Review

Alginate fibres: an overview of the production processes and applications in wound management

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Abstract: Alginate fibers are made from sodium alginate, which 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 for the treatment of exuding wounds. In order to deliver functional performances for advanced wound management products, many improvements have been made in recent years to enhance the absorption and gel-forming capabilities and the anti-microbial properties of alginate fibers. In addition, attempts have been made to use alginate fibers as a carrier to deliver zinc, silver and other active ingredients that are beneficial to wound healing. This paper reviews the development in the production of various fibers from alginate, and summarizes the production processes for calcium alginate, calcium/sodium alginate, sodium alginate, zinc alginate, silver alginate and other types of alginate fibers containing novel functional ingredients.

INTRODUCTION

Alginate is a natural polysaccharide extracted from brown seaweeds. Since it was discovered by Stanford in 1881, alginate has been used in a wide range of industries, such as food, textile printing, paper and pharmaceuticals, and for many other novel end-uses. As a water-soluble polymer, alginate is an excellent gel-forming material capable of holding a large amount of water. In recent years, alginate has been widely used in the wound management industry as a novel material for the manufacture of ‘moist healing’ products such as gels, foams and fibrous non-woven dressings that are used to cover wounds. In these applications, alginate materials are used either in the dry form to absorb wound fluid, or to donate water to a dry wound when used in the hydrated gel form. In either case, the interaction of the alginate materials and wound surface creates a moist local environment. It has been shown that, when wounds are kept in a moist but not wet condition, the migration of epithelial cells from the edge of the wound to the wounded area is faster than when wounds are kept in a dry state. Modern ‘moist healing’ wound dressings aim to create the moist conditions that can facilitate optimum healing.

Alginate fibers are particularly useful as raw materials for the production of highly absorbent wound dressings. In this particular field, the properties of alginate fibers are unparalleled in many respects.

First, as a natural polymer, alginate is non-toxic and safe to use on wound surfaces and in cavities. Second, when a water-insoluble calcium alginate fiber is placed in 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 haemostatic agent. Third, as a calcium alginate fiber slowly turns into a sodium alginate fiber, it absorbs a large quantity of exudates and turns itself into a gel, which helps keep a moist interface on the wound surface. Fourth, as a natural polymer, alginate is a renewable resource with unlimited supply in nature.

In the fiber form, it is also possible to process the alginate fibers into woven, non-woven, knitted and various composites to address specific wound management problems.

The present review aims to summarize the development of various types of alginate fibers and their use as a wound management material.

CHEMICAL STRUCTURES OF ALGINATE

Alginate can be found in brown seaweeds such as the species of ascophyllum, durvillaea, ecklonia, laminaria, lessonia, macrocystis, sargassum and turbinaria. Of these, the most important ones are laminaria, macrocystis and ascophyllum. On a dry weight basis, the alginate contents are 22–30% for Ascophyllum

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soluble sodium alginate. After filtration, the sodium alginate in various salt forms is converted into water-alkali solutions, typically NaOH, in which the natural from raw seaweeds by a treatment with aqueous α-seaweeds.

M/G ratios, of alginate extracted from various commercial brown seaweeds8–10 Table 1 shows the resulting in the differences in the physical properties of alginates prepared from various commercial brown seaweeds.

Because of the differences in the chemical structure of alginates, the properties of alginate extracted from different species of brown seaweeds vary greatly. Chemically, alginate is a linear polymeric acid composed of 1,4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. As can be seen in Fig. 1, these two acid residues are stereochemically very different as a result of their difference at C-5. Alginates extracted from different species of seaweeds differ in M and G contents, resulting in the differences in the physical properties of the respective alginate products. Table 1 shows the M and G contents of alginate extracted from seaweeds commonly used for the commercial extraction of alginate.

