The Conversion of Calcium Alginate Fibers into Alginic Acid Fibers and Sodium Alginate Fibers

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ABSTRACT: Alginate is a natural polymer extracted from brown seaweeds. Over the last two decades, alginate fibers have become well established in the wound management industry where their ion exchange and gel forming abilities are particularly useful in the treatment for exuding wounds. Alginate fibers are commonly made by extruding sodium alginate solution into a calcium chloride bath, producing calcium alginate fibers. To improve the gelling ability and the absorption capacity of calcium alginate fibers, this study used hydrochloric acid to convert calcium alginate fibers into alginic acid fibers, which was further converted into sodium alginate fibers by treating the fibers with sodium hydroxide in organic solvent. Results showed that alginic acid and sodium alginate fibers and fabrics can be readily made by treating the calcium alginate fibers and fabrics, respectively, with hydrochloric acid and sodium hydroxide. Improved gel blocking properties and absorption capacities were obtained with the sodium alginate fibers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4216–4221, 2006

Key words: alginate; ion exchange; hydrogel; absorption; wound dressing

INTRODUCTION

Alginate is a naturally occurring polymeric acid composed of two types of monomer units, i.e., α-L-guluronic acid [G] and β-D-mannuronic acid [M]. Figure 1 shows the chemical structures of the two types of alginic acids.

As a linear polymeric material, alginate can be made into fibers by the wet-spinning process, and a study by Speakman and Chamberlain in 1944 reported the detailed conditions for making alginate fibers with tensile properties similar to those of viscose rayon fibers.[1] Because of their tendency to dissolve under alkali conditions, alginate fibers had limited applications as a conventional textile material. Since the 1980s, however, alginate fibers have become widely used in the wound management industry as a novel wound management material.[2–8]. In this particular field, the properties of alginate fibers are unparalleled in many respects. First, as a natural polymer, alginate is nontoxic and safe to use on wound surfaces and in cavities. Second, when the water insoluble calcium alginate is placed on contact with wound exudates, the calcium ions exchange with sodium ions in the body fluid and calcium ions are released, which can act as a hemostatic agent. Third, as calcium alginate slowly turns into sodium alginate, it absorbs a large quantity of exudates and turns itself into a gel, which helps to keep a moist interface on the wound surface. Forth, as a natural polymer, alginate is a renewable resource with unlimited supply in nature. These unique properties of the alginate fibers are validated by the large varieties of alginate wound dressings now commercially available in the European and North American health care market.

In terms of the manufacturing process, calcium alginate fibers can be made via one of the most basic spinning processes. The spinning solution can be made by dissolving sodium alginate powder in water, and after degassing, a concentrated sodium alginate solution can be extruded through fine spinneret holes into a calcium chloride bath, whereby the sodium alginate is precipitated out in filament form as a calcium alginate fiber (the later being insoluble in water). The fibers can be washed and dried before they are further processed into nonwoven felt through conventional textile processes.

It has been known that the calcium alginate fibers can be chemically treated to convert them into a mixed salt containing both calcium and sodium ions.[9,10] In this process, the calcium alginate fibers are first washed with hydrochloric acid to replace part of the calcium ions with hydrogen ions. The hydrogen ions are then replaced with sodium ions by a treatment with sodium carbonate or sodium hydroxide. The resultant fiber contains both the water insoluble calcium

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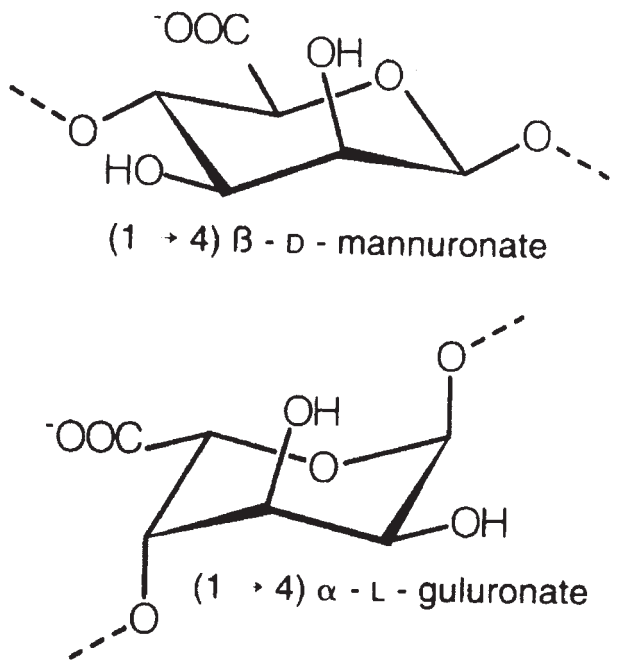

Figure 1 The chemical structures of α-L-guluronic acid and β-D-mannuronic acid.

alginate and the water soluble sodium alginate. Because sodium alginate is water soluble, the fibers become more and more absorbent when more and more sodium ions are introduced into the fibers.

