# Ionomer Studies of Polyethylene–Acrylic Acid Copolymer. I. Fiber Preparation and Properties

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## SYNOPSIS

Two EAA (Ethylene/acrylic acid) copolymers from Dow Chemical Company have been studied. Primacor resin (5980), having a mol wt of about 30,000 and an acrylic acid content of 19.2%, was converted into 10 and 20 denier per filament fibers to create a high surface area. Cold drawing and use of a fiber lubricant helped prevent sticking and blocking during spinning. The fiber was optimally swollen in a 0.5 N caustic at 55°C to produce an ion exchange fiber. Primacor resin (5980) in pellet form was reacted with alkali and was subsequently hammermilled into an ion exchange porous particulate. Physical and chemical properties, such as thermal properties, swelling, cation exchange activity and selectivity, tensile and elongation properties, among others, were determined on the fiber before and after conversion to specific metal (cationic) forms. The swollen fibers appeared to have more cation binding capacity than hammermilled pellets. The EAA polymers were colored by some metal cations. Some metal cations could be preferentially removed from solutions of mixed cations. Most fibers were weak, even after exchanging with multivalent ions, and did not have a precise melting point. Fiber tension and solution pH during the cationic exchange had an effect on the cation uptake, as well as on the physical properties obtained.
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## INTRODUCTION

The use of carboxylic acid groups, attached to polymer (fiber) substrates and used for ion exchange purposes, is well known. For example, polyethylene,[1] polypropylene,[2] and polyester fibers,[3] among others, have been electron beam irradiated and grafted with acrylic acid monomers to produce fibers having cationic exchange properties. Anionic exchange properties can be obtained using amino-containing monomers.[4] Such polymers have been known since 1966.[5] EAA polymers have good adhesive properties[6] and hydrophilicity.[7] The Dow Chemical Company, USA, began to produce nongrafted ethylene/acrylic acid (EAA) copolymer and the company had significantly increased its manufacturing capacity in 1982.[8] Some of the early work with the copolymer dealt with impact tensile behavior using partially ionized zinc and sodium salts.[9] EAA copolymers have been used in adhesives,[10] coatings,[11] molding compounds,[12] packaging films,[13,14] and have also been used to produce experimental ion exchange resins.[15] EAA copolymers are particularly versatile. They can be processed or applied either as thermoplastic melts or as a water-based solutions (suspension). Further, these polymers can be modified easily by reaction with various cations in solution or melt to provide marked changes in physical and chemical properties. The thermoplastic processing capability leads to a consideration of these polymers for use in fiber form, although fibers of low density polyethylene (LDPE), the major component of these EAA polymers, are generally inferior to fibers produced from other polymers (even high density polyethylene). Fibers of polyethylene, copolymerized with small to moderate amounts of acrylic acid, may provide some avenues for property improvement. Properties that might be changed (or added) by the use of acrylic acid as a comonomer include:

1. processibility (spinnability),
2. compatibility with other resins,

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3. adhesion,
4. ion exchange properties,
5. potential for derivatization reactions with the carboxyl groups,
6. hydrophilicity, and
7. dyeability.

Ionomer formation by reaction with various metal cations offers varied pathways to novel fiber systems.

Information on the physical and chemical properties of microporous particulates or fibers, which have been partially or fully saturated with metal ions, has not been published since its discovery by Vaughan and Guerra.[15] This work reports on the fiber extrusion and the physical and chemical properties of low mol wt EAA fibers and microporous particulates made from Dow's Primacor* 5980.

## EXPERIMENTAL

### Polymer

For this study, Primacor 5980 (Dow Chemical Company) was used. The polymer was EAA, containing 19.2% acrylic acid, having a melt flow index of 248, a mol wt of about 30,000, and a density of 0.958 $cm^3$; the acrylic acid residues are more or less randomly distributed along the polymer chain.[16]

### Fiber Extrusion

Fibers were extruded, both at Auburn University, and in the laboratories of Alex James and Associates in Greenville, South Carolina. The equipment at Auburn consisted of a $1\frac{1}{2}$-inch MPM melt extruder with a 24/1 L/D screw, coupled to a Zenith melt spinning pump, and a pack containing screen filters and a 34-hole spinnerette, having a nominal diameter of 0.017 inches. The molten threadline was solidified in a 6-foot, crossflow cooling zone and then was dropped 15 feet to godets and a Leesona 959 take-up. Extrusion temperature was 130°-135°C (final zone), with a take-up speed of 400 and 600 meters per min. Yarns were spun at (nominal) 400 and 800 denier. A water solution of 10% Carbowax 1500 was used as a spin finish. Subsequent drawing attempts were not successful, due to the tendency of the fibers to stick together (block) on the take-up package.

Fibers, subsequently produced in the laboratories of Alex James and Associates, were extruded on a $1\frac{1}{2}$-inch spin-draw machine at a temperature of 125°C (final zone). The polymer was pumped through a spin pack containing a 40-hole (round) spinnerette. The yarn was dropped through a crossflow cooling zone to a draw stand. A xylene-soluble nylon spin finish (made by Gouldston) was applied; the yarn was drawn (2.5 draw ratio) and then was taken up at 800 m/min.

### Physical Property Determinations

The linear density of yarn was measured by cutting 10 one-meter samples and weighing them on an analytical balance. The samples used for linear density measurements were subsequently tested on an Instron Universal Tester at 10 inches gauge length and an elongation rate of 100% per min.

### Swelling (Causticization)

A two-gram skein of EAA was placed in a 250 mL Erlenmeyer flask, fitted with a ground glass stopper. Two Hundred mL of 0.5 N sodium hydroxide (reagent grade) solution was added, and the sample was placed in a water bath maintained at the test temperature (±0.1°C). At intervals, the caustic solutions were removed and the fibers were exchanged 5 times with distilled water over 2 h, or until the water was neutral. The samples were air dried or reacted in the swollen state.

