Gel Swelling Properties of Alginate Fibers

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ABSTRACT: This article described a study on the gel-forming abilities of a number of different types of alginate fibers. The gelling abilities were assessed through the measurement on the release of calcium ions from the fibers and the absorption capacities in water and 0.9% saline solution. The effects of the chemical compositions of the alginate and the calcium and sodium contents of the fibers on the gelling abilities were studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1641–1645, 2004

Key words: alginate; fibers; wound dressing; ion exchange; hydrogels

INTRODUCTION

Alginate is a natural polymer composed of two monomers: α-L-guluronic acid and β-D-mannuronic acid. Figure 1 shows the chemical structures of these two monomers.

Alginate exists widely in brown seaweeds. Like cellulose, it acts as a reinforcing element in cell walls of brown seaweeds. Alginate is widely used in the textiles, food, and chemical industries as a thickening and gelling agent.[1]

Alginate fibers have had a long history. As early as 1944, Speakman and Chamberlain[2] reported a detailed process for the manufacturing of alginate fibers. Since the 1950s, alginate fibers have been used in the textile industries as draw threads and as home-decoration materials, taking advantage of their ability to dissolve in a dilute aqueous alkali solution and their nonflammable properties.

Since the 1980s, alginate fibers have been widely used in the manufacture of high-tech wound dressings. Alginate fibers have unique gel-forming characteristics whereby on contact with wound exudates, the sodium ions in the wound exudates can exchange ions with the calcium ions in the fiber, and as more and more sodium ions enter the fiber structure, the fiber absorbs increasing amounts of water and becomes a gel.[3] This property is ideal for the wound dressings industry where in recent years it has been shown that the ideal environment for wound healing is a moist but not wet condition.[4] For alginate wound dressings, as the water enters the fiber structure, the fiber becomes a gel and a moist environment is formed on the wound surface, thus providing an ideal moist condition for healing to take place. Many clinical trials have shown that alginate wound dressings not only have high absorption capacities, but also have the ability to promote wound healing.[5–9]

This article reports the investigation of the gel-swelling properties of several types of alginate fibers. It aims to quantify the ion-exchange process between the alginate fibers and the contacting solutions, and study the properties of the resulting gels.

EXPERIMENTAL

Three types of commercial alginate wound dressings were used in the present study. Under various trade names they were, respectively, Sorbsan from Maersk Medical, Algosteril from Laboratory Brothier, and Kaltostat from ConvaTec. The Sorbsan sample is made of calcium alginate fiber in a loose nonwoven format; the Algosteril sample is a needled felt of calcium alginate; and Kaltostat is made of calcium/sodium alginate fiber in a needled nonwoven format.

Several types of laboratory-made samples were also used in the present study. They were made with samples of alginate containing different proportions of α-L-guluronic acid and β-D-mannuronic acid. After chemical treatment, the samples can also be made to contain different amounts of calcium and sodium ions.

The calcium and sodium contents of the alginate fibers are expressed as the percentage of carboxylic acid group in either calcium salt or sodium salt, assuming that all the carboxylic acid group in the alginate sample exists in either of these salts. To measure the calcium and sodium contents, the fibers were first digested in 98% sulfuric acid solution, and the calcium and sodium contents were measured with an atomic absorption spectrometer. Assuming the w/w calcium content of the fiber is C_1 and the sodium content is C_2, the fiber calcium content equals $\{[C_1/20]/[(C_1/20)$

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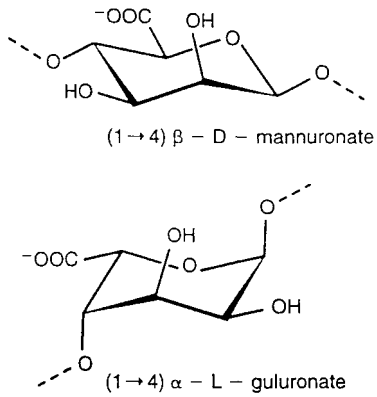

Figure 1 Chemical structure of guluronic acid (G) and mannuronic acid (M).

