Preparation and Properties of Alginate Superabsorbent Filament Fibers Crosslinked with Glutaraldehyde

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ABSTRACT: Superabsorbent filament fibers based on sodium alginate were prepared using glutaraldehyde as a crosslinking agent. Alginate was extruded into an aqueous hydrochloric acid coagulation bath to form continuous alginic acid gel fibers via a wet-spinning method. The alginic acid gel fibers were dehydrated by exchanging water with dioxane, crosslinked, then neutralized for better absorbency. Crosslinked alginate filaments exhibited a high saline solution and synthetic urine absorbencies, maintaining the integrity of the fiber structure. Maximum synthetic urine absorbency was obtained with the fiber crosslinked at a lower glutaraldehyde concentration compared with that required for maximum saline solution absorbency. This appears to be due to the crosslinking effect of calcium ions in the synthetic urine solution being absorbed. Strain and tenacity of the crosslinked alginate fibers decreased with an increasing amount of glutaraldehyde used in the crosslinking reaction. The decrease in tenacity was not significant while the strain showed an extensive decrease. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1797–1804, 2000

Key words: sodium alginate; wet spinning; alginic acid fiber; crosslinking; superabsorbent; absorbency

INTRODUCTION

Superabsorbent polymers (SAPs) are water-insoluble hydrophilic polymers, capable of absorbing large amounts of water, saline solution, or physiological fluids, that is, as high as 10–1000 times their own weight. Since the development of the first SAP, starch-*g*-polyacrylonitrile, in the 1970s,[1] superabsorbents have been used extensively in various product applications such as disposable diapers, sanitary napkins, additives for soil in agriculture and horticulture, water-blocking tapes, and medicine for drug-delivery systems, where water absorbency or water retention is important.[2–4] The most remarkable success has been in hygiene applications such as disposable diapers and sanitary napkins; over 80% of SAPs are currently consumed in these applications.

When SAPs are used in hygiene applications, they are added to pads in basically two ways: layered or blended. SAP powder can be sprayed on a fluff pulp matrix, which is then folded so that the polymer is located between the pulp layers in the absorbent structure. An absorbent structure can also be made by blending SAP powder and fluff pulp to form a homogeneous mixture.

In either method, containment of the powdered polymer within the loose, porous structure of the diaper is required. If the powdered material is not immobilized, it may bunch up or agglomerate, resulting in an uneven absorptive capacity and discomfort or may become air-borne, which can

then swell within the human air passage, causing health hazards. These drawbacks can be overcome by producing SAPs in the form of fiber. Another advantage of producing SAP fibers is that the amount of fluff pulp can be reduced to make the absorbent structure much thinner and lighter. Some patents on the preparation of SAP sheets or SAP fibers have been reported.[5–7] However, most patents describe immobilization of SAPs on filament or staple fibers, in which case the detachment of SAP powder may still be a problem.

SAPs can be grouped into two main classes based on their chemical structure: crosslinked synthetic polymers, such as crosslinked polyacrylate, polyacrylamide, or maleic anhydride copolymers, and hydrolyzed polyacrylonitrile graft copolymers of cellulose or starch. Among them, the commercially important superabsorbent polymers are sodium salts of crosslinked poly(acrylic acid) and hydrolyzed starch-g-polyacrylonitrile graft copolymers. These materials are generally considered to be resistant to attack by microorganisms. Since the major applications of SAPs are in disposable goods, they result in environmental pollution. Thus, research on biodegradable SAP material as a substitute for synthetic polymers presently used has recently been reported.[8]

In this work, we used alginate as the starting material to prepare biodegradable SAP fibers. Alginate is a collective term for alginic acid, its salts, and its derivatives. Sodium alginate is soluble in water, has carboxylate groups, and is biodegradable.[9] Alginic acid is a high molecular weight linear copolysaccharide composed of β-D-mannuronic acid and α-L-guluronic acid residues, in various proportions depending principally upon the seaweed species.[10,11]

Alginates are used in various applications such as thickening agents, chelating agents, emulsifiers, stabilizers, encapsulation, swelling, or suspending agents or used to form gels, films, and membranes.[12–15] Among alginate's characteristics, its gelation behavior is unique. It forms ionic gels in the presence of calcium or other multivalent metal cations and acid gels at pH below the pK_a value of the uronic acid residues.[16] Thus, alginate is processed into various forms such as beads or fibers by utilizing its gelation property.