The present work aims to study the treatment conditions for converting calcium alginate fibers into alginic acid fibers and sodium alginate fibers. The gelling abilities and absorption capacities of the resultant fibers with different chemical structures were also studied.

EXPERIMENTAL

The calcium alginate nonwoven felt was first converted into alginic acid by washing the felt with hydrochloric acid. A 0.5 mol/L aqueous HCl solution was prepared by measuring 42 mL of a 37% concentrated HCl solution and diluted to 1000 mL with distilled water. Six pieces of 5×5 cm^2 calcium alginate nonwoven fabrics were each treated with 50 mL of the 0.5 mol/L HCl solution for 0, 10, 20, 30, 60, and 90 min, respectively. After the treatment, the fibers were washed twice with distilled water and then twice with acetone. They were then dried in a 60°C oven for 4 h before being digested in 98% sulfuric acid solution. The fiber calcium content was analyzed by using atomic absorption spectrometer.

When preparing sodium alginate fibers, the calcium alginate nonwoven fabrics were first treated with excess amount of 0.5 mol/L HCl solution for 20 min and the fibers were washed twice with distilled water and then with acetone twice. They were then dried in a 60°C oven for 4 h. Eight samples of the alginic acid nonwoven fabrics were then placed in 8 conical flasks containing 50 mL of water/i-propanol mixture, with the water/i-propanol ratios at 10 : 0, 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, 4 : 6, and 3 : 7, respectively. An excess amount of NaOH was added into each solution and, after treating for 30 min at room temperature, the nonwoven fabrics were washed twice with acetone and dried at 60°C.

When studying the effect of treatment time, the alginic acid nonwoven fabrics were placed in a water/i-propanol mixture, with a water/i-propanol ratio of 7:3 and treated with excess amount of NaOH for 20, 30, 40, 50, and 60 min. The fibers were washed twice with acetone and dried at 60°C.

When studying the effect of treatment temperature, the alginic acid fibers were placed in a water/i-propanol mixture, with a water/i-propanol ratio of 7 : 3 and treated with excess amount of NaOH at 30, 40, and 50°C for 30 min. The fibers were washed twice with acetone and dried at 60°C.

When preparing fibers with different amount of calcium ions, the alginic acid nonwoven fabrics were placed in a water/i-propanol mixture, with a water/i-propanol ratio of 7:3 and treated with excess amount of NaOH at room temperature for 30 min. The nonwoven fabrics were washed twice with acetone and dried at 60°C to prepare the sodium alginate nonwoven fabric. These were then treated with different amount of calcium ions (using 0.14 mol/L aqueous $CaCl_2$ solution) to prepare calcium sodium alginate fibers. The 0.14 mol/L $CaCl_2$ solution was prepared by dissolving 7.770 g anhydrous $CaCl_2$ in 150 mL i-propanol followed by addition of distilled water to 500 mL. The sodium ions and calcium ions in the fibers were controlled theoretically at Na(I):Ca(II) = 0 : 10, 0.5 : 9.5, 0.8 : 9.2, 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 4 : 6, respectively. After treating for 30 min, the fibers were washed twice with acetone and dried at 60°C.

When testing the absorbency of the nonwoven alginate dressings, samples were cut to 5×5 cm^2 sizes and weighed (W) before being placed in petri dishes (90 mm in diameter) and wetted with 40 times their own weight of solution A (an aqueous solution containing 142 mmol of sodium chloride and 2.5 mmol of calcium chloride). The dish was then placed in a 37°C oven for 30 min. After that, the dressing was lifted out of the solution by holding it with a forcep at one corner. The solution was left to drip for 30 s and the wet dressing was weighed (W_1). The absorbency of the dressing is calculated as $(W_1 - W)/W$.

After testing the wet weight, the sample dressing was then wrapped in a piece of polyester fabric and placed in a centrifuge. After centrifuging for 5 min, the dressing was taken out and weighed again (W_2). Fi-

TABLE I
Effect of Treatment Time on Fiber Calcium Content*

Treatment time (min)	Fiber calcium content
0	8.61%
10	0.55%
20	Nil
30	Nil
60	Nil
90	Nil

A piece of 5 × 5 cm^2 nonwoven calcium alginate fibers was treated with 50 ml of the 0.5 mol/L HCl solution.

nally, the dressing was dried to constant weight at 105°C for 4 h and the weight was weighed (W_3).

