NOTE

A Study of Polyethylene Acrylic Acid Copolymers. II. Effect of Swelling Method and Ionomerization Tensions on Ion Absorption of PEAA Fibers

INTRODUCTION

PEAA fibers undergo significant swelling in 0.5*N* alkali solutions. The swelling is attended with significant fiber shrinkage of at least 30%. This shrinkage can be prevented by holding the fiber at constant length much like mercerization of cotton. In cotton mercerization, significant cellulose chain orientation occurs, resulting in a change of fiber properties such as its enhanced absorption of dye molecules.

We felt that changing the alkali swelling conditions of PEAA copolymer fibers results in similar differences in cation uptake and could result in differences in the final properties of the fiber. The alkali-exchanged PEAA fibers undergo additional shrinkage if allowed to react in the slack state during ionomerization (cation exchange) in the metal salt solution.[1] Again, this shrinkage can be prevented by holding the fibers at constant length. As a consequence, it may be possible to control the placement of ions within the fiber by the method of swelling (slack or tension) and/or the method of ionomerization (slack or tension). This research focuses on the copper ion location as a result of these four permutations of treatment. The first treatment is for the method of swelling, and the second treatment, for the ionomerization, as follows:

Tension–Tension
Tension–Slack
Slack–Slack
Slack–Tension

The copper-ion concentration was obtained at the edge, midregion, and center of the fiber by EDAX methods.

EXPERIMENTAL

Swelling

(A) General Information. A 0.25 g sample of the 22 Denier PEAA fibers was swollen at 55°C either completely slack or at constant length using the skein dyeing device and technique previously reported.[1] The skein during the "slack" treatments was allowed to react completely relaxed on the dyeing device through periodic adjustments as it was swollen in the 0.5*N* alkali hydroxide over the first 15 min. This enabled the yarn to be held in skein form without being so slack as to allow fibers to come loose from the skein holder and float free in the 0.5*N* caustic solution. This same skein holder could then be used to draw the swollen skein in a taut condition (after rinsing) for later ionomerization "at constant length" if desired. All alkali solutions were made to 0.5*N* (ACS reagent grade). Treatments were accomplished at a liquor ratio (solution to fiber) of 100/1.

(B) Alkali Metal Ionomers. Fibers that are swollen in alkali are removed from the reaction bath and rinsed (3×) with agitation in distilled or deionized water. If the samples are not to be further treated, they are dried on the dye frames. Fibers at the midpoint of the skeins (well away from contact points with the frames) are taken for study.

EDAX and Fiber Diameters

EDAX measurements were made at 20 kV and at 2000× magnifications (20 mm = 10 μm). A cut fiber bundle was examined and several fibers of cirricular cross section were selected for measurement (a cirricular cross section indicates a cut, perpendicular to the fiber axis). The area of the viewed screen spot was 18 × 22 mm, which calculated to an actual sample area of 24.75 μm^2. The fiber diameters were calculated from measurements on the scanning elec-

Table I Diameter (μm) of Various Fibers Swollen in 0.5*N* Sodium, Potassium, and Lithium Hydroxides

	Method of Swelling	
Metal Ion	Tension	Slack
Lithium	31.45	38.1
Sodium	37.0	44.3
Potassium	34.6	38.3

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Table II Diameter of Sodium Alkali Swollen and Copper-Ionomerized PEAA Under Various Treatment Conditions

Treatment Condition	Diameter (μm) %
Slack/Slack	67.3
Slack/Tension	55.5
Tension/Tension	56.3
Tension/Slack	63.3

tron microscope screen in mm at 1100×. From the diameter, the cross-sectional area of the fiber could be calculated. The percentage area of the fiber used for the EDAX measurements was held at about 0.7% of the "total cross-sectional area." A minimum of four separate fibers were measured at the edge midpoint and center of the fibers and the results averaged.

Ionomerization

If the fibers are to be ionomerized with copper, the rinsed samples are placed, without drying, directly into the buffered metal salt solution. For samples to be treated at constant length (under tension), the skein holder was set to prevent any significant yarn contraction during the copper exchange. For the "slack" treatments, the tension on the skein was slowly let off as virtually all the shrinkage occurred during the first 15 min of ionomerization in the 5% copper sulfate (ACS reagent grade) solution. The solution was buffered to pH 5 with sodium citrate and the treatment was at a liquor ratio of 300/1. The yarn contact time with the solution was 24 h at room temperature followed by rinsing (3×) with agitation in distilled or deionized water followed by air drying, while being held in either the "slack" or the "tension" state.