### Initial Swelling Rate Studies

For the rates of swelling studies, the EAA was spun into strands having diameters ranging from 0.0934 to 0.1230 inches. The time required for caustic penetration to reach a depth of 1000 $\mu$ was used to calculate the average swelling rate. The penetration depth was measured microscopically on cross sections of copper exchanged strands, by measuring the penetration depth of the blue color.[17]

### Ionomer Formation

One gram of the swollen fiber samples was placed into 500 mL of Copper Sulfate (5% reagent grade) and was allowed to exchange for 24 h, after which they were rinsed (5 times) in distilled water and air dried.

### Metal Ion Analysis

Analysis for copper was performed by emmission spectroscopy at the Dow Chemical Company Ana-

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lytical Laboratory at Freeport, Texas. Reproducibility of the analysis was found to be 0.02 to 0.08 milliequivalent/gram.

### Fiber Swelling

Yarn was swollen with lithium, sodium, or potassium hydroxide (0.5 N at 55°C) in either the slack state or under tension. In the slack state, the yarn skein was allowed to float freely in the reaction vessel or was attached through the eyelet made in a Nichrome or Chromel A wire. The eyelet had to be of a large enough diameter so as not to restrict the swelling or movement of the skein through the eyelet. Alternatively, a basket, fabricated from stainless steel or Chromel A hardware cloth[18] and fitted with a cover that could be wired to the top, could be employed for slack treatments. This technique allows yarns cut to specific lengths to be swollen (causticized). For yarns treated at constant length (under tension), a stainless steel dyeing skein holder (spiral-end stirrer) was employed. The holder had hooklike projections that were similar to the ones supplied with the Ahiba–Texomat automatic dyeing machine.[19] The device had a moveable collar, which allowed any level of tension from slack to constant length to be obtained during the reaction. The Ahiba–Texomat automatic dyeing machine further allowed the sample to be uniformly agitated during the treatment as well as to provide for precise temperature control. The EAA control was treated at 55°C for 2 h in distilled water.

### Cation Exchange in Fibers

Swollen skeins were placed in 5 g/L solutions of a soluble salt of the test cation, including the associated water of hydration (ACS grade or better). Solutions that exhibited a pH below 5 were buffered to pH 5 with sodium citrate. The salts employed in this study were: cobalt chloride, magnesium sulfate, calcium chloride, tin IV chloride, nickelous sulfate, aluminum sulfate, copper II nitrate, iron III chloride, and zinc chloride.

The swollen sodium neutralized EAA fibers were soaked in the solutions for at least 18 h, followed by rinsing (3×) in distilled water, and air drying. The fibers were allowed to react either by placing the skeins to soak loose in the reagent, or were they held at constant length (under tension) using the spiral-end stirrer described above.

### Fiber Annealing

The ionomer fibers were annealed (after cation exchange) at constant length (under tension) by placing them still-wrapped onto the reaction (spiral-end stirrer) assembly[19] in a forced air convection oven at 75°C for one h.

### Tensile Properties of Fibers

The tensile properties of the ionomer were measured on yarns of the 10 or 20 denier fiber, using a Instron Universal Tester at a 5-inch gauge length and 5 inches/min crosshead speed.

### Thermal Properties of Fibers

The thermal properties of ion-exchanged fibers were measured on a Perkin–Elmer Model DSC-2 Differential Scanning Calorimeter (DSC) under nitrogen at a 20°C/min scan rate over a temperature range of 50–300°C. Indium was used as a calibration and reference standard.

### Hammermilled EAA

Pellets of Primacor 5980 were swollen in caustic to yield an exchange capacity of 2.8 eq/Kg, followed by washing three to five times with deionized water. After draining, both the pellets and the hammermill were cooled to liquid nitrogen temperatures.[17] The pellets were hammermilled to 20–50 mesh. The final product had an imbibed water content of 70%, a bulk density of 32 lbs/ft$^2$, and a kinetic capacity ion exchange range of 45–70% of ultimate. The pH of interstitial water was between pH 8 and pH 9. This material was kindly supplied by Omni Tech International, Ltd. (Midland, Michigan).

### Scanning Electron Microscopy

Samples of air-dried swollen fiber or hammermilled products were dried in a vacuum oven at 40°C prior to SEM, since they were hygroscopic. The EAA materials were coated with a mixture of gold and palladium and were studied at magnifications of 100–200 times. An Amray 1000 SEM was employed using an accelerating voltage of 20 kv. Polaroid 55 PN film was used for the electron photomicrographs.[22]

### Ion Selectivity

Sodium-neutralized EAA fiber was buffered to pH = 5. The fiber was placed in contact with a solution

**Table I Physical Properties of EAA Fibers**

| Property | As-Spun | Spin-Draw |
|---|---|---|
| Linear density (g/9000 m) | 798 | 409 |
| Tensile strength (g) | 247 | 414 |
| Tenacity (g/denier) | 0.31 | 1.01 |
| Elongation at break (%) | 93 | 23 |

containing a known amount of cation calculated on a molar basis to load the polymer to approximately 50% of its exchange capacity. The fiber (1 g) was left in contact with the solution until equilibrium (about 24 h) was reached. The concentration of cations remaining in solution was determined by Ion Chromatography.[20] Thus, knowing the exchange capacity of the resin, the concentration of metal ions absorbed by the resin, and the amount left in solution, an equilibrium constant (*K*) for each metal was calculated. All reactions were assumed to form charge-balanced species with no complex ionic species formed. That is,

$$Cu^{2+} + 2\ R\text{-}COO^- \rightarrow Cu(R\text{-}COO)_2$$

and not

$$Cu^{2+} + 3\ R\text{-}COO^- \rightarrow Cu(R\text{-}COO)_3^-$$

The resulting pK values were arranged in order to produce the selectivity order.