Since alginate is biodegradable and its sodium salt is soluble in water, it was expected that it can be used as a substitute for acrylic acid polymers, without environmental problems. Alginate hydrogels are used commercially in the form of ionic gels crosslinked with multivalent metal cations, mostly Ca ions. However, calcium alginate shows low absorbencies due to its high crosslink density. It is expected that glutaraldehyde would be better than Ca^{2+} as a crosslinking agent in the preparation of a superabsorbent due to the following reasons: First, the control of the degree of crosslinking is much easier with glutaraldehyde compared with Ca^{2+}, where the reaction rate is very high. Second, higher crosslink length, which is favorable for absorbent behavior, can be obtained with glutaraldehyde compared with Ca^{2+}. There are some reports concerning the absorbency of crosslinked alginate. Yuk and coworkers prepared an absorbent fiber from a calcium alginate and poly(acrylic acid) mixture.[9] Moe and coworkers crosslinked alginate in the gel state by exchanging the water in the gel with ethanol or another solvent in which epichlorohydrin is soluble, but it was in the form of a bead.[17]

In this work, we prepared sodium alginate gel fibers by extruding an aqueous alginate solution into an acid coagulation bath where gelation was effected by the exchange of the sodium cation with proton. The gel fiber was then crosslinked with glutaraldehyde to reduce the solubility of sodium alginate such that it may function as a SAP. The absorbency behavior of these superabsorbent fibers in various salt solutions and their tensile properties were investigated.

EXPERIMENTAL

Materials

Sodium alginate (chemical grade) was obtained from KANTO Chemical Co. (Tokyo, Japan). Glutaraldehyde (25% by weight in water) was obtained from Sigma–Aldrich Ltd. (Milwaukee, WI). Reagent-grade hydrochloric acid, sodium hydroxide, sodium chloride, calcium chloride, urea, magnesium sulfate, dioxane, and methanol were used without further purification.

Preparation of Alginic Acid Gel Fiber

Alginic acid fibers were produced by wet spinning using an apparatus described in Figure 1. Spinning dope was prepared by dissolving 3% by weight of alginate in water and aging overnight at room temperature to remove all the air bubbles. The dope was then placed in a stainless-steel vessel and 1 kg/cm^2 pressure was applied with
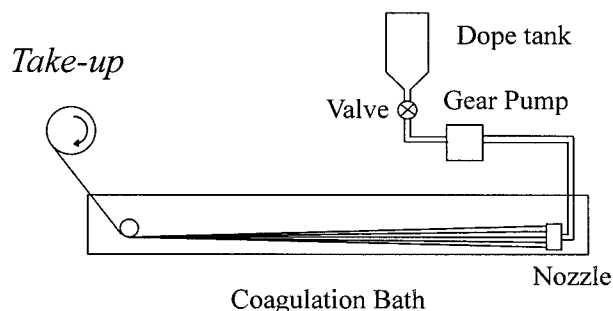
Figure 1 Schematic diagram of wet-spinning process.

nitrogen gas. The dope passed through a 100-mesh stainless-steel filter to a constant volume-metering pump and then to a spinneret with twelve 200-μm diameter holes. With the extrusion rate fixed at 0.53 cc/min, the dope was coagulated in a 1% HCl (35%) coagulation bath and the gel fibers were wound at a take-up speed of 2.0 m/min.

