Diametric Swelling and Hydrophilic Characteristics of Fibrous Acrylic Ion Exchanger

Mojdeh Zargaran,[1] Ahmad M. Shoushtari,[1] Majid Abdouss[2]

[1]*Textile Engineering Department, Amirkabir University of Technology, Tehran, I.R. Iran*
[2]*Chemical Department, Amirkabir University of Technology, Tehran, I.R. Iran*

Received 5 January 2008; accepted 16 March 2008
DOI 10.1002/app.28497
Published online 19 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In our previous works, modified acrylic fiber samples with highly ion-exchange ability were described. These fibers contain suitable functional groups such as amidoxime, amid, and amine groups in their molecular chains. In this work, swelling in fiber diameter and hydrophilic properties of the modified acrylic fiber samples, as important parameters affecting on ion-exchange efficiency, were investigated. The results showed that all modification treatments gave rise to diameter swelling ratio, but this does not mean that sample with highest swelling ratio in all cases can result in highest ability to ion-exchange. In other words, the relation between them was complicated, and several factors such as the kind and the size of ion adsorbent and crosslinking ability of chemical reagent were used for modification interfere in ion-exchange phenomena.The results of moisture adsorption indicate that incorporating functional groups by modification treatments enhance moisture adsorption in which samples with higher ion-exchange ability possess higher hydrophilic property. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3843–3847, 2008

Key words: ion-exchange fiber; diameter swelling; hydrophilic property; acrylic fiber; moisture regain

INTRODUCTION

Among well-known methods for removal or reduction of ions from solutions, adsorption and ion-exchange methods are highly efficient, simple, and economical, especially in diluted solutions.[1] However, among different types of ion exchangers, fibrous ion exchangers have attracted great interest in the recent years.[2,3] This can be related to their structure and characteristics such as high-specific surface, small cross section, uniformity in diameter (in macroscopic scale),[4] long length of fiber to diameter that prevents packing of the ion material to the surface of ion exchangers,[4,5] 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.[5,6] Moreover, they can be used in the purification of water and air from chemically active pollutants such as acids, bases, and acid anhydrides, and also they can be applied for the protection of respiratory organs from aggressive gases and vapors.[5]

Correspondence to: A. M. Shoushtari (amousavi@aut.ac.ir).
Contract grant sponsor: Industrial Development and Renovation Organization (IDRO).
Contract grant sponsor: Small Business Development Center (SBDC).

In the recent years, considerable research has been focused on the characterization and swelling behavior of super adsorbent polymers (SAPs).[6] SAPs are materials that can absorb or retain a liquid or fluid greater than 15 times their dry weight and release the retained liquid in a liquid or fluid form and by diffusion though the gel as water vapor or moisture.

To function as an absorbent for aqueous fluids, a polymer must have certain properties: (a) it must be hydrophilic, (b) the polymer must swell in aqueous fluids but must not dissolve, and (c) although it is not a strict requirement, absorbents should have some ionic character, because charge repulsion is an important factor in promoting polymer swelling in aqueous fluids.[7] Many kinds of SAPs have been commercialized, because they are widely applied not only in the fields of personal care products, biosorbent, and biomaterials,[8] but also in soil for agriculture,[9] wastewater treatment,[10–12] etc., where water absorbency or water retention is important.

In the previous work, a high efficiency ion-exchange acrylic fiber for ionic compounds adsorption was described, the functional groups incorporated into fiber structure was investigated, and then the ion adsorption ability and the amount of ion adsorption for different metal ions were studied[13,14]; and in another work,[15] modification treatments with hydroxylamine and hydrazine under optimized conditions in terms of functional group contents incorporated into acrylic fibers while keeping their shape and physical properties were indicated. It is noticed

TABLE I
Samples Specifications Prepared Under Optimized Condition [13–15]