# DISCUSSION

## Fiber Spinning Studies

Because of the low modulus, high elasticity, and tackiness of freshly spun EAA fibers, problems were encountered in the further processing of the yarn. Packages tended to be crushed as the yarn aged (or cooled) on the paper core. Backwinding of the yarn from the take-up packages was difficult because of numerous yarn breaks and filament separations. These difficulties were reduced, but not eliminated, by the addition of a Carbowax spin finish and by the minimization of the winding tension. The spin finish had two possible modes of action: reduction of the surface tackiness, and cooling of the yarn to ambient temperature before it was wound on the package. In spite of the difficulties, sufficient yarn was obtained for subsequent processing and study. Physical properties for the yarn appear in Table I.

Additional yarn was produced on a spin-draw machine at a 2.5 draw ratio. The physical properties also appear in Table I. As expected, the elongation-at-break of drawn yarn was much lower than the as-spun yarn, and the strength was higher. The drawn yarn behaved much less like a rubber band and the tackiness was much reduced. The drawn yarn could be backwound from the take-up packages with little difficulty.

## Tensile and Elongation Studies

The results of yarn tensile testing are shown in Tables II and III. The results show that, although dif-

**Table II Tensile Properties of Ionomer Fibers**

| Sample Identification | Denier (g/9000 m) | Tensile Strength (g) | Tenacity (g/den) | Elong. (%) | Average Modulus (g/den) | Initial Modulus (g/den) |
|---|---|---|---|---|---|---|
| EAA as-spun | 864 | 476 | 0.55 | 26 | 2.1 | |
| EAA control (TU)[a] | 700 | 290 | 0.41 | 87 | 0.47 | |
| Na EAA (TA) | 958 | 269 | 0.28 | 102 | 0.27 | 1.21 |
| Li EAA (TA) | 815 | 382 | 0.47 | 28 | 1.67 | 7.39 |
| K EAA (TA) | 1032 | 254 | 0.25 | 108 | 0.23 | |
| Cu EAA (TA) | 680 | 371 | 0.55 | 133 | 0.42 | |
| Zn EAA (TA) | 894 | 422 | 0.47 | 77 | 0.61 | 6.33 |
| Ca EAA (TA) | 830 | 470 | 0.57 | 32 | 1.77 | |
| Co EAA (TA) | 830 | 528 | 0.64 | 64 | 0.99 | |
| Mg EAA (TA) | 845 | 454 | 0.54 | 100 | 0.54 | 5.04 |
| Ag EAA (TA) | 809 | 445 | 0.55 | 97 | 0.57 | |
| Fe (3) EAA (TA) | 792 | 339 | 0.43 | 84 | 0.51 | |
| Al (3) EAA (TA) | 749 | 342 | 0.46 | 88 | 0.52 | |
| Sn (4) EAA (TA) | 756 | 305 | 0.40 | 84 | 0.48 | |
| Mg/Al (3/1) EAA (TA) | 735 | 439 | 0.60 | 114 | 0.52 | |

[a] Control was soaked in water at 55°C instead of caustic. (T) tension, (U) unannealed, and (A) annealed.

**Table III Effect of Annealing and Tension on the Properties of EAA Ionomers**

| Sample Identification | Denier (g/9000 m) | Tensile Strength (g) | Tenacity (g/den) | Elong. (%) | Average Modulus (g/den) |
|---|---|---|---|---|---|
| Na EAA (TA) | 958 | 269 | 0.28 | 102 | 0.27 |
| Na EAA (SA) | 967 | 284 | 0.29 | 91 | 0.32 |
| Na EAA (TU) | 958 | 261 | 0.27 | 102 | 0.26 |
| Na EAA (SU) | 967 | 274 | 0.28 | 85 | 0.33 |
| Na EAA (A) Unr. | 1103 | 276 | 0.25 | 144 | 0.17 |
| K EAA (TA) | 1032 | 254 | 0.25 | 108 | 0.23 |
| K EAA (SA) | 959 | 232 | 0.24 | 126 | 0.19 |
| K EAA (TU) | 1032 | 231 | 0.22 | 98 | 0.23 |
| Ca EAA (TA) | 830 | 470 | 0.57 | 32 | 1.77 |
| Ca EAA (SA) | 899 | 551 | 0.61 | 24 | 2.57 |
| Ca EAA (TU) | 722 | 404 | 0.56 | 15 | 3.73 |
| Mg EAA (TA) | 845 | 454 | 0.54 | 100 | 0.54 |
| Mg EAA (SA) | 909 | 580 | 0.63 | 92 | 0.69 |
| Mg EAA (SU) | 909 | 527 | 0.58 | 19 | 3.0 |
| Fe (3) EAA (TA) | 792 | 339 | 0.43 | 84 | 0.51 |
| Fe (3) EAA (SA) | 858 | 313 | 0.36 | 82 | 0.45 |
| Fe (3) EAA (TU) | 792 | 360 | 0.45 | 25 | 1.83 |
| Fe (3) EAA (SU) | 858 | 351 | 0.42 | 21 | 2.0 |
| Mg/Al 3/1 EAA (TA) | 735 | 439 | 0.60 | 114 | 0.52 |
| Mg/Al 3/1 EAA (SA) | 935 | 422 | 0.45 | 14 | 3.13 |
| Mg/Al 3/1 EAA (TU) | 735 | 372 | 0.51 | 19 | 2.62 |
| Ni EAA (SU) Unr. | 1146 | 454 | 0.39 | 13 | 3.1 |

NOTES: (T) Tension, (A) annealed, (S) slack, (U) unannealed, and (Unr) unrestrained.

ferences exist between the various EAA fibers (depending on the particular ion used), all of the fibers were weak (< 0.7 g/den). This is reasonable, considering the low mol wt of the starting polymer (reported to be approximately 30,000). Considering all factors (the small number of tensile samples per treatment, the imprecise nature of the tension control during treatment, and the low fiber strength), only generalizations may be drawn.