The fluid that is held by the nonwoven dressing is divided into two parts, i.e., those held in the textile structure between the fibers and those held inside the individual fibers. In the aforementioned experiment, $W_1 - W_2$ is the weight of fluid held between the fibers while $W_2 - W_3$ is the weight of fluid held within the fibers. The ratio of $(W_1 - W_2)/W_3$ and $(W_2 - W_3)/W_3$ were calculated to convert the absorbed fluid into gram fluid absorbed per gram of dry fiber, which can be used to compare different samples.

When testing the lateral wicking properties, a piece of 10 × 10 cm^2 nonwoven dressing was first placed on a flat surface, and 5 mL solution A was then dropped onto the dressing with a titration tube. The wicking properties are characterized by the diameter of the wet circle.

RESULTS AND DISCUSSION

Most of the alginate fibers in commercial applications are in the form of calcium alginate, which can be easily made by extruding sodium alginate solution into a coagulation bath containing calcium chloride. These fibers are then converted into nonwoven fabric by a carding and needling process. Once placed on wound surface, the calcium alginate fibers in the nonwoven fabric slowly converts into sodium alginate as a result of the ion exchange between sodium ions in the wound exudate and calcium ions in the fiber.[11,12]

Since sodium alginate is water soluble, by converting the calcium alginate fibers into sodium alginate in fiber form, it should be possible to produce a wound dressing with high gelling ability and absorption capacity. This can be achieved by first converting calcium alginate into alginic acid and then by treating alginic acid with sodium hydroxide. Because alginic acid is insoluble in water, the removal of calcium ions with hydrochloric acid can be carried out in an aqueous media. The reaction proceeds according to the following equation:[13,14]

$$\text{Calcium alginate} + 2\,\text{HCl} = \text{Alginic acid} + \text{CaCl}_2$$

TABLE II
Effect of i-Propanol Content on the Weight Changes During the Conversion of Sodium Alginate Fiber to Calcium Alginate Fiber

Water/i-propanol ratio	Weight of the alginic acid fiber (g)	Weight of the sodium alginate fiber (g)
10:0	0.539	
9:1	0.556	0.507
8:2	0.463	0.335
7:3	0.554	0.511
6:4	0.627	0.674
5:5	0.585	0.627
4:6	0.547	0.588
3:7	0.516	0.558

Empty cell denotes that fiber dissolves in water.

In this process, the alginate fibers remain in the solid state, while the calcium ions are washed into the solution. As can be seen in Table I, the calcium ions in the calcium alginate fibers can be easily washed off from the fibers by treating the fibers with an excess amount of 0.5 mol/L aqueous HCl solution at room temperature. No calcium ions were found in the fibers after 20 min of treatment.

Since sodium alginate is water soluble, when the alginic acid fiber is converted into sodium alginate fibers by treating it with NaOH, the resultant fiber will lose its fibrous form if the treatment is carried out in an aqueous media. Attempts were therefore made to convert the alginic acid fibers into sodium alginate fibers by treating the fibers with NaOH in solutions containing organic solvents. Table II shows the effect of water/i-propanol ratio on the properties of the resultant sodium alginate fiber. When no i-propanol was used, the fibers dissolve when NaOH was added, and hence it is impossible to make sodium alginate in fiber form. When the water i-propanol ratio was below 6:4, it was found that the weight of the sodium alginate fiber obtained after the treatment is generally lower than that of the original alginic acid sample. This indicates that some of the sodium alginate has dissolved during the treatment, as sodium alginate is theoretically heavier than alginic acid. These results show that to maintain the fibrous structure during the conversion process, the i-propanol content in the treatment solution should be 30% or above.