Crosslinking of Alginic Acid Gel Fibers with Glutaraldehyde

The alginic acid gel fiber was placed in dioxane solutions containing various concentrations of glutaraldehyde and 0.1% HCl (35%). The crosslinking reaction was allowed to proceed at 50°C for 4 h, unless otherwise specified. The crosslinked alginic acid fibers were neutralized in a methanol/0.4N sodium hydroxide mixture (80/20, v/v) at room temperature for 20 min. Crosslinked and neutralized alginate fibers were washed with 80% aqueous methanol, dehydrated in methanol, and then dried in a vacuum at 50°C for 1 day. Control samples were prepared following the same procedure excluding glutaraldehyde.

Absorbency

A fixed amount (0.03 ± 0.001 g) of the dried product was immersed in 50 mL of a saline solution (0.9% sodium chloride aqueous solution) and allowed to swell for 30 min. The unabsorbed saline solution was drained through a 300-mesh wire gauze and water on the surface of the swollen SAP was removed using filter paper. The swollen SAPs were weighed, then precipitated in acetone and dried at 50°C under a vacuum. The absorbency was calculated with the following equation:

$$\text{Absorbency} = \frac{\text{wt swelled gel} - \text{wt dried sample}}{\text{wt dried sample}}$$

The absorbency of the fibers in synthetic urine was also determined. The synthetic urine was prepared from 970.0 mL deionized water, 19.4 g urea, 8.0 g sodium chloride, 0.6 g anhydrous calcium chloride, and 2.05 g magnesium sulfate heptahydrate. The percentage of solubles (weight loss) was calculated with the following equation:

$$\text{Weight loss (\%)} = \frac{m - m'}{m} \times 100$$

where m is the weight of the dried fibers before immersion, and m', the weight of the dried fibers after immersion.

Kinetics of Swelling

A technique based on the demand wettability method was adopted (Fig. 2).[18] A graduated burette with an air inlet at the bottom was connected by a flexible tube to a cell on which a 300-mesh wire gauze was attached. After filling with the saline solution, the burette was closed at the top and air was introduced while the fibers absorbed the saline solution to eliminate hydrostatic pressure. About 40 mg of the fibers were placed on the mesh and the amount of the saline solution adsorbed by the sample was measured.

Moisture Regain

The weight of a sample of fibers was measured after conditioning at 20°C and 65% relative humidity for 24 h and then measured again after drying to calculate the moisture regain:
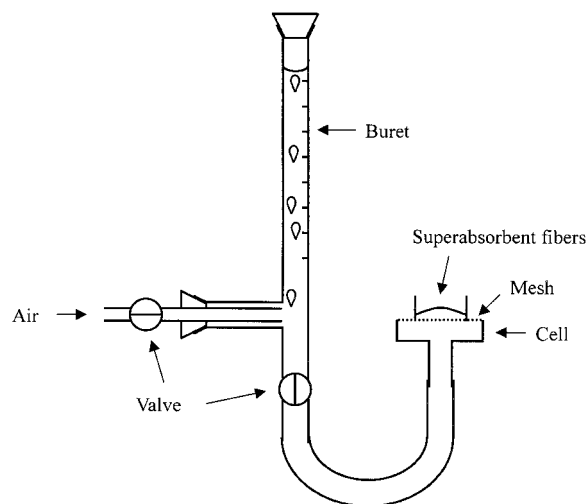
Figure 2 Demand wettability test apparatus.

$$\text{Moisture regain } (\%) = \frac{\text{weight of water}}{\text{dry weight}} \times 100$$

Morphology

Morphological analysis of the fibers was performed by scanning electron microscopy (SEM, JSM-840A, JEOL Ltd.).

Tensile Properties

Tensile properties of the fibers were determined on an Instron tensiometer (Series IX Automated Materials Testing System 1.00, Instron Corp.) according to ASTM method D2101-82. The gauge length was 20 mm and the crosshead speed was 50 mm/min. All samples were preconditioned at 20°C and 65% relative humidity for 24 h prior to testing.