$+ (C_2/23)]\} \times 100\%$, whereas the fiber sodium content is $\{[C_2/23]/[C_1/20 + (C_2/23)]\} \times 100\%$ (Note: one calcium ion binds with two carboxylic acid groups.)

The gel-swelling abilities of the alginate fibers were measured by placing 0.2 g fiber in 100 mL of either distilled water or 0.9% w/w aqueous sodium chloride solution (normal saline). After 1 h, the fibers were separated from the contacting solution and placed in a centrifuge tube with the bottom half-filled with knitted viscose rayon fabric to contain the spinoff solution. Centrifugation was carried out at 1200 rpm for 15 min. After that, the fiber (W_1) was dried at 105°C to constant weight (W_2). The gel swelling ratio is expressed as the ratio between the weight of the wet sample and that of the dry sample (i.e., W_1/W_2).

To measure the gel strength, 2 g of alginate fibers were first cut to a length of about 5 mm. They were placed in a beaker with 50 mL distilled water. After stirring for a few minutes, 10 mL of a 9% w/w aqueous trisodium citrate solution was added into the above mixture. The resultant mixture contained about 3% alginate and 1.5% trisodium citrate. After thorough mixing, the mixture was left for 5 min before measuring the gel strength on a Stevens gel strength meter.

The ion exchange of alginate fibers with contacting solution was conducted with solution A as the contacting medium. The British Pharmacopoeia[10] specifies solution A as an aqueous solution containing 142 mmol of sodium chloride and 2.5 mmol of calcium chloride. About 1 g fiber was placed in 40 mL of solution A and was conditioned at 37°C for 30 min. After separating the fiber from the solution, the calcium and sodium contents in the solution were measured by an atomic absorption spectrometer.

If the calcium content in the original solution is C_1 ppm, and that after the ion exchange process is C_2 ppm, then the calcium ions released per gram of fiber is $40 \times (C_2 - C_1) \times 10^{-6}$ g/g.

The absorption capacities of the dressings were measured according to the method as specified in the British Pharmacopoeia monograph for alginate dressings and packings. A piece of 5 × 5-cm dressing (W_1) was placed in a flat-bottom petri dish 90 mm in diameter, to which was added a quantity of solution A 40 times the weight of the dressing. After conditioning at 37°C for 30 min, the sample was lifted from one corner and held in the air for 30 s before the weight of the sample was measured (W_2). The absorption capacity is expressed as $(W_2 - W_1)/W_1$ g/g.

The changes in the fiber length after wetting were measured under an optical microscope. A piece of fiber about 2 mm in length was wetted with either distilled water or 0.9% saline, and the length change is expressed as (wet length − dry length)/dry length × 100%.

RESULTS AND DISCUSSION

Because alginate is a copolymer of guluronic acid (G) and mannuronic acid (M), and because these two isomers have significantly different stereochemical structures, the G and M contents of the fiber have a significant effect on the gelling abilities of the alginate fibers. As shown in Figure 2, the GG block is able to form a space between the two monomer units, which is ideal for fitting in the calcium ion. As the calcium ion forms salt with carboxylic acid groups in two neighboring GG blocks, it can create a strong crosslink between the two polymer chains, causing gelation when calcium ions are in contact with the sodium alginate solution. For this reason, alginate high in G content can form strong and firm gels, whereas those rich in M contents tend to form weak and soft gels. The MM block adopts a flat structure and its ability to bind calcium ions is low.

Figures 3–5 show the structures of the Sorbsan alginate fiber when dry, wet in distilled water, and wet in 0.9% saline, respectively. From these figures it can be seen that, whereas the fiber swelled only slightly in water, there was significant swelling in 0.9% saline. It is clear from Figure 5 that on contact with the sodium-containing solution, there was a rapid ion-exchange process and a large quantity of water was absorbed into the fiber to form a fibrous gel.