Sample	Optimized treatment condition
One step modification treatments (with one reagent)	
AAF	Raw acrylic fibers treated with hydroxylamine hydrochloride and calcium carbonate (2 : 1.5 by weight) using of 50 cc distilled water and 1gr fiber sample (L:G 50:1) at 70°C for 30 min.
HAF	Raw acrylic fibers treated with 2% hydrazine (on weight of fiber) and liquor ratio (L : G 50 : 1) in boiling water, for 80 min
EDAAF	Raw acrylic fibers treated with 2% ethylene diamine (on weight of fiber) and liquor ratio (L : G 50 : 1) in boiling water, for 80 min
HMDAAF	Raw acrylic fibers treated with 2% hexamethylene diamine (on weight of fiber) and liquor ratio (L : G 50 : 1) in boiling water, for 80 min
UAF	Raw acrylic fibers treated with 5% urea (on weight of fiber) and liquor ratio (L : G 50 : 1) in boiling water, for 80 min
Two step modification treatments (with two reagent)	
HAAF	HAF sample treated with hydroxylamine hydrochloride under condition described for AAF
EDAAAF	EDAAF sample treated with hydroxylamine hydrochloride under condition described for AAF
HMDAAAF	HMDAAF sample treated with hydroxylamine hydrochloride under condition described for AAF
UAAF	UAF sample treated with hydroxylamine hydrochloride under condition described for AAF

that these fibers are not super adsorbent but, in the literature, moisture adsorption and good swelling characteristics are important properties needed for suitable ion adsorbent material.[7,16,17] However, only few works discussing above subjects have been described. In this work, the swelling ratio, moisture adsorption, and their relations with ion-exchange ability for different modified ion-exchange acrylic fiber samples were investigated.

EXPERIMENTAL

Raw materials and reagents

Modified commercial acrylic fibers, prepared according to Refs. 13 and 14, were used. All chemicals consisting of hydrazine hydrate (80%), hydroxylamine hydrochloride, urea, ethylene diamine, hexamethylene diamine, and dimethyl formamide (DMF) used in this work, were laboratory reagent grade and supplied from Merck Co.

Treatment procedures

Treatment with chemical reagents

According to our previous work,[13,14] acrylic fiber samples were treated with different chemical reagents such as hydrazine, hydroxylamine, urea, ethylene diamine, and hexamethylene diamine to obtain modified ion adsorbent fibers, and in this work, samples prepared under optimized condition were selected and presented briefly in Table I.

Adsorption 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 concentration of 0.1*M* were prepared. Then, 10 mL of each metal solution was added to 100 mg of dry modified fibers at the room temperature (25°C) and left them for 30 min to reach the equilibrium state.[14] The quantity of ions adsorbed by modified fibers, using atomic absorption spectrometer (AAS), was calculated as follows:

$$Q = V(C_1 - C_2)/W \quad (1)$$

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).

Characterization and measurement procedures

Swelling ratio measurement

For measuring the diameter swelling of fiber samples, the changes in the fiber diameter were studied. For this purpose, in each sample, first, one primary fiber group ($n_1 = 5$) was selected, and the diameter of each fiber sample was measured using projection microscope. Then, according to statistical methods, the real number of the samples (n) needed for measuring with error limit of 0.001 by applying formula (2) was obtained.

$$n = \left[\frac{Z \times SD}{E}\right]^2 \quad (2)$$

where n is the number of samples that needed for measuring, E is the error limit, Z, for the numerous samples ($n > 30$), was exploited from the table of

TABLE II
Results of Primary Diameter Measurements of Fibers

Samples	n_1	Average diameter (mm)	SD	n
Raw	5	0.01700	0.00068	2
HAF	5	0.01900	0.00137	8
HAAF	5	0.02000	0.00306	36
AAF	5	0.02310	0.00108	5
UAF	5	0.02150	0.00137	8
UAAF	5	0.02375	0.00217	19
EDAAF	5	0.01920	0.00153	5
EDAAAF	5	0.02080	0.00201	5
HMDAAF	5	0.01941	0.00145	5
HMDAAAF	5	0.02100	0.00205	5

normal distribution, and, for $n < 30$, it was obtained from t distribution table at confidence limit of 95%. SD is the standard deviation, which can be calculated by formula (3).

$$\mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \tag{3}$$

where x_i is the number of samples and x is the arithmetic mean.

The diameter swelling ratio was calculated according to the following formula:

$$a = \frac{D - D_0}{D_0} \tag{4}$$

where D and D_0 are the diameters of modified and raw fiber samples, respectively.

Scanning electron microscopy

To investigate the appearance, surface defects, and confirm the swelling results of treated fiber samples with chemical reagents, typical micrographs of some fibers before and after treatments were obtained by scanning electron microscopy (SEM) PHILIPS XL30.

Moisture regains measurement

For measuring the moisture regain (hydrophilic property) of fiber samples, the changes in the fiber weight before and after drying for 50 min in which no further reduction in weight was observed under 80°C were calculated.

