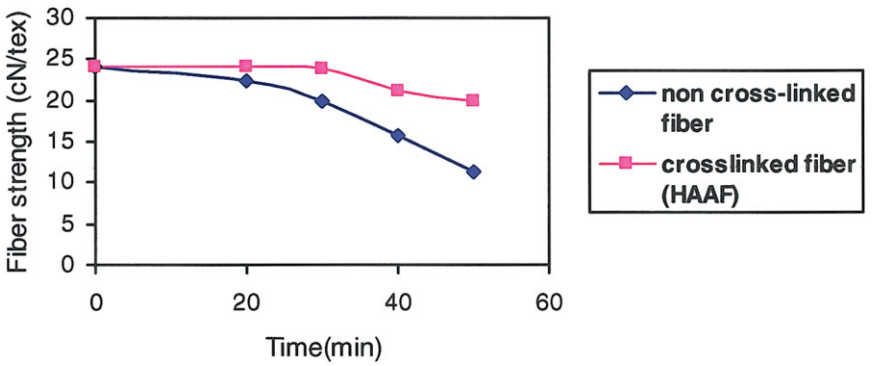


Figure 5 Effect of reaction time on strength of amidoximated fiber in noncrosslinked and crosslinked fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ylamine hydrochloride and reaction time, on the content of the amidoxime groups, respectively. As can be seen from Figures 2 and 3, by increasing the concentration and reaction time, the content of amidoxime group increases sharply with the concentration and time at the beginning period of reaction;[10] however, it tends to steady values after passing the conditions of 75 g/L, and 60 min. These results, which are in good agreement with others work, can be related to the high molecular diffusion of $HONH_2$ from the solution into the fiber at the beginning period of reaction while decreases and reaches to a steady state at the mentioned conditions of concentration and time. Therefore, to reach suitable amount of the amidoxime group, it is not effective to increase the concentration higher than 75 g/L and the reaction time more than 60 min.

Figure 4 shows the relationship between the content of the amidoxime groups and the time at various temperatures. In general, by increasing of the treatment time in amidoximation process, increasing of AO groups' content, in all samples, but with different trends, were observed. However, as can be seen in Figure 4, though the amidoxime groups content increase with reaction temperature, but at temperatures over 70°C, the content of the amidoxime groups become similar in all samples. Therefore, to save energy and keep fiber properties at safe side, 70°C can be selected as optimum temperature.

Mechanical properties

The effects of crosslinking and amidoximating treatments on the mechanical properties are shown in Table I.

In amidoximated fiber, when noncrosslinked fiber is used, the strength of fiber decreases remarkably (Fig. 5).

In general, by increasing hydrazine concentration, drop in all mechanical properties, especially in strength and elongation, can be observed. However, at concentration of 4% (by weight of fiber) and treatment temperature of 95°C, still reasonable properties (only 5.79% decrease in strength and 11.13% in elongation) can be obtained. It should be emphasized that at lower temperatures (<90–95°C) no crosslinking reaction can occur while at higher temperatures (>95°C), corresponding to literature, cyclic compounds might be formed by side reaction leading to fiber properties deterioration such as flexibility, strength, and swelling ratio.[8]

In noncrosslinked fiber when the concentration is increased to >75 g/L, and treatment time to >60 min, the content of the amidoxime group increases slowly and tends to a steady value (Figs. 2 and 3). Therefore, it is reasonable to choose the amount of 75 g/L for concentration and 60 min for reaction time as optimum conditions.

Table II presents the effect of amidoximation reac-

TABLE II
Effect of Reaction Time on Mechanical Properties of HAAF Fiber Samples

Experimental conditions	Tenacity (cN/tex)	Elongation at break (%)	Work at rupture (cN × cm)	Initial modulus (cN/tex)
Raw	24.05 (7.16)	33.49 (9.91)	3.08 (3.90)	325.36 (9.86)
20 min	24.04 (6.61)	27.75 (4.06)	2.62 (4.82)	323.65 (6.56)
30 min	23.85 (7.83)	25.60 (8.71)	2.41 (5.17)	320.71 (7.20)
40 min	20.23 (10.10)	22.65 (10.82)	2.08 (7.14)	327.57 (3.62)
50 min	19.94 (4.11)	21.95 (15.85)	2.19 (2.26)	333.10 (4.43)

Values in parentheses show CV% of samples.