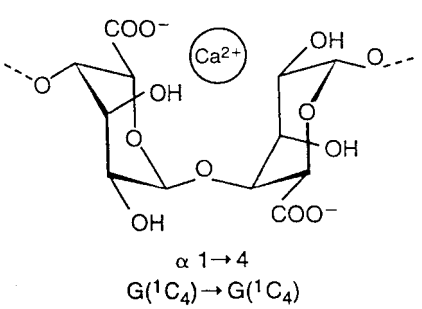

Figure 2 Stereochemical structure of the GG block.

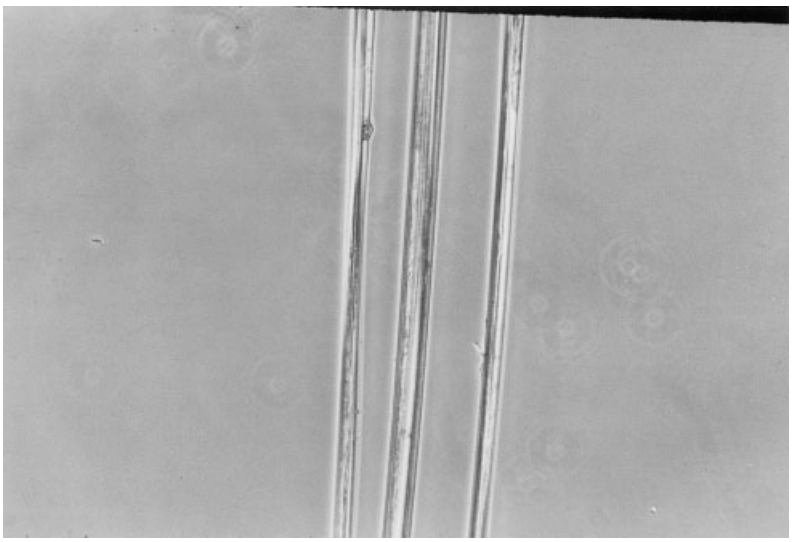

Figure 3 Surface structure of the alginate fiber when dry (×200).

Table I shows the gelling abilities of three types of alginate fibers with different M/G contents. The high G alginate fiber has about 70% G and 30% M, whereas the high M alginate has about 65% M and 35% G. After the ion-exchange process in solution A, the solution in contact with the high G alginate fiber contained about 317.6 ppm calcium ions, whereas the solution in contact with the high M alginate fiber contained 561.0 ppm calcium ions, almost twice as much as that for the high G alginate fiber. This result clearly demonstrates that the high M alginate fiber exchanges ions more readily with the sodium-containing solution, and its gelling ability is much better than the high G alginate fiber.

The design of the Sorbsan dressing makes use of this easy gelling ability of the high M alginate fibers. The Sorbsan dressing is a loose unneedled felt. After they are used on exuding wounds, these dressings can be easily removed from the wound bed with a rinse of warm saline solution, thus reducing the pain associated with the removal of wound dressings. Unlike Sorbsan, the Algosteril dressing is made of high G alginate. Its ion-exchanging ability with the wound exudate is limited and it is more difficult to form a gel than Sorbsan. However, the Algosteril fibers are stronger than Sorbsan when wet, and because it is in a needled format, it can be removed from the wound surface in one piece by using a forcep. During clinical use, both dressings have their own unique characteristics.