![Chemical structures of β-D-mannuronic acid and α-L-guluronic acid.](image)

**Figure 1.** Chemical structures of β-D-mannuronic acid and α-L-guluronic acid.

<table>
<thead>
<tr>
<th>Type of seaweed</th>
<th>Mannuronic acid (%)</th>
<th>Guluronic acid (%)</th>
<th>M/G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascophyllum nodosum</td>
<td>60.0</td>
<td>40.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Laminaria digitata</td>
<td>59.0</td>
<td>41.0</td>
<td>1.43</td>
</tr>
<tr>
<td>Laminaria japonica</td>
<td>69.3</td>
<td>30.7</td>
<td>2.26</td>
</tr>
<tr>
<td>Macrocystis pyrifera</td>
<td>61.0</td>
<td>39.0</td>
<td>1.56</td>
</tr>
<tr>
<td>Laminaria hyperborea, fronds</td>
<td>56.0</td>
<td>44.0</td>
<td>1.28</td>
</tr>
<tr>
<td>Laminaria hyperborea, stems</td>
<td>30.0</td>
<td>70.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**Table 1.** Percentages of mannuronic acid and guluronic acid, and M/G ratios, of alginate extracted from various commercial brown seaweeds.

Because its polymeric structure contains two types of monomer acids, alginate can be regarded as a block copolymer of β-D-mannuronic acid and α-L-guluronic acid. It has been shown that the polymer chain is made up of three kinds of blocks. The GG blocks contain only units derived from L-guluronic acid, the MM blocks are based entirely on D-mannuronic acid and the MG blocks consist of alternating units from D-mannuronic acid and L-guluronic acid. It was demonstrated from X-ray studies on the fibers of poly(mannuronic acid) and those from alginic acid rich in guluronic acid content that the spacings along the fiber axis are 10.35 Å for mannuronic polymer and 8.72 Å for guluronic polymer.

In addition to the G and M contents, it has been shown that the physical properties of alginates also depend on the relative proportions of the three types of blocks. For example, the formation of gels by the addition of calcium ions mainly involves the GG blocks. Hence, under otherwise same conditions, the higher the GG contents, the greater the gel strength.

The industrial utilization of any particular alginate will depend on its properties and therefore on its uronic acid composition; it is therefore important to quantify the relative proportions of the uronic acids. Various methods have been developed to measure the ratio of mannuronic acid to guluronic acid (the M/G ratio), as well as the MM, GG and MG/GM contents of alginate samples. In particular, accurate determination of G, M, MM, GG and MG/GM contents can be measured by $^1$H NMR and $^{13}$C NMR. Table 2 shows the percentages of the three principal types of block structures in alginates prepared from various commercial brown seaweeds.

<table>
<thead>
<tr>
<th>Type of seaweed</th>
<th>MM segments (%)</th>
<th>GG segments (%)</th>
<th>MG/GM segments (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascophyllum nodosum</td>
<td>38.4</td>
<td>20.7</td>
<td>41.0</td>
</tr>
<tr>
<td>Laminaria digitata</td>
<td>49.0</td>
<td>25.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Laminaria japonica</td>
<td>36.0</td>
<td>14.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Macrocystis pyrifera</td>
<td>40.6</td>
<td>17.7</td>
<td>41.7</td>
</tr>
<tr>
<td>Laminaria hyperborea, fronds</td>
<td>43.0</td>
<td>31.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Laminaria hyperborea, stems</td>
<td>15.0</td>
<td>60.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

**Table 2.** Percentages of the three principal types of block structures in alginates prepared from various commercial brown seaweeds.

 DOI: 10.1002/pi
PREPARATION OF SPINNING SOLUTIONS
In the wet-spinning process in which alginate is converted from powder into fiber form, alginate is first dissolved in water to form a homogenous solution. Sodium alginate is typically used as the raw material, since it is easily soluble in water. In preparing a spinning solution, it should be pointed out that the properties of the alginate fibers depend on a number of factors, such as the molecular structure and molecular weight of the alginate, the coagulation bath composition, the processing temperatures and speeds, etc. As the first step in the production process, the spinning solution has an important effect on both the production efficiency and the product performances. Some of the factors involved in the preparation of an alginate spinning solution are discussed below.