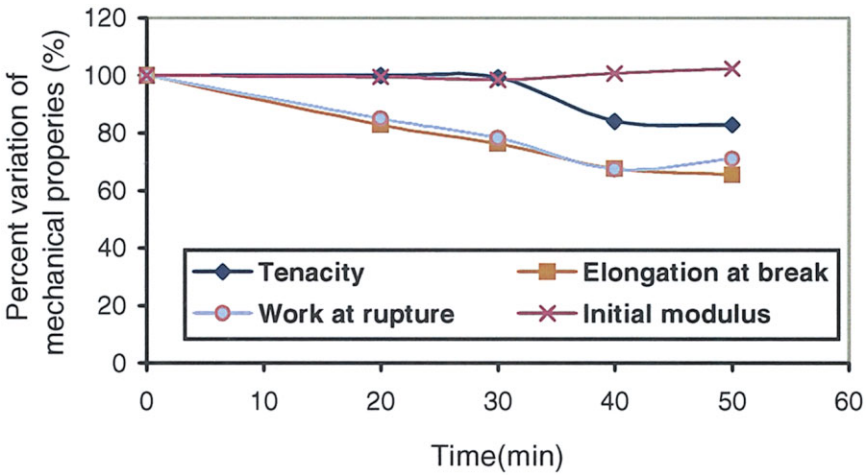


Figure 6 The changes of HAAF mechanical properties with respect to RAF sample. All mechanical properties of RAF sample were considered as 100. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion time on mechanical properties of HAAF fiber sample. In this experiment, first, the fibers were treated with hydrazine under optimum conditions, and then with hydroxylamine under constant concentration 75 g/L at different reaction times. In general, increasing of the amidoximation reaction time reduces mechanical fiber properties; however, as can be seen in Table II and Figure 5, in the HAAF sample, which was treated to hydrazine and hydroxylamine under 50 min reaction time, still acceptable mechanical properties can be observed.

Figure 6 shows the changes in tenacity, elongation at break, work at rupture, and initial modulus of modified samples (HAAF) with respect to RAF samples. Basically, by increasing the amidoximation reaction time, all mechanical properties were reduced, but the reduction in elongation (34.46%) and work at rupture (28.9%) is higher than tenacity (17.09%), while in initial modulus, no obvious changes were observed.

Ion adsorption quantity

The quantities of copper and iron ions remained in metal solutions after treatment with raw and modified acrylic fiber samples were measured. The values of adsorbed ions in initial and reused modified fiber samples are shown in Figure 7. For comparison efficiency and speed of ion adsorption between raw and modified fiber samples, the adsorption reaction time 30 min was used for all of them. As can be seen in the raw acrylic fibers, the content of copper and iron ions adsorbed was negligible; however, in the modified samples, the HAF and HAAF, high level of ion adsorption was observed, which can be related to the existence of functional groups. In addition, among all tested samples, the HAAF one by adsorption, respectively, 775 and 780 mg/g for copper and iron ions shows maximum efficiency in ion adsorption, and this can be related to assisting amidoximation treatment along with hydrazide groups, which can considerably increase the number of efficient functional groups in the chain structure comparing to HAF sample.

Figure 7 also clearly shows that the HAAF sample, which is objected one time to ion desorption process and then immersed again in the metal solutions, still has high efficiency in adsorbing metal ions.

Thermal properties

The differential scanning calorimetry (DSC) curves for raw acrylic fibers, pretreated fibers with hydrazine (HAF) and treated fibers with hydrazine and hydroxylamine (HAAF) are illustrated in Figure 8, and the results are summarized in Table III.

The DSC curves of the raw sample demonstrate clearly the suddenness and intensity of the liberated heat. It is noticeable that the nature of the exotherm, which is associated with the reactions of the nitrile

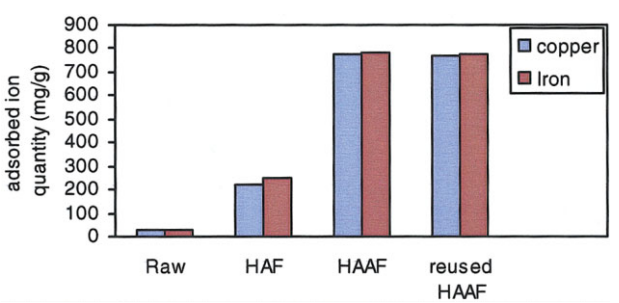


Figure 7 The quantities of copper and iron ions adsorbed by various acrylic fiber samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