TABLE III
Effect of NaOH Treatment Time on Fiber Properties

Time (min)	Absorption capacity of the resultant nonwoven fabric (g/g)
20	17.29
30	17.85
40	17.54
50	17.36
60	17.24

TABLE IV
Effect of Treatment Temperature on Fiber Properties

Temperature (°C)	Absorption capacity of the resultant nonwoven fabric (g/g)
Room temperature	17.85
30	17.74
40	13.23
50	11.18

Table III shows the effect of NaOH treatment time on the properties of the resultant sodium alginate dressing. It can be seen that after the treatment, the resultant fabric has a fairly high absorption capacity. In the range of time studied, treatment time did not have a significant effect on the absorption capacity, which shows that the treatment is a fairly quick process. In view of the results in Table III, for further studies, the conversion was carried out at room temperature for 30 min. In Table IV, it can be seen that when the NaOH treatment was carried out at different temperatures, the resultant dressing had significantly different absorption capacities. Fibers treated at room temperature has an absorption capacity of 17.85 g/g, while under otherwise similar conditions, the sample treated at a higher temperature of 50°C had an absorption capacity of only 11.18 g/g.

Table V shows the conditions for preparing alginate fibers with different calcium contents. Sodium alginate fibers were first prepared in the procedure described in the previous sections and seven samples of the sodium alginate fibers were treated with different amount of calcium chloride solution in 70/30 water/i-propanol mixture. The calcium contents were analyzed with atomic absorption spectroscopy, and as can be seen in Table V, the seven samples contained various amount of calcium ions, ranging from 1.46%, 1.75%, 2.73%, 3.34%, 5.77%, 7.29% to 8.58%.

It has been known previously that for the production of alginate fibers and wound dressings, increased absorption capacity can be obtained by incorporating sodium ions into the calcium alginate fibers. For example, the Kaltostat brand alginate wound dressing is made of alginate fibers with a mixed salt of about 80% calcium and 20% sodium alginate. Test results have shown that this type of calcium sodium alginate wound dressings are more absorbent than the pure calcium alginate wound dressing such as Sorbsan.[11,12] In the present study, it has been shown that the absorption properties of the alginate fibers and dressings are closely related to the sodium and calcium ion content of the fiber. As can be seen in Figure 2, the gel swelling ratio in both water and solution A decreased with the increase in calcium content. This shows that as the calcium ion is a divalent metal ion, when the fiber is rich in calcium ion instead of sodium ion, the fiber is crosslinked more and it is difficult for it to swell when wet. On the other hand, sodium alginate is water soluble and when the calcium alginate is converted into sodium alginate, it is able to pull water into the fiber, resulting in a high gel swelling ratio. It is interesting to note that the gel swelling ratio is generally lower in solution A than in water, due to the high ionic strength in solution A.

Table VI shows the absorption properties of nonwoven felt made of calcium alginate fiber, alginic acid fiber, and sodium alginate fiber. To prepare these samples, the original calcium alginate nonwoven felt was first washed with excess amount of hydrochloric acid solution to convert it into alginic acid, which is then treated with excess amount of sodium hydroxide for the further conversion into sodium alginate. As can be seen in Table VI, the sodium alginate nonwoven felt had the highest absorption capacity of 18.90 g/g, while the alginic acid nonwoven felt could only absorb 10.41 g/g. This is understandable as the sodium alginate can readily pull water into its fibrous structure and hence can hold a large amount of water. For the calcium alginate fiber, when it is placed in contact with solution A, the sodium ions in the solution can slowly convert part of the fiber into sodium alginate, thereby helping it to absorb liquid. For the alginic acid fiber, the carboxylic acid group in the fiber is in acid form and it is not possible for the fiber to convert into

TABLE V
Conditions for Preparing Alginate Fibers with Different Calcium Contents

Weight of sodium alginate fiber (g)	n/mol	Volume of 0.14 mol/L $CaCl_2$ solution (mL)	Volume of 70/30 water i-propanol solution (mL)	Weight of the sample after treatment (g)	Calcium content of the fiber (%)
0.503	0.00253	0.9	8.1	0.504	1.46
0.504	0.00254	1.8	7.2	0.507	1.75
0.484	0.00224	3.2	5.8	0.465	2.73
0.541	0.00250	5.3	3.7	0.501	3.34
0.498	0.00231	6.5	2.5	0.456	5.77
0.433	0.00200	7.2	1.8	0.405	7.29
0.483	0.00223	7.9	1.1	0.471	8.58

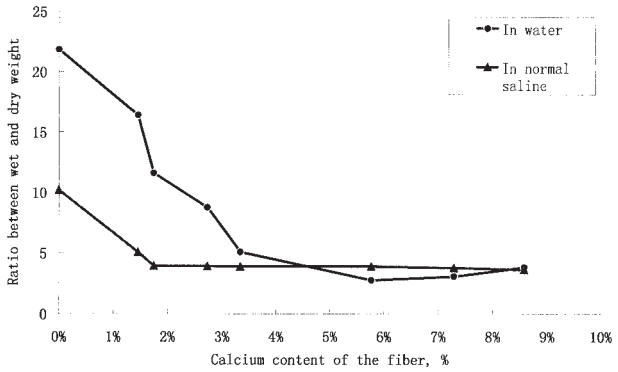

Figure 2 Gel swelling properties of alginate fibers with different calcium ion contents.