1. Certain ions caused a marked increase in fiber stiffness (modulus). This change may have resulted from increased strength or decreased elongation or a combination of the two. Cations, which produced the most marked increase in stiffness, were Li, Ca, Co, Fe(3), Al(3), mixed Mg/Al, and Ni. The calcium ionomer was so brittle that tying a hard knot in the yarn produced failure. Neither the stiffness of the monovalent Li, nor the flexibility of the polyvalent Zn, Mg, and Sn(4), were easily explained.
2. The few samples tested unannealed showed small changes in tensile strength from the annealed fibers, but sometimes a marked reduction in breaking elongation resulted. This naturally results in an increased modulus.
3. Yarn tension during caustic treatment was also variable in its effect. The slack Mg/Al had a relatively high modulus as compared to the sample treated at constant length. Again this result is primarily due to a reduction in breaking elongation. Other ionomers showed small effects of tension. Since the "slack" fibers were not totally unrestrained in their shrinkage and since the control of tension was not precise, further experiments will be required to reveal the effect of tension.
4. Initial modulus (Young's modulus) was calculated for several samples and tended to track with average modulus, although at a higher level.

## Swelling Studies

A caustic concentration of 0.5 N was found to produce the maximum swelling rate (Fig. 1). The decrease in the rate of swelling at high alkali concentrations may be due to osmotic forces and/or ionic strength of the swelling solution. For example, the

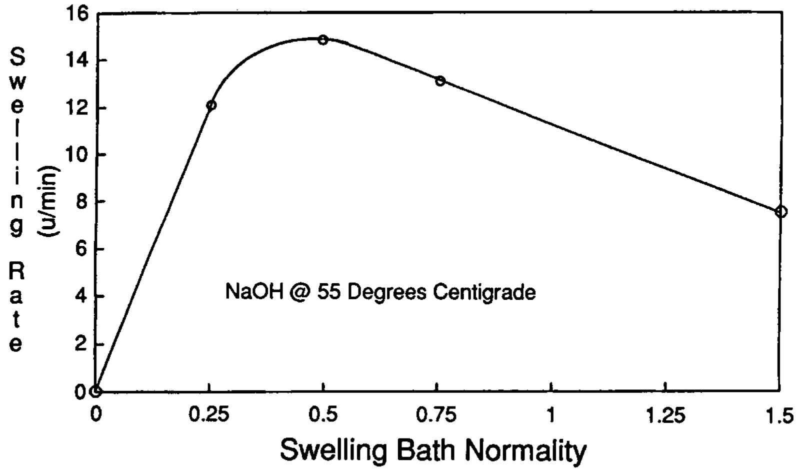

**Figure 1** Effect of NaOH concentration on swelling rate of Primacor 5980.

swollen fibers were elastomeric and thus may have been sensitive to osmotic forces.[17]

### Swelling Temperature

Bath temperatures, used to attempt to swell the fibers, ranged from 26°C to 65°C (Fig. 2). At temperatures above 65°C, that is, about 70°C and higher, the EAA polymer began to undergo dissolution into a dispersion. Even at somewhat lower temperatures, some low mol wt solubles were leached from the more swollen fibers at the higher temperature. Characterization of the leachates[17] showed the dissolved material to be a low mol wt EAA with an acrylic acid content (determined by titration) of 30.5% (vs. 19.2% originally). Consistent with this analysis was the fact that, at temperatures higher than 60°C, there was greater swelling than at 55°C (Fig. 3), but the ion absorption capacity of the swollen fiber was somewhat reduced. Overall, the best swelling temperature appeared to be at 55°C in order to avoid the leaching or dispersion problems. At temperatures lower than 55°C, less swelling was obtained and the ion exchange capacity was considerably reduced (Fig. 3).

### Rate of Swelling

The rate of swelling of EAA monofilament is shown in Figure 4. The average swelling rate (or penetra-