Molecular weight of the alginate powder
In theory, a higher molecular weight would result in a higher level of inter-chain bonding and a greater fiber strength. During the preparation for spinning dope, it should be noted that as the molecular weight increases, the solution viscosity increases sharply, making it difficult to dissolve a high concentration of alginate in a given amount of water. Although alginate is a natural polymer, manufacturers can control the molecular weight (or degree of polymerization, DP) by varying the severity of the extraction conditions to produce products with viscosities in a 1% solution ranging from 10 to 1000 mPa s, with a DP range of 100–1000 units. In order to extrude the alginate solutions through spinneret holes to form filaments, the spinning solution typically has a viscosity in the range 10 000–20 000 mPa s, which can be obtained either from a high concentration solution made of alginate with a low molecular weight, or a low concentration with a high molecular weight. For the production of alginate fibers, in order to balance the production efficiency with product performance, the raw material typically has a viscosity in 1% solution in the range 40–100 mPa s.4

Concentration of the spinning solution
The viscosity of the alginate solution increases sharply as the concentration increases. McDowell7,21 found a useful empirical equation which can be applied to a wide variety of alginates:

$$\log_{10}(\text{viscosity}) = a\sqrt{\text{concentration}} - b$$

where a is a constant related to the DP of the alginate and b is a constant for a particular type of alginate. It should be noted that higher concentrations are normally preferred in the wet-spinning process for a high production efficiency and generally good fiber properties, since as-made fibers from a spinning solution with a high solid content have a higher wet strength and are relatively easy to carry out the stretching and washing processes. However, high solution viscosities make it difficult to remove bubbles in the solution brought in during the mixing process. For practical reasons, wet-spinning processes typically use aqueous solutions containing 5–6% sodium alginate as the spinning solution.

Temperature of the solution
The viscosity of alginate solutions decreases as temperature increases, at a rate of about 2.5% per degree Celsius. Since viscosity drops sharply on heating, it is useful to heat a solution during the dissolution process. However, if alginate solutions are kept above 50°C for several hours, depolymerization may occur, giving a permanent loss of viscosity and molecular weight. During the preparation of alginate spinning solutions, it is usual to use high-shear mixers and the solution temperature is raised.
by the heat generated from high levels of shearing. This is beneficial since the reduced viscosity helps the bubbles to rise from the spinning solution. However, a prolonged storage of the alginate solution at high temperatures will have a detrimental effect on its molecular weight.

**pH of the solution**
The viscosity of alginate solutions is unaffected over the range pH = 5–11. Below pH = 5, the free –COO⁻ ions in the chain start to become protonated, to –COOH, and as the electrostatic repulsion between chains is reduced, they are able to come closer and form hydrogen bonds, producing higher viscosities. When the pH is further reduced, a gel will form, usually between pH = 3 and 4. Above pH = 11, slow depolymerization occurs on storage of alginate solutions, giving a fall in viscosity. For the wet-spinning of alginate, the spinning dope is normally prepared by dissolving sodium alginate in deionized water, with pH at around 7.

**PRODUCTION OF CALCIUM ALGINATE FIBERS**
In terms of the manufacturing process, calcium alginate fiber 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 to remove the bubbles in the solution, a concentrated sodium alginate solution can be extruded through fine spinneret holes into a calcium chloride bath, whereby sodium alginate is precipitated out in filament form as a calcium alginate fiber (the later being insoluble in water). The as-made fibers can then be stretched, washed and dried to produce calcium alginate fibers. Figure 3 shows schematically a small wet-spinning production line.

It should be pointed out that solutions of sodium alginate can react with many di- and trivalent cations to form gels; hence it is possible to use a variety of metal ions to precipitate sodium alginate solution during the wet-spinning process. In the production of alginate fibers, calcium has found greatest popularity as the divalent ion for gel formation, mainly because its salts are cheap, readily available and non-toxic. Zinc chloride has also been used for the production of zinc alginate fibers.

Figure 4 shows the egg-box model for alginate gel formation. During the extrusion process where sodium alginate is extruded into a calcium chloride bath, the buckled chain of guluronic acid units acts as a two-dimensional analogue of a corrugated egg-box with interstices in which the calcium ions may pack and be coordinated, and while calcium ions help to hold the alginate molecules together, their polymeric nature and their aggregation bind the calcium ion more firmly, resulting in a firm gel structure. As can be seen in Fig. 5, the structure of the guluronic acid block gives distances between carboxyl and hydroxyl groups which allow a high degree of coordination of the calcium ion.