RESULTS AND DISCUSSION

Absorption Properties of Crosslinked Alginate Fibers

Superabsorbent polymers consist of polyelectrolytes or other highly hydrophilic polymeric matrices, usually bearing crosslinking sites along the macromolecular chains to prevent dissolution. The presence of crosslinking allows swelling of the three-dimensional network and gel formation without polymer dissolution. Sodium alginate is soluble in water, but has carboxyl and hydroxyl groups that can be crosslinked to produce a water-insoluble hydrophilic polymer. Crosslinked alginate is known to absorb various aqueous solutions.[17,19–21]

In this work, crosslinks were introduced to alginate by reacting the hydroxyl groups with the aldehyde group of glutaraldehyde which is commonly used in the crosslinking of polysaccharides.[22–24] Yeom and Lee crosslinked dry alginate film with glutaraldehyde in acetone to ascertain the pervaporation separation property.[23,24] In our preliminary experiments on the selection of the reaction medium, reaction in dioxane resulted in better crosslinking efficiency than in methanol, acetone, or MEK. Alcohols and ketones are known to react with aldehyde and hydroxyl groups, respectively. Thus, they appear to interfere with the reaction between the hydroxyl groups of alginate and glutaraldehyde. Higher crosslinking efficiency in the case of dioxane is due to the absence of these interfering reactions.
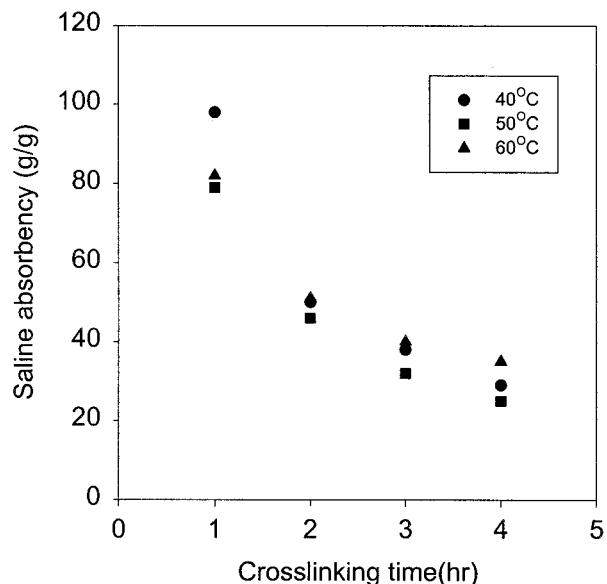
Figure 3 Saline absorbency as a function of crosslinking time and temperature. Crosslinking condition: glutaraldehyde 3%, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4*N* NaOH solution/MeOH 20/80 (v/v).

Absorbency was measured to indirectly estimate the degree of crosslinking of alginate fibers, as quantitative measurement of crosslinks in alginate fibers was not possible. It is well known that a water-soluble polymer becomes insoluble as crosslinks are introduced and that the absorbency decreases as the degree of crosslinking of the insoluble polymer increases. Plots of the saline absorbency as a function of crosslinking time at different crosslinking temperatures are given in Figure 3. It shows that the absorbency decreases with increasing crosslinking time, suggesting that the number of crosslinks introduced to alginate fibers increases with increasing crosslinking time. After 3 h, the extent of absorbency reduction decreased.