Because trisodium citrate has a strong chelating capacity for metal ions, a 1.5% aqueous trisodium citrate

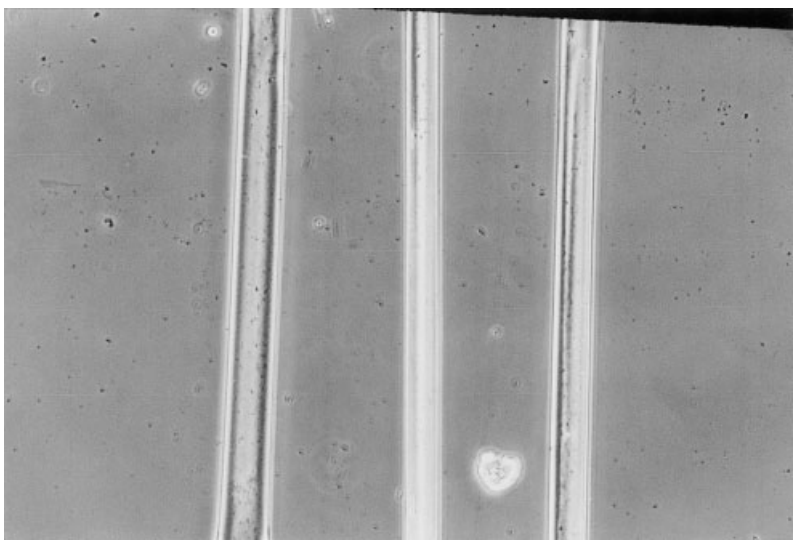

Figure 4 Surface structure of the alginate fiber when wet in distilled water (×200).

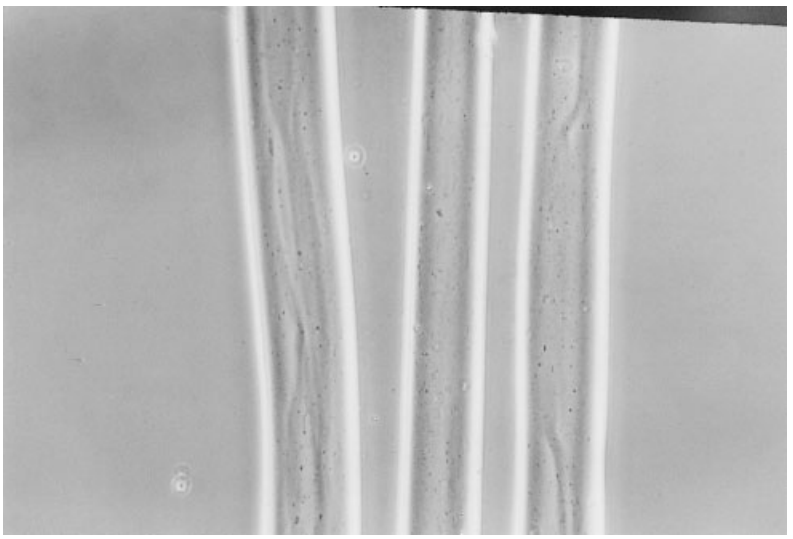

Figure 5 Surface structure of the alginate fiber when wet in 0.9% saline (×200).

solution was used to convert the high G and high M calcium alginate fibers into gel. From Table I, it can be seen that, because the high G alginate has a strong calcium-binding ability, the gels formed from the high G alginate fiber have a much higher gel strength than that of the high M alginate fiber. This high gel strength of high G alginate also has an additional benefit during the production process. After extruding into a calcium-containing coagulation bath, the high G alginate is able to form threads with high wet strength, and thus it is easier to process than the high M alginate.

Table II shows the gel swelling ratio and the absorption capacities of Sorbsan, Algosteril, and Kaltostat. It is clear that the Algosteril sample performs more poorly than either Sorbsan or Kaltostat. This is because Algosteril is a calcium alginate made of high G alginate. Compared to the high M Sorbsan, the high G alginate in Algosteril firmly binds calcium ions, and it is difficult for the ion exchange, thus gelling, to take place. Algosteril has poor gel-forming properties. The gel swelling ratio in 0.9% saline is only 5.2 g/g compared to the 13.9 g/g for Sorbsan. Kaltostat is also made of high G alginate; however, during the production process, a portion of the calcium ions in the Kaltostat fiber is already replaced by sodium ions, with the proportion of carboxylic acid group in calcium or sodium salt at about 80/20. The 20% sodium introduced during the production process significantly increased the gel swelling ratio in water: the value for Kaltostat is roughly four times that of Algosteril. After the introduction of 20% sodium, the absorption capacities were also significantly increased, with Kaltostat absorbing 17.3 g/g solution A, compared to 16.7 g/g for Sorbsan and 14.2 g/g for Algosteril.