RESULTS AND DISCUSSION

The effect of the alkali metal on the swelling of EAA is shown in Tables I and II. The ultimate fiber diameter depends upon whether or not the fiber is held under tension or allowed to react slack during the swelling in the 0.5*N* alkali. It is felt that because of the high liquor ratio employed the concentration of either the alkali or copper solutions do not materially change during the swelling or ionomerization sequence. In each case, it was found that the fiber diameters are greater when the fibers are allowed to react under slack conditions regardless of the alkali metal employed (Table I). The 0.5*N* sodium hydroxide appears to give greater fiber swelling than either 0.5*N* potassium or 0.5*N* lithium. It is not known, however, whether the 0.5*N* solutions of these alkali metals is the optimum concentration conditions for swelling PEAA. Alternatively, sodium, for some reason, has greater swelling power with PEAA than does the larger potassium or smaller lithium ion. It is not uncommon for one alkali metal ion to exhibit greater swelling power with fibers. For example, lithium hydroxide causes greater swelling of cotton at lower concentrations than do the sodium or potassium alkali metals.[2] This is thought to be due to the differences in hydration for these ions. Only the sodium-swollen PEAA was studied for location of copper ions.

The alkali-swollen PEAA fibers undergo additional swelling when the fibers are ionomerized (exchanged) with metal ions. Again, the largest increases in diameters occurs when the ionomerization is done under slack conditions (Table II). This is typical of fiber-swelling phenomena in textile fibers where an increase in diameter is accompanied by fiber shrinkage.

The amount of copper ions at three locations in the fiber (edge, midregion, and center) was determined by EDAX methods. The EDAX concentration of copper in each region was normalized to the edge. The results are given in Table III, whereas the typical EDAX patterns developed are shown in Figures 1 and 2. Apparently, the final copper distribution does not follow the levels of sodium or potassium in the fiber (Table IV). The amount

Table III Final Ion Concentration (EDAX) of Copper and Sulfur in the Sodium Alkali Swollen and Copper-Ionomerized Fibers[a]

0.5*N* Sodium Hydroxide Treatment/Copper Ionomerization Treatment	Fiber Position					
	Copper			Sulfur		
	Edge	Mid	Center	Edge	Mid	Center
Slack/Slack	1.00	0.78	0.78	1.00	1.87	3.37
Slack/Tension	1.00	0.48	0.38	1.00	0.43	0.18
Tension/Slack	1.00	1.10	1.14	1.00	2.18	2.76
Tension/Tension	1.00	0.64	0.66	1.00	0.92	1.31

[a] Normalized to the edge of the fibers.

Table IV Final Ion Concentrations (EDAX) of Alkali Metals in the Swollen, Rinsed, and Air-Dried Fibers[a]

Treatment	Fiber Position	
	Edge	Center
0.5*N* Sodium Hydroxide	Sodium	
Slack	1.0	1.06
Tension	1.0	1.16
0.5*N* Potassium Hydroxide	Potassium	
Slack	1.0	1.01
Tension	1.0	1.01

[a] Normalized to the edge of the fibers.

of sodium found at the center of the fiber is slightly higher for sodium mercerized fiber than for mercerization with potassium. In this fiber ionomer, the distribution appears to be surprisingly uniform regardless of the method of swelling. The distribution of copper for the sodium hydroxide swollen PEAA shows considerable scatter (Table III).

Except for the tension/slack treatment, most of the ionomerized copper is located near the edge of the fiber. If one looks at the amount of sodium present for exchange, there is greater sodium level at the fiber center for the tension-related treatments and, thus, it may be the reason for the higher levels of copper at this same location (Table III).

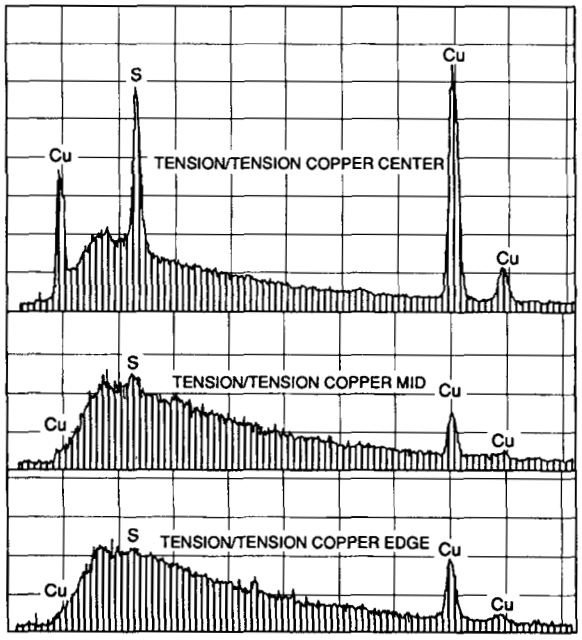

Figure 1 Typical EDAX patterns for copper-ionomerized PEAA fibers-treated tension/tension at three locations.