Superabsorbent polymers swell extensively in an aqueous solution, as polymer coils extend and swell in consequence of the electrostatic repulsion of negative or positive charges. Absorbency depends mainly on the osmotic pressure, ionic repulsion, and elasticity of the polymer network.[25] The presence of ionic groups and its density are very important factors in a superabsorbent polymer. Prior to neutralization, alginic acid fibers have carboxylic acid groups which dissociate only partially at neutral pH. Carboxylic acid groups need to be converted to carboxylate groups to
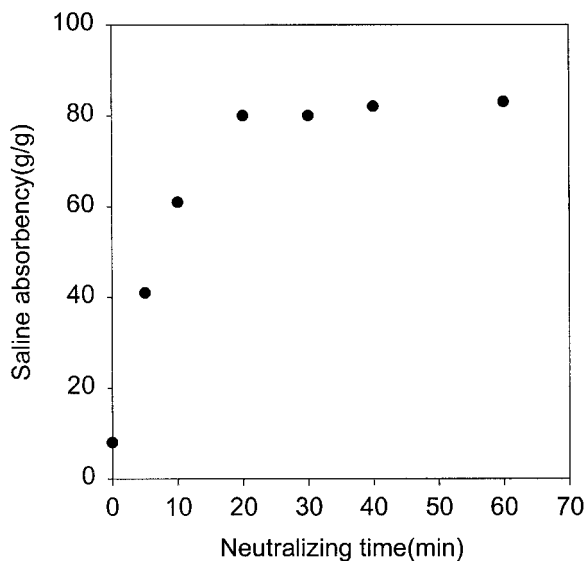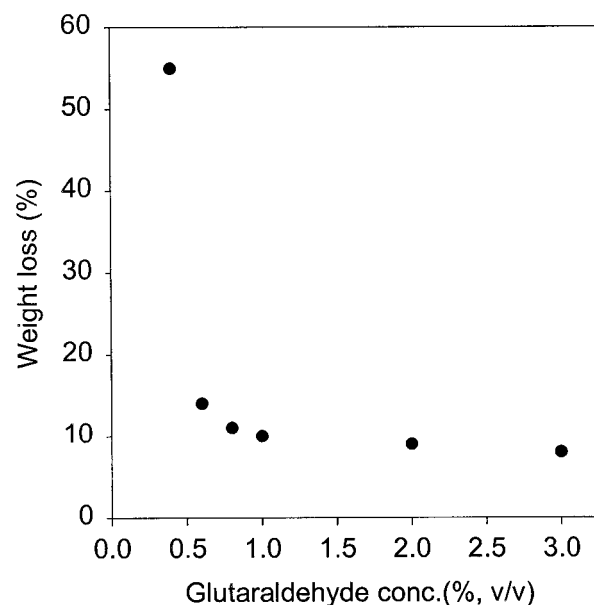
Figure 4 Saline absorbency as a function of neutralization time. Crosslinking condition: 50°C × 1 h, glutaraldehyde 3%, 0.1% HCl (35%); neutralization condition: 30°C, 0.4N NaOH solution/MeOH, 20/80 (v/v).

Figure 5 Weight loss of alginate fibers crosslinked at various concentrations of glutaraldehyde after immersion in saline solution. Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

ensure higher degrees of dissociation and higher absorbency. Absorbency reached a maximum value at a neutralization time of 20 min (Fig. 4), suggesting that approximately 20 min is sufficient for neutralization.

Sodium alginate itself is soluble in an aqueous solution unless the pH of the solution is lower than is the pK_a of alginate. It is expected that uncrosslinked or insufficiently crosslinked alginate polymer chains will dissolve in an aqueous solution, allowing it to be extracted from the polymer network, and thereby reduce the absorbency. A plot of the soluble polymer percentage versus crosslinking agent concentration is given in Figure 5. The alginate fiber crosslinked with 0.4% glutaraldehyde did not retain the fiber structure after immersion in an aqueous saline solution with about half of the polymer being soluble. When greater than 0.6% glutaraldehyde was used in the crosslinking reaction, the soluble polymer percentage decreased with increasing glutaraldehyde concentration, but the differences between samples were not significant. Saline absorbency of crosslinked alginate fibers increased with decreasing glutaraldehyde concentration within the range where the fiber structure was retained after swelling (Fig. 6).