RESULTS AND DISCUSSION

Diameter swelling characteristic

The results of diameter changes of modified fiber samples treated with hydrazine, hydroxylamine, urea, ethylene diamine, and hexamethylene diamine under optimized condition in comparison with raw fiber sample were calculated and shown in Tables II and III.

After obtaining the needed number measurements (n), final assessments were carried out, and the results were given in Table III.

According to the earlier results, the average diameter of fiber samples treated with hydroxylamine, hydrazine, urea, ethylene diamine, and hexamethylene diamine are higher than raw fiber samples. This can be related to the diffusion of reacting molecules among fiber molecular chains and also break of inter molecular bonds causing reduction in polar bonds of acrylic fiber chains. In other words, this phenomenon can be explained by the reaction of chemical reagents with nitril groups of the fiber causing easier movement of chains and higher free volume in the chain fiber structure.

On the other hand, incorporating hydrophilic functional groups such as amidoxime, amine, and amid groups in molecular structure of acrylic fibers can enhance moisture adsorption. Water molecules adsorbed by these functional groups can bring about distance between molecule chains and, therefore, give rise to diameter swelling ratio. In one-step treated samples (HAF, EDAAF, HMDAAF, AAF, and UAF), the swelling results show that AAF and

TABLE III
Results of Final Diameter Measurements of Fibers

Sample	Average diameter (mm)	Sd	Variance	Number of sampling (n)	Variation range	Diameter swelling ratio
Raw	0.0170	0.00068	0.00000	5	0.00125	–
HAF	0.0190	0.00137	0.00000	5	0.00250	0.1176
HAAF	0.02076	0.00205	0.00000	36	0.01000	0.2212
AAF	0.02310	0.000108	0.00000	5	0.00250	0.3588
UAF	0.02219	0.00209	0.00000	8	0.00500	0.3053
UAAF	0.02504	0.00269	0.00001	19	0.01000	0.4729
EDAAF	0.01920	0.00153	0.00000	5	0.00145	0.129
EDAAAF	0.02080	0.00201	0.00000	5	0.00234	0.223
HMDAAF	0.01941	0.00145	0.00000	5	0.00324	0.142
HMDAAAF	0.02100	0.00205	0.00000	5	0.00651	0.235

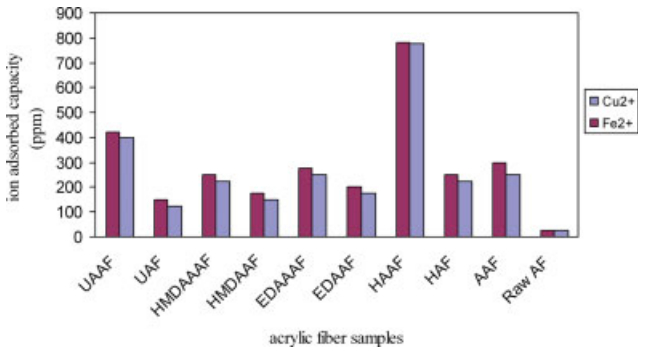

Figure 1 Ion adsorbing amount for copper and iron ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UAF present higher swelling ratio comparing to samples treated with diamines. This observation can be explained by this discussion that in modified fibers with diamines (HAF, EDAAF, and HMDAAF samples) the crosslinkages formed between molecular chains of fibers decrease the chains mobility and prevent the adjusted chain to keep distance from each other, and therefore swelling procedure cannot take place properly.[11] Similarly, in two-step modification-treated samples, in comparison with HAAF, EDAAAF, HMDAAAF, and UAAF, the fibers with crosslink bonds present lower swelling ratio than UAAF.

Between non-crosslinking samples (AAF and UAF), the AAF sample, which poses amidoxime functional group, present higher hydrophilic property comparing to UAF sample. Therefore, the kind of functional group is more important for the adsorbed moisture and swelling effect.

Meanwhile, the results indicate that in non-crosslinked fiber samples (UAAF, UAF, and AAF fibers), UAAF fibers have more hydrophilic functional groups and the greatest swelling ratio among samples. Therefore, the number of functional group is also more important for the adsorbed moisture and swelling effect.

By considering the results shown in Table III and Figure 1, basically, it can be said that increase in swelling ratio can be related to higher ion adsorption ability of fiber sample as can be noticed in UAAF sample, which has higher swelling ratio compared to UAF, HAF, and AAF samples, thereby showing higher ion adsorption ability to both kind of Cu^{2+} and Fe^{2+} ions.