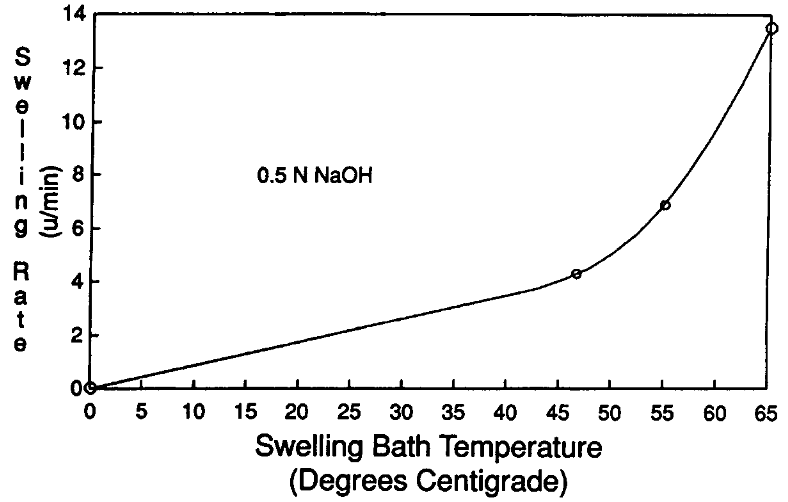

**Figure 2** Effect of bath temperature on swelling rate of Primacor 5980 fibers.

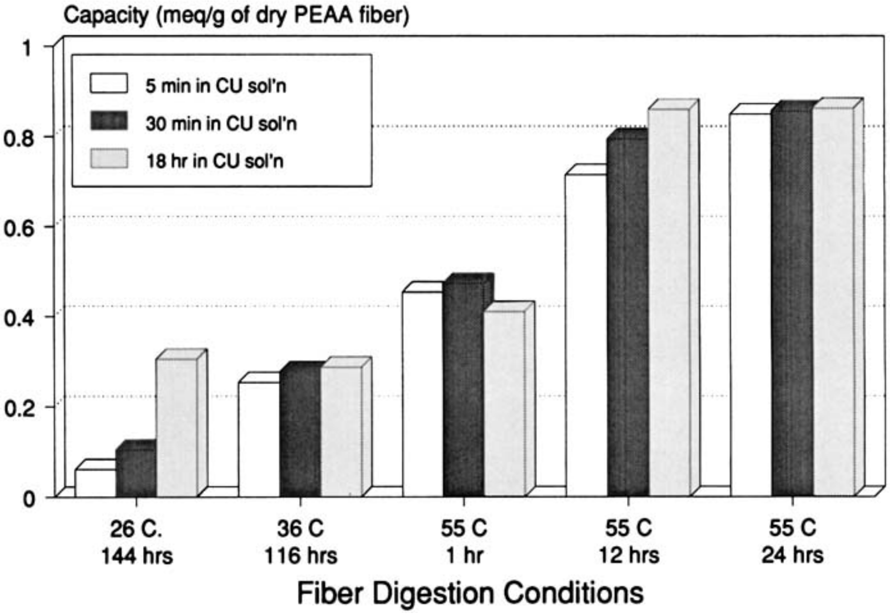

**Figure 3** Fiber digestion conditions.

tion rate for the caustic) was found to be 13.5 $\mu$/min. Lower mol wt EAA material (e.g., 16,800) was found to have a higher swelling rate (about 33.3 $\mu$/min).[17] In practical terms, the swelling rate of a 10 to 20 denier fiber (diameter of 70–100 $\mu$) should be rapid, and short exposure times (from Fig. 4) should be sufficient for the causticization reaction to be complete. This appeared to be the case. The fibers were highly gelatinous when swollen, but could be redried to an easily handled fiber.

### Effect of Denier on the Exchange Capacity

There appeared to be a slight effect of denier on the exchange capacity of the swollen fibers (Fig. 5). The smaller (10 denier) fiber had greater surface area than the larger (20 denier) fiber. Longer digestion times may have allowed for greater opportunity for smaller mol wt materials to leach from the swollen material once maximum swelling had been achieved. Only 1 h was required for maximum swelling for the

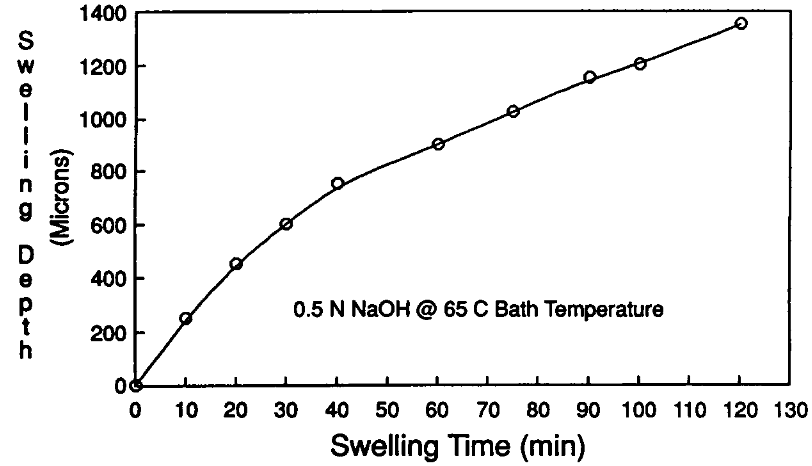

**Figure 4** Caustic swelling of Primacor–Adhesive Polymer 5980.

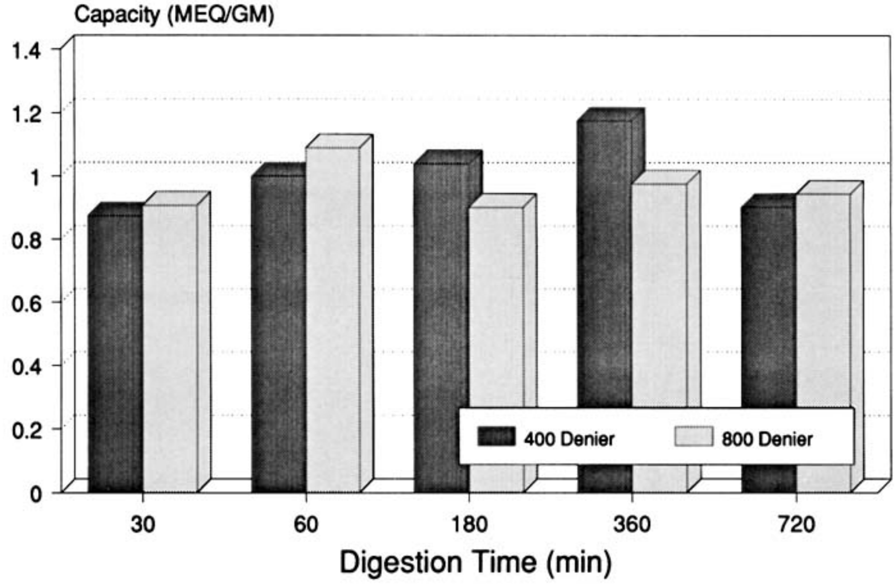

**Figure 5** Copper cation capacity vs. digestion time at 55°C.

larger fiber (800 denier) yarn, while 3 h were required for the smaller fiber (400 denier yarn). This may have been due to the fact that the draw ratio may have differed and thus the relative orientation of the two fibers. In any case, it may be wise to run the caustization reaction for at least 3 h since two fibers may be different. Also, by comparison of Figures 3 and 5, it was apparent that swollen but never dried fiber had a higher exchange capacity than swollen and dried fiber. Apparently, once the fiber underwent collapse during drying, some exchange sites were lost due to inaccessibility; [also for dry fiber to achieve a reasonable exchange rate within 5 min, long reaction times (24 h) in the caustic solution were required] (Fig. 3). The copper ionomer of the EAA was bright blue-green. The sodium and potassium ionomers were essentially white. The neutralized EAA fibers tended to stick together upon drying. Fibers, ionomerized with copper while in the swollen state, had less sticking upon drying.

## pH of Cation Exchange

The cationic exchange with sodium neutralized hammermilled EAA was pH sensitive. Tests, in which the exchange solution, containing 400 ppm $Cu^{++}$, and in which the pH was adjusted with $H_2SO_4$, showed that at low pH, the cation exchange was suppressed (Table IV).[17] At pH below 2, polymer ionization was depressed and the capacity was reduced.