During the production of calcium alginate fibers, calcium ions from the coagulation bath diffuse into the fiber to form a swollen fibrous gel. Thomas et al. studied the diffusion of calcium ions during the wet-spinning process. Their results showed that the gelling time of calcium alginate fiber varied linearly with alginate concentration, increased markedly with fiber radius and decreased with increasing calcium concentration. It is interesting that the gelling time is independent of the guluronic acid and mannuronic acid contents. Gelling time for a given sodium alginate filament can be calculated from the following empirical equation:

\[
T = \frac{ER^2}{4DC + ER/2KC}
\]

**Figure 4. Egg-box model for alginate gel formation.**
where $T$ is the gelling time (s), $R$ the radius of fiber (m), $E$ the stoichiometric constant (kmol m$^{-3}$), $D$ the diffusivity (m$^2$ s$^{-1}$), $C$ the calcium chloride solution strength (kmol m$^{-3}$), and $K$ the mass transfer coefficient (m s$^{-1}$).

Experimental results showed that when the fiber radius increased from 0.65 to 3.0 mm, the time required for gelling increased from 200 to 3500 s. For a wet-spun filament, the typical radius is about 100 µm, and the time required for coagulation is about 5 s.

Speakman and Chamberlain$^{25}$ made a detailed study on the production of calcium alginate fibers. They made fibers from a series of alginates with different molecular weights, characterized with different times of fall of a steel ball. As can be seen in Table 3, when the ball falling time increased from 2.0 to 174.0 s, indicating a large change in molecular weight, the fiber strength varied between 1.45 and 1.68 g d$^{-1}$. This shows that the properties of the alginate fibers were not seriously affected by the changes in molecular weight.

Table 4 shows the properties of calcium alginate fibers made from spinning solutions with different solid contents. The best result was obtained when the solid content was 3.92%. As the concentration increased, solution viscosity became too high and it was difficult to spin the fiber. However, fibers made with a high concentration of alginate had a good luster, with the cross-section assuming a circular shape. As can be seen in Fig. 6, when the solid content increased from 2.25 to 8.88%, the cross-section of the fibers changed from an irregular shape to a circular shape.

**PRODUCTION OF CALCIUM SODIUM ALGINATE FIBERS**

Alginate fibers are mainly used for the production of wound dressings, where absorption of wound fluid is a key performance criterion. During the development of alginate wound dressings, calcium alginate fibers were chemically treated to convert them into a mixed salt containing both calcium and sodium ions, the calcium ions giving the fiber wet integrity, the sodium ions giving the fiber absorbency. In the process for making calcium sodium alginate fibers, the calcium alginate fibers are first washed with hydrochloric acid to replace part of the calcium ions with hydrogen ions. The calcium ions giving the fiber wet integrity, the sodium ions giving the fiber absorbency. In the process for making calcium sodium alginate fibers, 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 calcium and 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.26

In order to make alginate fibers with different amounts of sodium ions, the calcium alginate fibers can be treated with aqueous solutions containing different amounts of Na2SO4. Na2SO4 is used because the solubility of CaSO4 in water is only 0.209 g per 100 mL at 30 °C; hence it can easily replace calcium ions from the alginate fibers. Table 5 shows the calcium and sodium contents after the calcium alginate fibers were treated with aqueous solutions containing various levels of Na2SO4. It is clear that, as the Na2SO4 concentration increases, more and more calcium ions were replaced by sodium ions. Gel-swelling results show that whilst the original sample swelled only a little in water, with a gel-swelling ratio of 1.8, there were significant increases in the gel-swelling ratio as more and more calcium alginate was converted into sodium alginate. As can be seen in Fig. 7, gel-swelling ratio rose as the fiber sodium content increased, with the 0.7% Na2SO4-treated sample showing a gel-swelling ratio of 21. Figure 8 shows photomicrographs of alginate fibers with various levels of sodium contents. It is clear that the sodium contents in the alginate fibers have a significant effect on the absorption and gelling properties of the fiber.27

Table 5. Effect of Na2SO4 concentration on fiber calcium content and gel-swelling ratio27

<table>
<thead>
<tr>
<th>Na2SO4 concentration (%)</th>
<th>Fiber Ca(II) content (%)</th>
<th>Fiber Na(I) content (%)</th>
<th>Alginic acid as Na(I) salt (%)</th>
<th>Gel-swelling ratio in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>8.35</td>
<td>0.20</td>
<td>2.0</td>
<td>1.8 ± 0.15</td>
</tr>
<tr>
<td>0.1</td>
<td>6.55</td>
<td>1.25</td>
<td>14.2</td>
<td>6.5 ± 0.45</td>
</tr>
<tr>
<td>0.2</td>
<td>6.45</td>
<td>1.6</td>
<td>17.7</td>
<td>8.5 ± 0.65</td>
</tr>
<tr>
<td>0.5</td>
<td>5.65</td>
<td>1.55</td>
<td>22.2</td>
<td>11.1 ± 0.80</td>
</tr>
<tr>
<td>0.7</td>
<td>5.95</td>
<td>2.65</td>
<td>27.9</td>
<td>21.0 ± 1.50</td>
</tr>
</tbody>
</table>