This observation can be explained by this fact that by swelling of fiber diameter, the molecular chains enhance their distance from each other. Therefore, the diffusion of metal solution can take place easier, the contact time between metal ions and functional groups is increased, and, consequently, the ion adsorption capacity gives rise. But these results cannot be generalized to all samples. For example, crosslinked fiber samples (HAF and HAAF) although show lower swelling ratio in comparison with UAF and UAAF, respectively, but present higher ion adsorption ability. So, it can be concluded that ion adsorption ability is very complicated and depends on various factors, mainly, mechanism of network structure formation by crosslinking treatments,[15] the type of functional groups incorporated in the fiber structure, ions settlement manner, history of fiber structure morphology, and characteristics of ions. But it can be said that with forbearance crosslinking effect and prevention effect of it to swelling, the samples with higher swelling ratio have higher ability to ion-exchange.

Moisture adsorption

Figure 2 shows the percentage of increased moisture adsorption of fiber samples compared to raw acrylic fiber. The results show that incorporating functional groups into the fiber to produce ion-exchange fiber can enhance moisture adsorption property. This phenomenon can be related to incorporating hydrophilic groups into the fiber. Because functional groups incorporated to fibers are hydrophilic, therefore, beside ion-exchange ability, the moisture adsorption of treated fibers was increased.

The relation between ion-exchange ability and moisture adsorption is apart from crosslinked and non-crosslinked samples is direct, and samples with highest ion-exchange ability have highest moisture adsorption.

The SEM images

SEM was used to examine the external surface of the fiber before and after treating with solutions (Fig. 3).

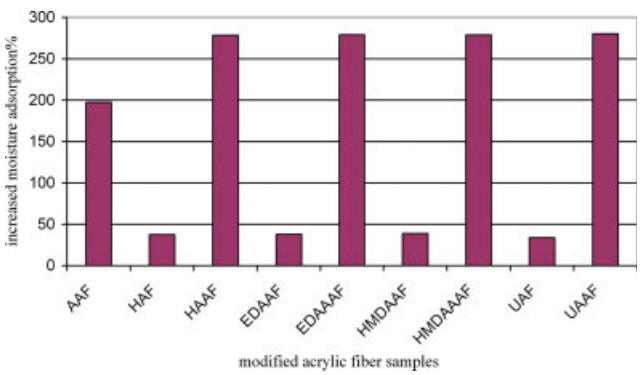

Figure 2 Percentage of increased moisture adsorption of fiber samples comparison to raw acrylic fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