Since sodium alginate is rapidly crosslinked with Ca ions, a CaCl$_2$ solution is commonly used as a coagulation solution in spinning sodium al-

ginate.[26,27] It is likewise expected that further crosslinking of alginate fibers crosslinked with glutaraldehyde can occur in a synthetic urine so-
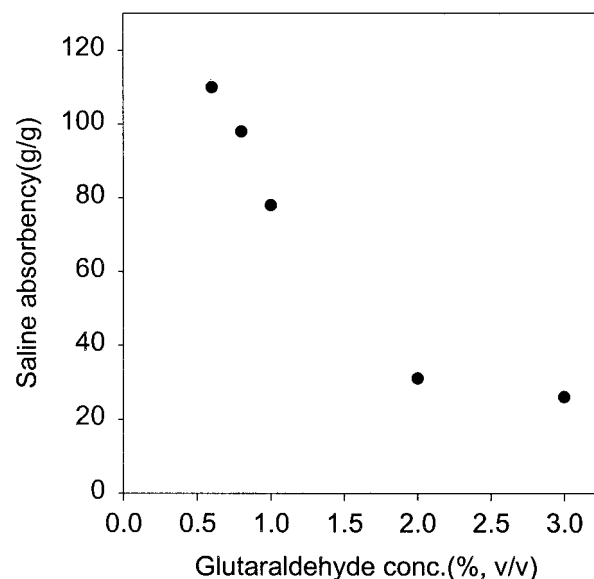
Figure 6 Saline absorbency of alginate fibers crosslinked at various concentrations of glutaraldehyde. Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).
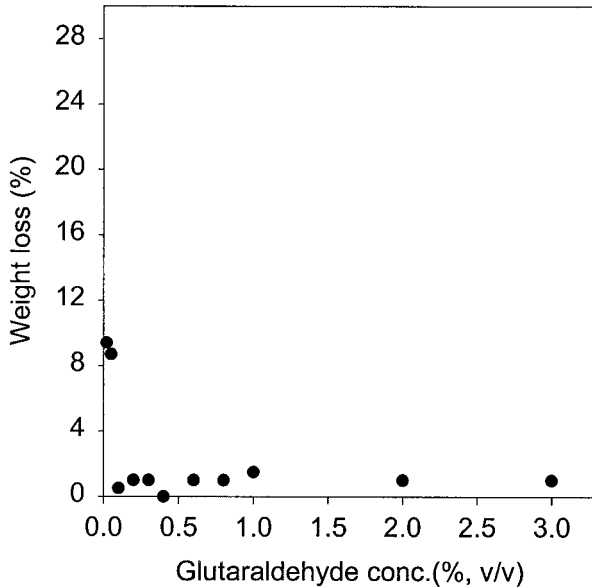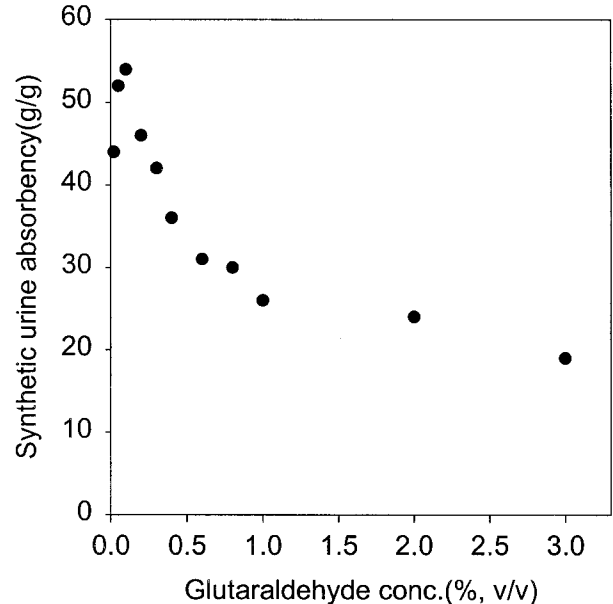
Figure 7 Weight loss of alginate fibers crosslinked at various concentrations of glutaraldehyde after immersion in synthetic urine solution. Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

Figure 8 Synthetic urine absorbency of alginate fibers crosslinked at various concentrations of glutaraldehyde. Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

lution where Ca ions are present. Figure 7 shows the amount of soluble polymers in crosslinked alginate fibers on immersion in a synthetic urine solution. Only small amounts were soluble in synthetic urine, including fibers crosslinked with very small amounts of glutaraldehyde which were soluble in an aqueous saline solution or in water. The maximum value of the absorbency for the synthetic urine solution was obtained with fibers crosslinked with a much lower glutaraldehyde concentration than that in the case of the saline solution (Fig. 8).