In the fiber study, therefore, the pH of the cationic exchange solutions were maintained at pH 5, using sodium citrate as buffer with the exception of the Tin IV solution. This salt could not be buffered, due to the precipitation on the addition of the citrate. This salt was used as prepared and had a pH of about 2. A minimum of 18 h was required to insure complete take-up of the cation.

## Ionomerized Yarns

In most cases, the skein (containing the 34 filaments/strand) after removal from the ion exchange bath could not be easily separated again into yarns for testing. Some of the skeins tended to stick together when dried. In those that did not stick, the individual filaments migrated between yarns and it was impossible to distinguish one yarn from another. A reasonable level of twist would probably prevent yarn migration, but not the sticking problem. The solution attempted here was to wind yarns onto a pronged dye stirrer and to try to keep the strands separate from one another. This approach proved reasonably successful. It was recognized early in the testing that the level of tension in the yarn had a marked effect on the penetration of both caustic and any other of the cations that were exchanged for the alkali metal. The most desirable treatment condition for maximum reaction was slack, but this caused severe problems in the separation of the yarns after treatment. Two conditions of tension were tested:

**Table IV Effect of pH on the Sodium EAA Capacity for Copper**[a]

| pH (Feed) | eq/Kg (Dry Polymer) | Wt % $Cu^{++}$ (Dry) |
|---|---|---|
| 1 | 0.21 | 0.62 |
| 2 | 0.63 | 2.06 |
| 3 | 0.81 | 2.56 |
| 4 | 0.94 | 3.00 |
| 5 | 1.17 | 3.71 |
| 6 | 1.32 | 4.20 |
| 7 | 1.39 | 4.42 |

[a] Polymer: Hammermilled EAA made from Primacor 5980; feed: 400 ppm $Cu^{++}$; bed: 20 inches; flow rate: 12 Bed Volumes/h; leakage: less than 0.1 ppm.

one at constant length, the other with 10 to 20% shrinkage allowed. Neither of these conditions was completely slack since the yarn shrunk about 30% (when unrestrained) in the hot caustic. Further, the yarns underwent additional shrinkage during ionomerization if allowed to react in the slack state.

## Coloration of EAA by Ionomerization

Some cations, when reacted with sodium EAA, produced light to deep coloration (Table V). In general, most ions yielded clear (white) fiber after cation exchange. If the salt used in the ionomerization was colored, then, generally, the exchanged EAA form will also be colored, but not necessarily the same color. For example, cobalt chloride produces a red solution, but the EAA ionomer color form is bright purple. Iron II yields a yellow solution, but a dark red-brown ionomer. Copper sulfate is a blue-green salt but the ionomer is not exactly the same shade. The use of the sodium (or other alkali metal) EAA might provide a spot test for specific ions, due to the coloration obtained.

## Ion Selectivity

Selectivity differences between carious cations (inferred from equilibrium constants) were found to exist as follows:

$$\mathrm{Hg} \gg \mathrm{Fe}^{+++} > \mathrm{Pb} > \mathrm{Cr}^{+++} \gg \mathrm{Cu} > \mathrm{Cd} \gg \mathrm{Al}$$
$$> \mathrm{Zn} = \mathrm{Ag} = \mathrm{Mn} = \mathrm{Ni} = \mathrm{Co} > \mathrm{Ca} > \mathrm{Sr} > \mathrm{Ba}$$
$$> \mathrm{Mg} \gg \mathrm{K} = \mathrm{Na} = \mathrm{Cs} = \mathrm{Rb} > \mathrm{Li}$$

These differences in exchange capacity may allow one ion to be selectively removed from others. There was also some shifting of position within the major groups at different pH values[21] because the chemistry of some ions may change with pH. In general, the most optimum pH values for cation exchange with neutralized EAA fiber ranges from 5–9.

Table VI illustrates the use of sodium EAA to polish a commercial waste stream containing 0.5% Sodium Sulfate.[21] In other tests, 100 ppm of $Pb^{++}$ could be removed from concentrated magnesium brine.[17] This study indicates that maintaining a pure ionomer form may not be possible. For example, the magnesium ionomer might easily be replaced by ions higher on the selectivity scale, should the sample ever come into contact with water containing other ions. Further, the colorless magnesium ionomer form could become discolored should iron, cobalt, etc., be the replacement cation. Further still, the selectivity may vary, depending upon which other ions are in the solution. For example, even though $Hg^{++}$ selectivity is high, the EAA may be swamped if other multivalent ions (e.g., $Ca^{++}$, $Mg^{++}$) are present in concentrations higher than the $Hg^{++}$.

## Thermal Properties

The low crystallinity of the polymer (because of both the copolymerization and swelling techniques) pro-

**Table V Colors Developed During Ionomerization of Neutralized EAA**

| Salt Solution Employed | Salt Color | Fiber Color Developed |
|---|---|---|
| Cobalt chloride | Red | Bright purple |
| Magnesium sulfate | Colorless | Colorless |
| Calcium chloride | Colorless | Colorless |
| Tin IV chloride | Colorless | Colorless |
| Nickelous sulfate | Blue-green | Pale lime-green |
| Aluminum sulfate | Colorless | Colorless |
| Copper II nitrate | Blue | Blue-green |
| Iron II sulfate | Blue-green | Dark brown |
| Iron III nitrate | Pale violet | Pale red-brown |
| Chromium trioxide | Dark yellow | Pale yellow |
| Barium nitrate | Colorless | Colorless |
| Silver nitrate | Colorless | Colorless |
| Mercuric nitrate | Colorless | Colorless |
| Li, NA, K, Ce, Rb hydroxide | Colorless | Colorless |
| Stannous chloride | Colorless | Colorless |
| Zicronyl nitrate | Colorless | Colorless |
| Lanthanum nitrate | Colorless | Colorless |

**Table VI Polishing of a Commercial Waste Stream Containing 0.5% Sodium Sulfate to Meet EPA Permit Requirements[a,21]**

| Cation Removed | In Feed (ppm) | In Effluent (ppm) | % Metal Removal |
|---|---|---|---|
| As | 0.15 | ⟨0.05⟩ | 66 |
| Cd | 0.14 | ⟨0.05⟩ | 64 |
| Pb | 0.90 | ⟨0.05⟩ | 94 |
| Sb | 1.50 | ⟨0.10⟩ | 93 |
| Zn | 0.11 | ⟨0.05⟩ | 54 |

[a] Analysis by ICP; flow rate: 9–15 Bed Volumes/h; pH: 5–6; contact time: 4–6.5 min; bed: 20 in. deep.

duced an uneventful DSC trace. There was typically a broad endotherm between about 50° and 110°C. The highest point of this broad endotherm was typically within the range of 80° to 100°C. Exothermic decomposition began at about 200°C for the EAA fiber, and higher (if at all) for the ionomers. The potassium EAA had an unexplained endotherm in the range of 130°C–160°C.