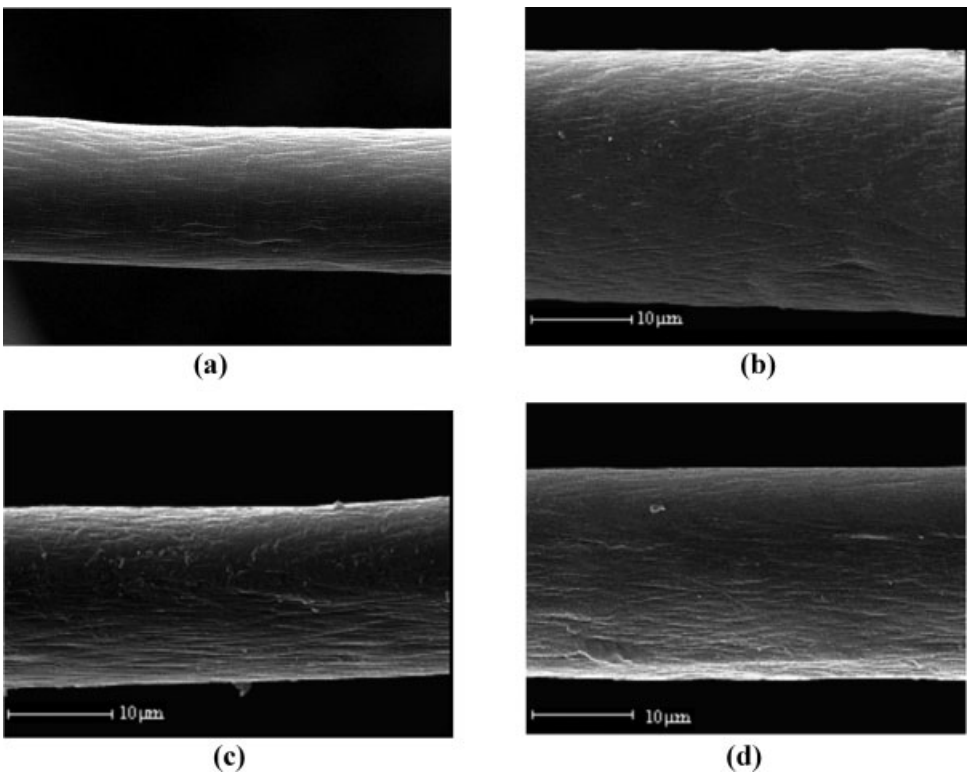

Figure 3 The SEM images of (a) raw acrylic fiber, (b) modified one (UAAF), (c) HAF, (d) HAAF.

CONCLUSION

According to swelling measurements of diameter, typical SEM micrographs and considering adsorption results, it can be concluded that samples with higher diametric swelling ratio show higher ion adsorption capability. Enhancement in swelling ratio can be related to higher ion adsorption ability in modified fiber samples, but this does not mean samples with highest swelling ratio can adsorb the highest amount of all kinds of ions. The swelling and hydrophilic characterization results indicate that ion adsorption phenomena in fibrous materials is very complicated and depends on various factors such as mechanism of network structure formation by crosslinking treatment, type of functional groups presented in fiber structure, ion settlement manner, and characteristics of adsorbed ions. So to find out accurate relationship between swelling ratio and ion adsorption ability for fibrous materials, more intensive studies should be carried out.

From moisture adsorption results, it can be said that in addition to creation of ion-exchange ability, the moisture adsorption of treated fibers were also increased because functional groups incorporated to fibers are hydrophilic. Direct relation between ion-exchange ability and moisture adsorption, whether the sample is crosslinked or non-crosslinked type can be observed by which samples with highest ion-exchange ability have highest moisture adsorption.

References

1. Rether, A.; Schuster, M. React Funct Polym 2003, 57, 13.
2. Ruixia, L.; Jinlong, G.; Hongxiao, T. J Colloid Interf Sci 2002, 248, 268.
3. Zhang, B. W.; Fischer, K.; Bieniek, D.; Kettrup, A. React Polym 1994, 24, 49.
4. Borrell, P.; Harrison, P. D.; Marriott, J. C. Cationic fibers suitable for ion-exchange materials and their production, European patent application. Eur. Pat. 0,194,766, A1 (1986).
5. Soldatov, V. S.; Shunkevich, A. A.; Sergeev, G. I. React Polym 1988, 7, 159.
6. Yiamsawas, D.; Kangwansupamonkon, W.; Chailapakul, O.; Kiatkamjornwong, S. React Funct Polym 2007, 67, 865.
7. Kiatkamjornwong, S.; Chomsaksakul, W.; Sonsuk, M. Radiat Phys Chem 2000, 59, 413.
8. Saraydin, D.; Unver-Saraydin, S.; Karadag, E.; Koptagel, E.; Guven, O. Nucl Instr Meth B 2004, 217, 281.
9. Karadag, E.; Saraydin, D.; Caldiran, Y.; Guven, O. Polym Adv Technol 2000, 11, 59.
10. Duran, S.; Solpan, D.; Gun, O. Nucl Instr Meth B 1999, 151, 196.
11. Karadag, E.; Uzum, O. B.; Saraydin, D. Eur Polym J 2002, 38, 2133.
12. Can, H. K.; Kirci, B.; Kavalak, S.; Guner, A. Radiat Phys Chem 2003, 68, 811.
13. Zargaran, M.; Shoushtari, A. M.; Abdouss, M. J Polym Sci Technol (in Persian) 2005, 18, 235.
14. Shoushtari, A. M.; Zargaran, M.; Abdouss, M. J Appl Polym Sci 2006, 101, 2202.
15. Zargaran, M. M.Sc. Thesis, Amirkabir University of Technology, Iran, 2004.
16. Bilba, N.; Bilba, D.; Moroi, G. J Appl Polym Sci 2004, 92, 3730.
17. El-Sawy, N. M.; Hegazy, E. A.; El-Hag Ali, A.; Abdel Motlab, M. S.; Awadallah-F, A. Nucl Instrum Methods Phys Res B 2007, 264, 227.