Figure 9 shows the absorption rates for a series of crosslinked alginate fibers in a saline solution. Fibers crosslinked at a higher glutaraldehyde concentration reach a steady state in a shorter time than do those crosslinked at a lower glutaraldehyde concentration, as reported previously.[28] All fibers show very rapid absorption behavior reaching a steady state within 20 s.

Physical Properties

Physical properties of the sodium alginate fibers crosslinked with various concentrations of glutaraldehyde are shown in Table I. Sodium alginate fibers shrunk extensively during drying, as can be deduced by comparing the measured linear den-

sity with the theoretical value calculated from the amount of extrusion, the take-up speed, and the diameter of the bottle used in winding. For exam-
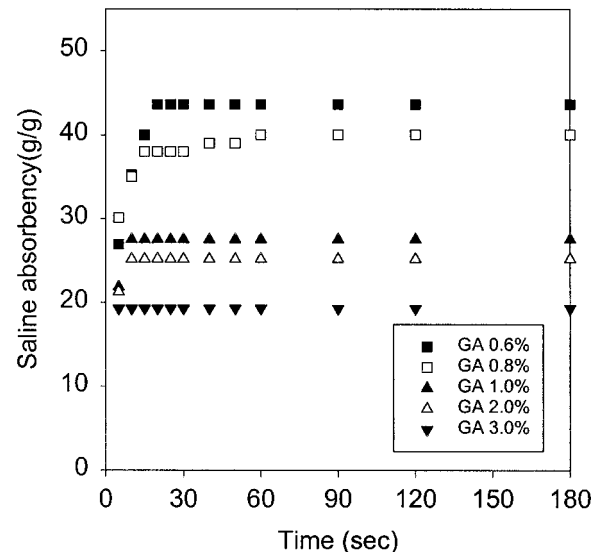
Figure 9 Saline absorption rate by the demand wettability method of alginate fibers crosslinked at various concentrations of glutaraldehyde. Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

Table I Physical Properties of the Alginate Fibers Crosslinked at Various Concentrations of Glutaraldehyde

|	Concentration of Glutaraldehyde (%, v/v)	Linear Density (denier)	Moisture Regain (%)
SA	0	8.7	22.9
CSA04	0.4	8.3	24.1
CSA06	0.6	8.2	24.4
CSA1	1.0	8.0	24.4
CSA2	2.0	8.0	24.1
CSA3	3.0	7.8	25.8

SA: sodium alginate fiber; CSA: crosslinked sodium alginate fiber; crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

ple, the linear density of noncrosslinked sodium alginate fibers is about 1.2 times the theoretical value (7.3 denier). The linear densities decreased with increasing glutaraldehyde concentration used in the crosslinking reaction. It is inferred that crosslinks introduced in alginate fibers impart dimensional stability to fibers and reduce their contraction. Moisture regain increased with increasing the glutaraldehyde concentration, contrasted to linear density. The moisture regain difference between fibers crosslinked with different concentrations of glutaraldehyde may also be possibly due to the different degrees of shrinkage. It is inferred that fiber shrinkage makes the fibers dense and thereby reduces the moisture regain. The change in density can be inferred from the micrograph of the cross section of the fibers (Fig. 10).