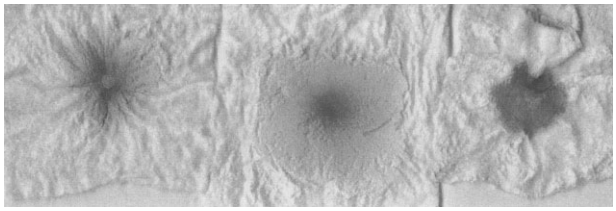

Figure 3 Lateral wicking of solution A on (from left to right) calcium alginate, alginic acid, and sodium alginate nonwoven fabrics.

the water holding sodium alginate, hence it has the lowest absorption capacity among the three samples.

Under detailed analysis, it can be seen that calcium alginate fiber, alginic acid fiber, and sodium alginate fiber differ greatly in their absorption characteristics. In Table VI, $(W1 - W2)/W3$ measures the amount of liquid held between fibers, while $(W2 - W3)/W3$ measures the amount of liquid held inside the fiber structure. It can be seen that under the same testing conditions, the sodium alginate fiber can absorb 24.71 g/g water into the fiber structure, as compared to 4.49 g/g for the alginic acid fiber and 2.28 g/g for the calcium alginate fiber. Because of the ion exchange process, the calcium alginate fibers swell more in the presence of solution A, with the gel swelling ratio rising from 2.28 g/g in water to 6.67 g/g in solution A. On the other hand, the gel swelling ratio of the alginic acid fiber decreases from 4.49 g/g in water to 3 g/g in solution A.

The different absorption characteristics of the three types of fibers has a significant effect on the gel blocking properties of the nonwoven felt. When 5 mL normal saline is dropped onto the three types of felt, the diameters of the wet circle are 5.5, 7.5, and 4.0 cm, respectively, for the calcium alginate, alginic acid, and sodium alginate nonwoven felts, as is illustrated graphically in Figure 3. In clinical circumstances, if the fluid from the wound bed is absorbed by the wound dressing and held in place, it can help reduce the spreading of wound exudate to the healthy skins surrounding the wound site, thereby reducing the so-called wound maceration. In the present study, experimental result has shown that under otherwise same conditions, the sodium alginate felt has the best gel blocking properties, while the alginic acid felt has the worst. This is in accordance with the absorption properties of the respective fibers. The sodium alginate fibers are capable of a high degree of swelling when wet in water, hence it can block the spreading of fluid. On the other hand, for the alginic acid fiber, the fibers can swell only slightly when wet, which means that the pores within the nonwoven structure remain open when wet, hence allowing the rapid spreading of liquid on the nonwoven felt.

CONCLUSIONS

This study has shown that calcium alginate fibers and nonwoven fabrics can be converted into alginic acid and sodium alginate in the solid state, providing an indirect method for making fibers and nonwoven felts of alginic acid and sodium alginate. The calcium ions in the alginate fibers can be readily washed off with dilute aqueous hydrochloric acid solution, while sodium alginate fibers can be made by treating the alg-

TABLE VI
A Comparison of the Properties of Calcium Alginate, Alginic Acid, and Sodium Alginate Fibers and Nonwoven Fabrics

Sample		Original calcium alginate nonwoven felt	Calcium alginate nonwoven felt[a]	Alginic acid nonwoven felt	Sodium alginate nonwoven felt
Absorbency	$(W_1 - W)/W$	16.74	14.74	10.41	18.90
Swelling in water	$(W_1 - W_2)/W_3$	20.63	15.59	10.96	11.24
	$(W_2 - W_3)/W_3$	3.62	2.28	4.49	24.71
Swelling in normal saline	$(W_1 - W_2)/W_3$	13.96	13.58	11.35	[b]
	$(W_2 - W_3)/W_3$	9.08	6.67	3.00	[b]
Diameter of the wet area (cm)		4.5	5.5	7.5	4.0

[a] After washing with water and acetone.
[b] The fibers became gelly and lost the fibrous structure during the tests.

inic acid fibers with sodium hydroxide in an organic solvent. Experimental results showed that the sodium alginate fibers and fabrics are more absorbent than the calcium alginate fibers and fabrics, which is again more absorbent than the alginic acid fibers and fabrics.

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