Table III shows the absorption capacities and calcium release of three types of alginate fibers containing different levels of sodium ions. It is clear that as the sodium contents increased, there were corresponding increases in the absorption capacities of the

TABLE I
Calcium Release, Absorption Capacities, and Gel Strength of Three Types of Alginate Fibers

Parameter	High G Fiber	Mid G Fiber	High M Fiber
Ratio of M/G	~ 0.4	~ 1.6	~ 1.8
Fiber calcium content, %	98.2	96.8	96.3
Ca(II) content in extraction solution, ppm	317.6	459.9	561.0
Calcium release, %	0.9	1.42	1.88
Gel swelling ratio in water, g/g	2.68 ± 0.26	6.1 ± 0.88	5.70 ± 0.38
Gel swelling ratio in 0.9% saline, g/g	8.48 ± 0.61	14.52 ± 0.73	15.88 ± 0.64
Gel strength, g	85.1	25.7	32.5

TABLE II
Absorption Behavior of Sorbsan, Algosteril, and Kaltostat

Property	Sorbsan	Algosteril	Kaltostat
Fiber calcium content, %	~ 95	~ 98	~ 80
Absorption capacities in solution A, g/g	16.7	14.2	17.3
Gel swelling ratio in water, g/g	2.2	1.8	7.7
Gel swelling ratio in 0.9% saline, g/g	13.9	5.2	5.9

TABLE III
Absorption Capacities and Calcium Release of Three Types of Alginate Fibers Containing Different Levels of Sodium Ions

Property	High-calcium fiber	Mid-calcium fiber	High-sodium fiber
Fiber calcium content, %	~ 98.2	~ 76.6	~ 54.3
Ca(II) content in extraction solution, ppm	317.6	230.2	136.3
Calcium release, %	0.9	0.56	0.18
Gel swelling ratio in water, g/g	2.68 ± 0.26	24.15 ± 0.86	20.65 ± 2.68
Gel swelling ratio in 0.9% saline, g/g	8.48 ± 0.61	13.43 ± 1.13	18.60 ± 0.95
Gel strength, g	85.1	19.9	7.5

dressings. The gel swelling ratio in 0.9% saline increased from 8.48 g/g for the high-calcium fiber to 18.60 g/g for the high-sodium fiber. This result suggests that one way of improving the absorption and gelling properties of the alginate wound dressing is to introduce sodium ions into the fiber.

Table IV shows the changes of fiber length after wetting in distilled water and 0.9% saline solution. It is clear that, because the high G alginate has strong calcium binding and poor gelling ability, the fiber has a firm structure and good dimensional stability when wet. On the other hand, the high M type alginate fiber gels more easily, and as the fiber absorbs water during gelling, the oriented structure is disrupted, resulting in contraction of the fiber length. For similar reason, the fibers with high sodium contents gel more easily and have significant shrinkage in fiber length when wet.

TABLE IV
Changes in Fiber Length in Water and 0.9% Saline

Fiber type	In water	In 0.9% saline
High G high calcium alginate fiber	+0.99%	−6.15%
High M high calcium alginate fiber	−3.29%	−8.95%
High G high sodium alginate fiber	−9.21%	−12.01%
High M high sodium alginate fiber	−13.89%	−16.22%

CONCLUSIONS

This article reported the investigation of the gelling abilities of various alginate fibers. Results show that the gelling ability is affected by the guluronic acid and mannuronic acid contents, and the calcium and sodium contents of the fiber. High M alginate fibers exchange ions more readily than high G fibers, and thus they have better gelling abilities than those of high G fibers. By introducing sodium ions into the fiber, the gelling ability and absorption capacities can be improved for the high G alginate fibers.

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