### Hammermilled Particulate vs. Fiber

The copper ion exchange capacity of swollen hammermilled PEAA pellets vs. swollen PEAA fibers is summarized in Table VII. The fibers absorbed about 30% more copper ions (and probably other ions as well) than the hammermilled particulates. Since the polymer in both fiber and particulate is the some, the difference in ion absorption was most likely due to the higher swelling and surface area of the fibers as compared to the particulate.

### Scanning Electron Microscopy (SEM)

Fibers and hammermilled EAA particulates were studied by SEM methods. Typical results are shown in Figures 6 and 7. The hammermilled sodium particulates showed a layering, resulting from impact with the blades of the hammermill, which tended to improve the absorption of ions from solution by increasing the total surface area of the particulates. The potassium ionomerized fibers, when swollen, neutralized, and air dried, appeared to have a definite skin-core cross section. The presence of visible ridges on the lateral fiber surfaces was also consistent with a skin at the fiber surface.

## CONCLUSIONS

Optimum swelling for PEAA fiber occurred in 0.5 N caustic at 55°C and about 1 h exposure time. These conditions yielded the highest cation exchange for copper. At low temperatures (26–50°C), little swelling occurred, while at the higher temperatures (60°C and above), some low mol wt fractions were lost. The fibers were highly gelatinous when swollen and the multistrand yarns were difficult to separate into their individual fibers. The dried fibers had a tendency to stick together. Conversion to the copper ionomer from the swollen state eliminated the fiber–fiber stickness, but resulted in a blue-green fiber.

As-spun fibers had high propensity for blocking. Blocking can be considerably reduced by drawing at least 2.5 times and by using a fiber lubricant. Drawing also increased tensile strength (and tenacity) and decreases elongation at break.

EAA fibers, or hammermilled particulates, in the alkali metal form had a high surface area-to-volume ratio and produced rapid exchange rates with other metal ions. EAA fibers, swollen in potassium hydroxide, had a definite skin-core cross section. The EAA fibers had higher selectivities for mercury and iron$^{+3}$ than for barium and magnesium. All metal cations will be ultimately exchanged for the alkali metal. Various ions could cause the EAA fibers to become highly colored and may have offered the possibility for colorimetric tests for these ions in solutions. The exchange rates were highly pH sensitive, with the best exchange occurring at a pH of between 5–9. Because the swollen polymer was amorphous in nature and had low mol wt, the fibers were weak ($<$ 0.7 g/den) and they did not have a

**Table VII Comparisons Between Copper Capacities of Hammermilled Vs. 22 Denier Sodium–EAA Yarn[a]**

| Sample | Measurements (meg/gm) | Average |
|---|---|---|
| Hammermilled | 1.80[17]<br>1.76 | 1.78 |
| | 1.79[21]<br>1.85 | 1.82 |
| Melt spun fiber | 2.37<br>2.39 | 2.38 |

[a] Each product was exposed to a 5% solution of $Cu^{++}$ allowing 20 min equilibration time.