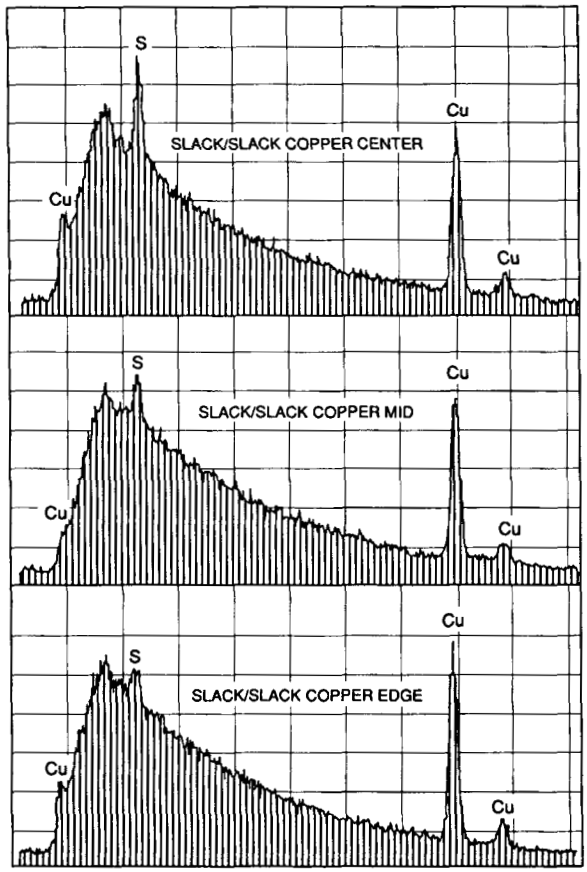

Figure 2 Typical EDAX patterns for copper-ionomerized PEAA fibers-treated slack/slack at three locations.

The EDAX also indicated that high levels of sulfur ions were present in the copper-ionomerized fiber and may account for the scatter observed in copper distribution at the edge, mid, and center of the fibers. The sulfur could be present only as sulfate ions since copper sulfate was used as the copper-exchange reagent. The method of treatment had a considerable effect on the amount of sulfur (sulfate) that was present. EDAX indicated that there were no sodium ions present in any of the (copper) ionomerized samples; hence, complete exchange had occurred in the 24 h reaction time and all the sodium was removed from the fiber probably as either the hydroxide or sulfate. A possible mechanism for the sulfate entrapment is shown in Figure 3. This mechanism could also account for the higher levels of copper present in the tension/slack treatment. Lithium cannot be detected by the EDAX method; hence, only swelling information could be obtained for this swelling method (Tables I and II).

CONCLUSIONS

Sodium hydroxide, 0.5N, has greater swelling power with PEAA than do similar concentrations of potassium or

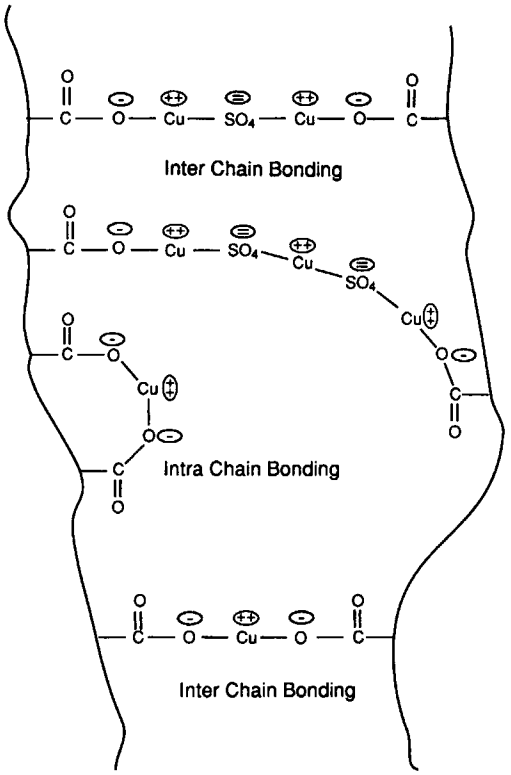

Figure 3 Possible Mechanisms for sulfur entrapment by copper-ionomerized PEAA fibers.

lithium hydroxides. This may be because optimum levels of alkali have not been determined for the potassium or lithium ionomers. As expected, the method of swelling as well as the method utilized for copper exchange (slack or with tension) gave different amounts of copper measured at the edge, mid, and center of the fiber. Sodium concentrations were higher at the center of the fiber than those of potassium. The distribution of potassium ions in the PEAA fiber appears to be more uniform than that of sodium. Because EDAX does not give reliable results with lithium, only swelling comparisons (ultimate diameter) could be obtained. Exchanging of sodium with copper sulfate gave considerable levels of sulfur (located principally at the fiber center) from the sulfate ion. The sulfate anion is most likely prevented from diffusion by ionic interactions between the copper and copper acrylate species, especially when the fiber is held under tension conditions where chain alignment may promote such interactions.

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