Figure 8. Photomicrographs of alginate fibers with (a) 2.0%, (b) 17.7% and (c) 27.9% sodium alginate, wet in water (×200).

**PRODUCTION OF SODIUM ALGINATE FIBERS**

Sodium alginate fibers can be produced by extruding a sodium alginate solution into an organic solvent bath. Kobayashi et al.28 made extensive investigations and found that it is possible to produce sodium alginate fibers by extruding an aqueous sodium alginate solution into a coagulating bath containing a large quantity of a hydrophilic organic solvent in which sodium alginate is insoluble. The prompt displacement of water in the spinning solution by the organic solvent produces continuous filaments of sodium alginate.

To prepare sodium alginate fibers, a 5% aqueous sodium alginate solution is first made by adding the sodium alginate powder to distilled water and stirring for about 4 h. The solution is filtered through a 200-mesh filter cloth to prepare a dope. After being stored overnight under reduced pressure, the dope was extruded at a rate of 12 g min−1 into a coagulating bath of varied non-solvents at 18 °C, through a spinneret...
plate with 1000 holes, each having a diameter of 0.1 mm. The resultant fibers were rolled at a rate of 0.5 m min⁻¹ onto a godet roller. The fibers were immersed in acetone, and then dried at 100 °C.

Table 6 shows the properties of the resultant sodium alginate fibers made with different types of coagulation bath. It appears that although sodium alginate fibers can be made by extruding its solution into various organic solvents, the fiber tenacities are generally low. The highest tenacity of 0.338 g d⁻¹ obtained with isopropanol is much lower than a typical fiber tenacity of about 1.8 g d⁻¹ for calcium alginate fiber.

In another experiment, sodium alginate solution was extruded into acetone at 13 °C at a rate of 16.4 g min⁻¹ through a spinneret plate with 1000 holes, each having a diameter of 0.1 mm. The resultant fibers were rolled onto a godet roller with a diameter of 11.2 cm at varied rotation rates. Table 7 shows the fineness and strength of the sodium alginate fibers made with different take-up speeds. It is clear that as the take-up speed increases, the fibers were drawn finer and since there is more orientation of the polymeric molecules along the fiber axis, there was also a significant improvement in the fiber strength.

PRODUCTION OF ALGINIC ACID FIBERS

Alginic acid fibers can be made by either a direct extrusion of sodium alginate solution into an aqueous bath containing sulfuric acid, where sodium alginate precipitates out as water-insoluble alginic acid, or by the conversion of calcium alginate fiber into alginic acid fiber in fiber form. Because alginic acid is insoluble in water, the removal of calcium ions with hydrochloric acid can be carried out in an aqueous medium. The reaction proceeds according to the following equation:

\[
\text{Calcium alginate} + 2\text{HCl} \rightarrow \text{alginic acid} + \text{CaCl}_2
\]

Table 6. Properties of sodium alginate fibers made with different types of coagulation bath

<table>
<thead>
<tr>
<th>Coagulating bath</th>
<th>Fiber fineness (denier)</th>
<th>Fiber tenacity (g d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>5.463</td>
<td>0.236</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.734</td>
<td>0.250</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>4.491</td>
<td>0.338</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.410</td>
<td>0.312</td>
</tr>
</tbody>
</table>

Table 7. Properties of sodium alginate fibers made with different take-up speeds

<table>
<thead>
<tr>
<th>Rotation rate (rpm)</th>
<th>Fiber fineness (denier)</th>
<th>Fiber tenacity (g d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.90</td>
<td>0.447</td>
</tr>
<tr>
<td>8</td>
<td>2.94</td>
<td>0.811</td>
</tr>
<tr>
<td>16</td>
<td>1.54</td>
<td>0.602</td>
</tr>
<tr>
<td>24</td>
<td>0.95</td>
<td>0.969</td>
</tr>
<tr>
<td>32</td>
<td>0.71</td>
<td>1.100</td>
</tr>
</tbody>
</table>

In this process, the alginate fibers remain in the solid state, whilst the calcium ions are washed into the solution. It has been shown that 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⁻¹ aqueous HCl solution at room temperature. No calcium ions were found in the fibers after 20 min of treatment.