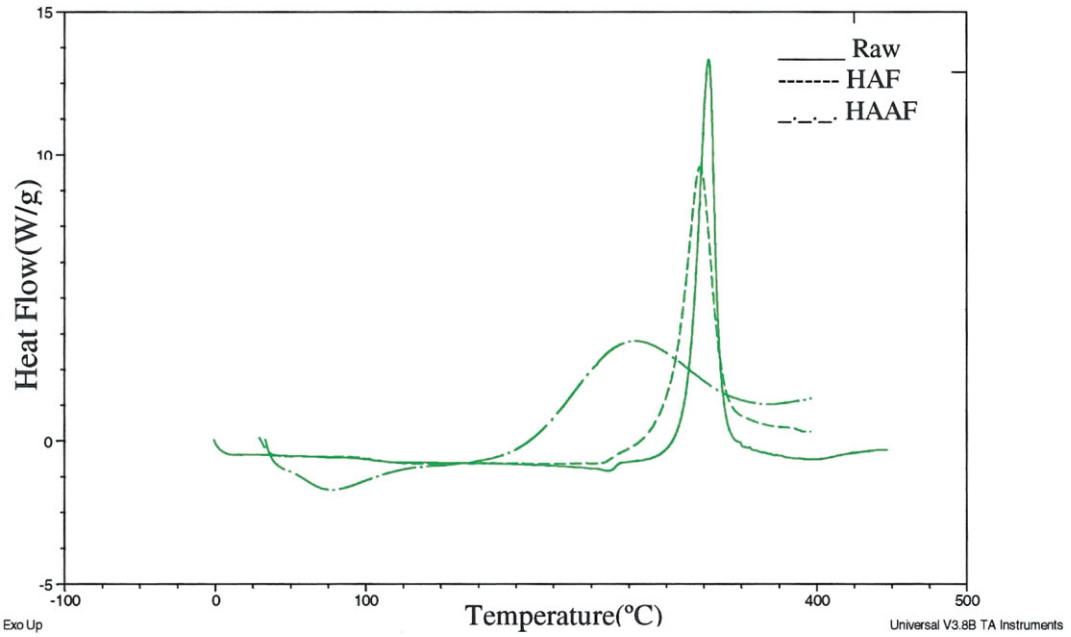


Figure 8 DSC curves for RAF, HAF, and HAAF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

groups (cyclization and intermolecular nitrile polymerization), differs significantly from raw sample to the HAF and also to HAAF samples. Comparison of the curves shows that the exothermic peak temperature starts at a high value for raw sample, and then it is reduced for HAF and HAAF samples while the peak width is increased. In the case of the HAF sample, the crosslinking treatment on the fibers results in significant effects on the thermal degradation behavior. The further broadening in the exothermic peak and the decrease in the peak temperature and a lower heat output compared to raw sample may indicate that crosslinking in some way, during the exothermic process, enhances the nitrile cyclization, which will consequently reduce any fragmentation reactions.

SEM investigations

Scanning electron microscopy (SEM) was used to examine the external surface of the fiber before and after modification. As can be seen from Figure 9, original acrylic fiber has comparatively smooth surface [Fig. 9(a)], and with modified fiber (HAAF), no obvious changes comparing to that of the raw fiber was observed [Fig. 9(b)]. This observation can give another reason for the fact that why the HAAF sample can still keep its mechanical properties after modification treatment, effectively.

CONCLUSIONS

A new type of ion-exchange crosslinked acrylic fiber is successfully prepared by modifying of a polyacrylonitrile (PAN) fiber with hydrazine and hydroxylamine at alkaline pH. This fiber can remove strongly metal ions, such as copper and iron ions, from aquatic solutions. Ion adsorbed by the fiber can be desorbed thoroughly by molar nitric acid solution under described condition. Therefore, these fibers can be reused with high efficiency.

The results show that by increasing the reaction time, temperature and concentration of hydroxylamine hydrochloride, amidoxime groups content increase in all samples, but with noncrosslinked fibers

TABLE III
The Effect of Cross-Linking and Amidoximation Treatments on DSC Characteristics of Acrylic Fiber Samples

Sample	Exothermic heat (J/g)	Peak (°C)	Peak width (°C)	Exothermic intensity (%)[a]	Onset (°C)
Raw	640.2	277.69–367.27	89.58	100	328.32
HAF	738.4	264.42–374.85	110.43	69.08	322.54
HAAF	772.9	199.49–373.43	173.94	22/23	275.96

[a]The values of exothermic intensity are relative; the peak of control sample set to 100%.

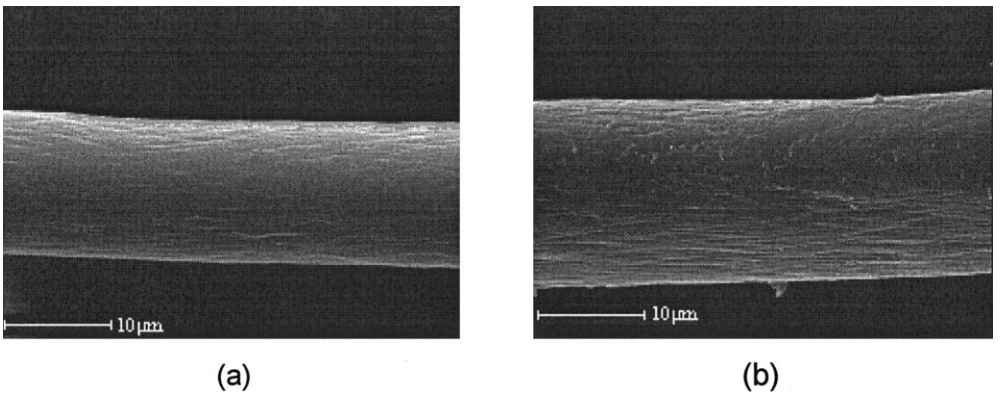


Figure 9 SEM images of (a) the original and (b) modified acrylic fiber (HAAF) (×2000),

intensive drop in the mechanical properties were observed; however, in crosslinked samples, specially in the sample prepared under optimum conditions of reaction, good ion adsorption capacity with keeping mechanical properties were achieved.

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