The values of the tenacity and strain with increasing glutaraldehyde concentration are listed in Table II. As expected, the strain decreased noticeably, with the tenacity exhibiting only a slight decrease with increasing amounts of the glutaraldehyde used in the crosslinking reaction. The reduction in tenacity was ascribed to an uneven crosslink distribution resulting in weak points, similarly to the decrease in tenacity of crosslinked cotton fabric (durable press finish).[29–31]

CONCLUSIONS

Alginate superabsorbent filament fibers were prepared by a two-step method. In the first step,
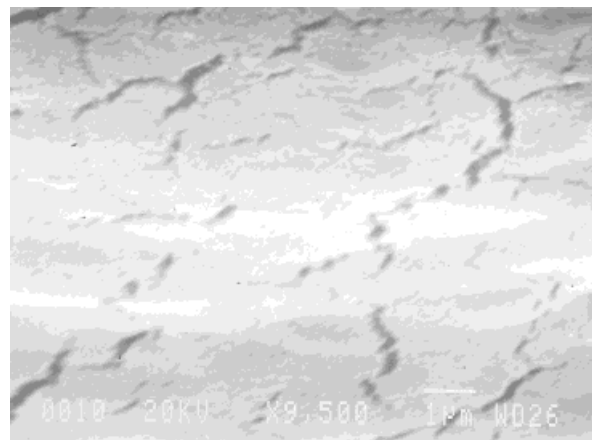
(a)
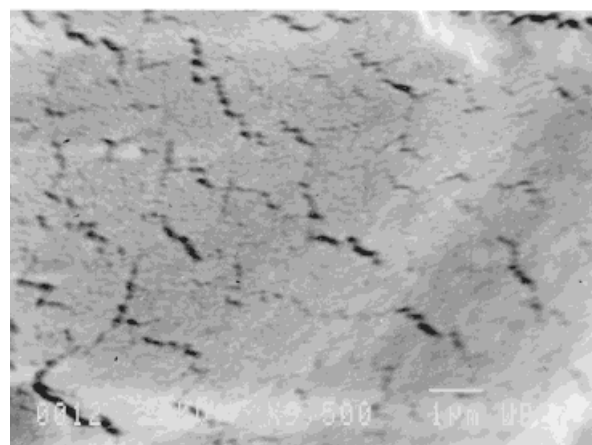
(b)

Figure 10 SEM micrographs of cross sections of alginate fibers: (a) SA; (b) CSA3.

alginic acid gel fibers were prepared by wet-spinning into a HCl coagulation bath, utilizing the acid gelation property of the alginate. In the second step, alginic acid fibers were crosslinked with

Table II Tensile Properties of the Alginate Fibers Crosslinked at Various Concentrations of Glutaraldehyde

	Tenacity (g/den)	Strain (%)
SA	1.16	27.1
CSA04	1.14	25.0
CSA06	1.12	24.6
CSA1	1.05	21.4
CSA2	1.02	19.8
CSA3	1.00	17.5

Crosslinking condition: 50°C × 4 h, 0.1% HCl (35%); neutralization condition: 30°C × 20 min, 0.4N NaOH solution/MeOH 20/80 (v/v).

glutaraldehyde after exchanging water in the gel with dioxane and then neutralized to increase absorbency.

Crosslinked alginate fibers exhibited a high saline solution and synthetic urine absorbencies. Absorbency of alginate fibers in saline and a synthetic urine solution increased with decreasing glutaraldehyde concentration up to a certain concentration, under which the crosslinked alginate fibers were partially soluble in water. Above this range, crosslinked alginate fibers retained their shape after swelling in saline or the synthetic urine solution. The maximum value of absorbency for the synthetic urine solution was obtained with fibers crosslinked at a much lower glutaraldehyde concentration than that for the saline solution, as the calcium ions in the synthetic urine solution introduced additional crosslinks to alginate.

With increasing glutaraldehyde concentration, the strain and tenacity of superabsorbent fibers decreased. However, the difference in the tenacity between fibers crosslinked with different concentrations of glutaraldehyde was insignificant.

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