PRODUCTION OF ZINC ALGINATE FIBERS

In clinical practice, zinc ions can generate immunomodulatory and anti-microbial effects, as well as activation of matrix metalloproteinases that facilitate auto debridement and keratinocyte migration, and topical applications of zinc-containing wound dressings are common in wound management. Topical zinc oxide has been found to aid treatment of leg and pressure ulcers.

Since alginate is a polymeric acid, it is easy for alginate fibers to carry zinc ions by forming salt with zinc ions. Zinc alginate fibers can be made by a direct extrusion of sodium alginate solution into a zinc chloride coagulation bath, or by treating calcium alginate fibers with aqueous zinc chloride solution where, after the ion exchange between calcium ions in the fiber and zinc ions in the solution, the fiber becomes a mixed calcium and zinc alginate. Table 8 shows the zinc content and zinc release results for alginate fibers treated with zinc chloride. It is clear that after the calcium alginate fibers were treated with ZnCl₂ solutions, both the high-G and high-M calcium alginate fibers contain a significant amount of zinc ions. When placed in solution A (a solution with similar levels of calcium and sodium ions to body fluid, defined in the British Pharmacopoeia as an aqueous solution containing 142 mmol of sodium chloride and 2.5 mmol of calcium chloride), the zinc ions can be replaced by sodium ions in the contacting solution in a similar way to calcium ions, resulting in the release of zinc ions.

Table 8. Zinc release from ZnCl₂-treated alginate fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>High-G calcium alginate fiber</th>
<th>High-M calcium alginate fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca content after ZnCl₂ treatment (%)</td>
<td>2.75</td>
<td>3.05</td>
</tr>
<tr>
<td>Zn content after ZnCl₂ treatment (%)</td>
<td>7.75</td>
<td>10.5</td>
</tr>
<tr>
<td>Zn content in extract solution, after 60 min (ppm)</td>
<td>461</td>
<td>495</td>
</tr>
<tr>
<td>Zn content in extract solution, after 24 h (ppm)</td>
<td>441</td>
<td>632</td>
</tr>
<tr>
<td>Zn content in extract solution, after 48 h (ppm)</td>
<td>449</td>
<td>640</td>
</tr>
</tbody>
</table>
from the zinc-containing alginate fibers is easier with high-M type alginate fiber. After 48 h in contact with solution A, the zinc contents were 640 and 449 ppm, respectively, in the high-M and high-G alginate samples.

**PRODUCTION OF SILVER-CONTAINING ALGINATE FIBERS**

Silver has a long history as an anti-microbial agent, especially in the treatment of burns. While metallic silver is relatively inactive, silver ions are effective against a wide range of bacteria. When low concentrations of silver ions accumulate inside cells, they can bind to negatively charged components in proteins and nucleic acids, thereby effecting structural changes in bacterial cell walls, membranes and nucleic acids that affect viability. Although silver is a highly effective anti-microbial agent, it has a limited toxicity to mammalian cells. In recent years, silver has been gaining importance in the wound management industry, and a number of silver-containing wound dressings have been developed. These function by the sustained release of low concentrations of silver ions over time, and generally appear to stimulate healing, as well as inhibiting micro-organisms. A number of laboratory studies have shown the excellent anti-microbial performances of silver-containing wound dressings.

Since alginate wound dressings are highly absorbent, they are mainly used on highly exuding wounds where microbial infection is common. By incorporating silver ions into alginate fibers, it is possible to obtain highly absorbent wound dressings with good anti-microbial properties.

Since alginate is a polymeric acid, it can form salt with silver ions. However, unlike calcium alginate, which is highly insoluble in water, silver is a monovalent ion and when sodium alginate solution is extruded into a silver nitrate solution, it is difficult to form silver alginate fiber. A mixed solution of calcium chloride and silver nitrate can be used to produce fibers that are a mixture of calcium alginate and silver alginate. Table 9 shows the calcium and silver contents of alginate fibers made with a mixed coagulation bath containing calcium and silver ions.