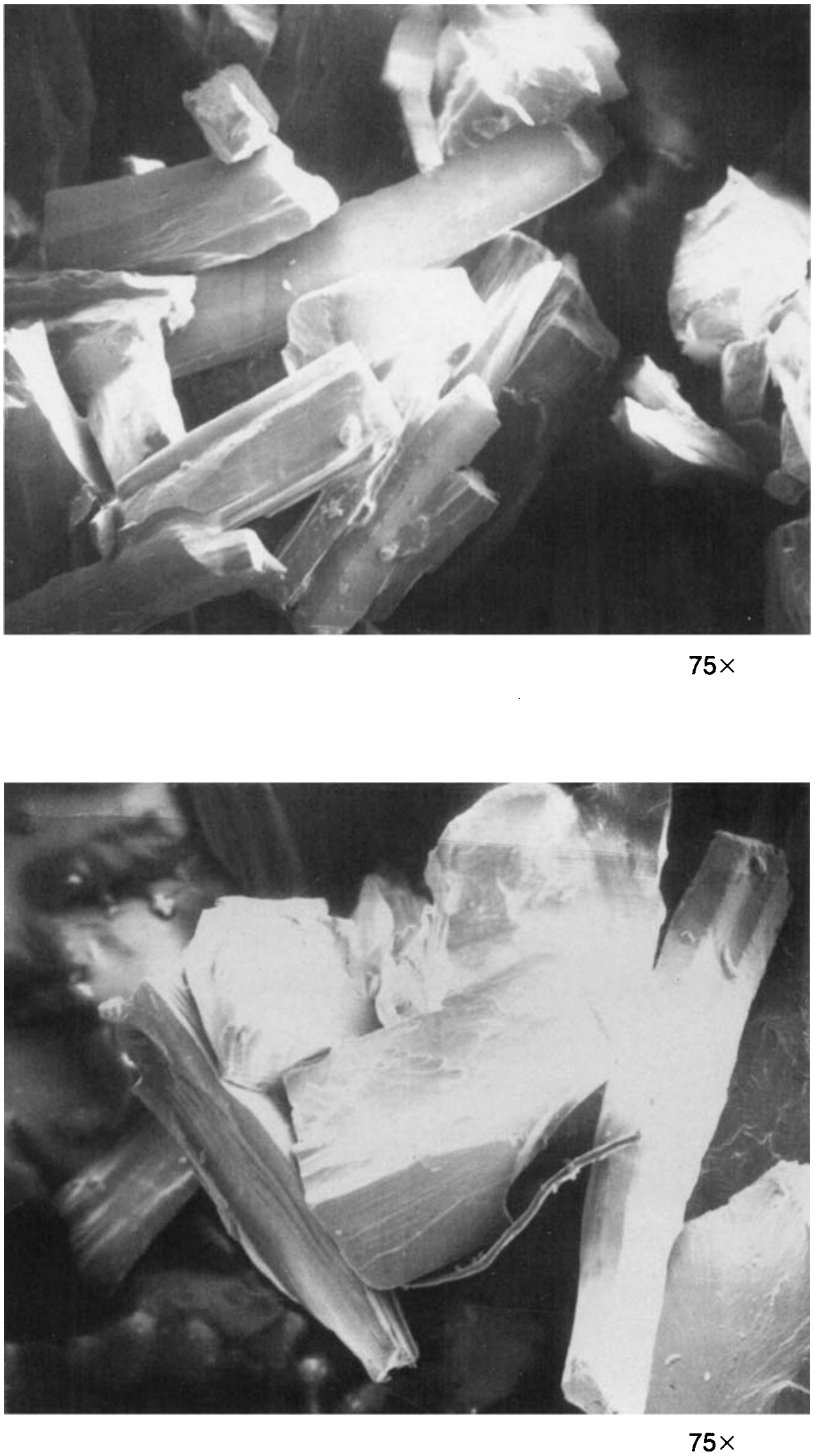

**Figure 6** Hammermilled PEAA pellets (sodium swollen 20–50 mesh).

definitive melting point; hence their primary advantage was that they had higher exchange capacities than the hammermilled particulates. Whether the fiber was swollen in the slack (relaxed state) or under tension had an effect on the ion exchange rate. Also, the fibers tended to undergo further shrinkage

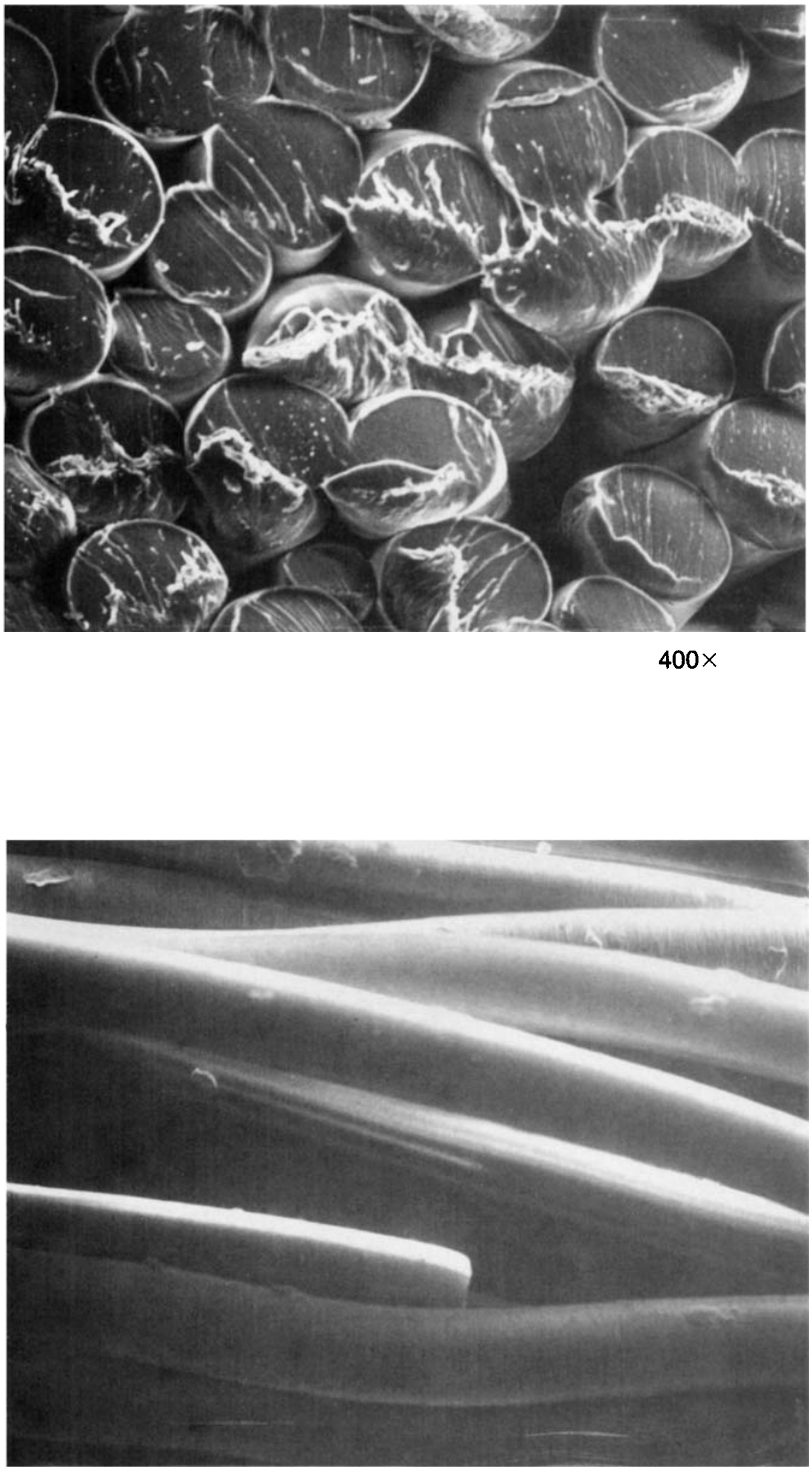

**Figure 7** Potassium swollen and air dried 22 Denier PEAA fibers.

during cation exchange and the amount of metal uptake could be reduced if the yarns were exchanged under tension.

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