![Table 9](https://example.com/table9.png)

In order to attach silver ions onto the alginate fibers, calcium alginate fibers can be treated with aqueous solutions of silver nitrate. The silver ions in the solution exchange with calcium ions in the fiber, resulting in the formation of calcium alginate fiber containing silver ions. These fibers are highly anti-microbial. However, due to the oxidative power of the silver ions, they are sensitive to light exposure and can become dark-to-black in appearance.

Adding particles of water-insoluble silver compounds into the alginate fiber is one way to avoid oxidation and maintain the white physical appearance that is highly desirable for a biomedical material. Le et al. developed a method to incorporate silver sulfadiazine (SSD) into alginate fibers by mixing water-soluble sodium sulfadiazine with sodium alginate to form a spinning solution, which was then extruded into a 2% calcium chloride solution containing silver nitrate. During the fiber-forming process, sodium alginate reacts with calcium ions to form the filament, whilst sodium sulfadiazine reacts with silver ions to form SSD, which is deposited inside the fiber structure. Alternatively, after sodium sulfadiazine and sodium alginate are dissolved to form a spinning solution, silver nitrate is added into this solution before extrusion. In this process, the SSD particles formed through the reaction between sodium sulfadiazine and silver nitrate is dispersed in the spinning solution. When extruded to form fiber, the SSD particles are embedded in the fibers.

As mentioned before, although silver is a highly effective broad-spectrum anti-microbial agent, it is also highly oxidative to organic materials. Skin discoloration and irritation associated with the use of silver nitrate is well known. In order to protect the host material from oxidation and discoloration, some novel silver-containing compounds have been developed in recent years and these have been made into fine particles that can be blended with fiber-forming polymers during extrusion.

AlphaSan RC5000 is a silver sodium hydrogen zirconium phosphate. This microbiologically active ingredient is a synthetic inorganic polymer. Under a scanning electron microscope, it resembles cube-shaped crystals, with an average particle size of about a micrometer. It consists of a three-dimensional, repeating framework of sodium hydrogen zirconium phosphate, with many equally spaced cavities containing silver. Silver (at 3.8% by weight) provides the main anti-microbial properties, while the framework matrix acts to distribute silver evenly (without clumping or pooling) throughout the individual fibers where the AlphaSan particles are added.

When AlphaSan RC5000 is mixed with sodium alginate solution, the fine particles can be evenly distributed in the spinning solution under a high rate of shearing. Because the particles are very fine, they can
be suspended uniformly while the solution is extruded to form fibers. Since the sodium hydrogen zirconium phosphate framework prevents the silver ions from oxidizing the alginate, this type of silver-containing alginate fiber remains white even after sterilization through irradiation.\textsuperscript{40}

When alginate fibers containing AlphaSan RC5000 particles are in contact with wound exudates, the silver ions can be released into the wound exudate by three mechanisms. First, there is an ion exchange between the silver ions in the fiber and the sodium and calcium ions in the wound fluid. Second, silver ions can be chelated by protein molecules in the wound fluid. Third, AlphaSan particles attached on the surface of the fibers can also be detached from the fibers and get into the wound exudate.

Table 10 shows the results of the silver ion concentration when alginate fiber containing 1% AlphaSan RC5000 is placed in contact with normal saline or human serum. It can be seen that the silver ions are slowly released into the solution, acting as an anti-microbial agent. More silver ions can be seen to release into human serum, suggesting the high silver-binding abilities of protein components in the wound exudates.\textsuperscript{41}

Figure 9 shows the anti-microbial action of silver-containing alginate fibers against \textit{Pseudomonas aeruginosa}. There was a 100% reduction in bacteria count within 5 h when the fibers were placed in contact with solutions containing the bacteria. Under similar test conditions, the silver-containing alginate fibers had far better anti-microbial effect than other common alginate fibers.\textsuperscript{41}

<table>
<thead>
<tr>
<th>Table 10. Silver concentrations in contact solutions\textsuperscript{41}</th>
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<tbody>
<tr>
<td><strong>Duration of contact</strong></td>
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<tr>
<td>30 minutes</td>
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<tr>
<td>48 hours</td>
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<td>7 days</td>
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**Figure 9.** Anti-microbial action of silver-containing alginate fibers against \textit{Pseudomonas aeruginosa}.

**PRODUCTION OF ALGINATE FIBERS CONTAININGPECTIN AND CARBOXYMETHYL CELLULOSE**

By blending other water-soluble materials into the spinning solution, it is possible to improve the absorption capacity of alginate fibers by breaking the regular structure of the fibers and making it easy for ion exchange to take place. Qin and Gilding\textsuperscript{42} prepared fibers from a mixture of alginate, carboxymethyl cellulose (CMC) and pectin. A spinning dope was prepared by mixing 12 kg of sodium alginate, 1.5 kg of CMC and 1.5 kg of high-methoxy pectin in 235 L of water. After storage at room temperature for two days to remove the bubbles, fibers were produced by extruding the dope through a 40,000-hole spinneret (hole diameter 70 µm) at 12 m min\(^{-1}\). The as-spun fibers were taken up at 7.2 m min\(^{-1}\) and then stretched at 80 °C to 9 m min\(^{-1}\). The fibers were then washed with water before they were dried by first passing the fibers through an acetone bath and then drying with heated air. Finally, the dry tow was crimped and cut to produce staple fibers. In another example, fibers were made from alginate and CMC by first mixing 13.5 kg of sodium alginate and 1.5 kg of CMC in 235 L of water. The fibers could be spun and carded into a non-woven dressing. The alginate/CMC dressing as produced in this way had an absorbency of 19 g g\(^{-1}\) as compared to 17 g g\(^{-1}\) for dressings made from fibers without the addition of CMC under exactly the same processing conditions.

**PRODUCTION OF OTHER NOVEL ALGINATE FIBERS**

From a wet-spinning point of view, the production process for alginate fibers is one of the cleanest processes used for manmade fibers. The dissolution of sodium alginate takes place in pure water and at neutral pH, whilst coagulation can take place in a dilute aqueous CaCl\(_2\) solution, again at a neutral pH and at room temperature. This makes it easy for alginate to be used as a carrier for biologically active compounds that can be added into the fibers and still maintain their bioactivities in the finished fibers.

Fan \textit{et al.}\textsuperscript{43} prepared fibers from alginate and gelatin blends by spinning their solution through a viscose-type spinneret into a coagulating bath containing aqueous CaCl\(_2\) and ethanol. The highest tensile strength was obtained when the gelatin content was 30 wt% of the overall solid content. The water retention values of the blend fibers increase with increasing gelatin contents. There was strong interaction and good miscibility between alginate and gelatin molecules, as a result of intermolecular hydrogen bonds.

Wang \textit{et al.}\textsuperscript{44} prepared fibers from blends of alginate and soy protein by spinning their solution through a viscose-type spinneret into a novel coagulating bath containing aqueous CaCl\(_2\), HCl and ethanol. Fibers with 10% soy protein isolate had a tensile strength of...
14.1 cN tex$^{-1}$ in the dry state and 3.46 cN tex$^{-1}$ in the wet state, with elongation at break of 20.71 and 56.7%, respectively.

Kobayashi et al.\textsuperscript{45} used alginate fibers for enzyme immobilization. They spun an aqueous mixture of sodium alginate and enzymes into divalent metallic ion solution as a coagulating bath to produce enzyme-containing fibers. The entrapment yields of enzymes, such as glucoamylase, cyclodextrin glucanotransferase, endo-polygalacturonase and protease, were higher in the calcium alginate fibers than those found in calcium alginate beads made under similar conditions. It was found that the yields increased with increasing extrusion rate through the spinning nozzle because at a higher extrusion rate the polymeric molecules are more highly oriented along the fiber axis, which can help prevent leakage of the entrapped enzymes.

**SUMMARY**

Alginate is a natural polysaccharide with an abundant supply in nature. By processing alginate into fibers, it is possible to obtain novel biomaterials that can be processed further into woven, knitted, non-woven and many other forms of composite structures. Because alginate is a polymeric acid, alginate fibers can be used as a carrier to deliver zinc, silver and other bioactive metal ions for wound care and other novel applications. In addition, since processing takes place in an aqueous solution and in an aqueous coagulation bath at a neutral pH, many bioactive materials, such as drugs and enzymes, can be combined into the alginate fibers, without loss of their bioactivity.

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**REFERENCES**
