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Alginate fibers

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3.1 Introduction

Historically, the use of seaweed extracts for food and medicine can be traced back as far as 3000 BC. Alginate in one form or another is used in the food industry, pharmaceuticals and textiles.[1] Stanford,[2] a British scientist, is reputed as the pioneer in scientific literature of alginate. In 1880 he described a new process for the extraction of iodine and salts from seaweed. The residual material, after extraction, which was unaltered in appearance, was found to contain a substance that had not been isolated before. He named this substance 'algin'. He obtained his first soluble 'algin' by extracting seaweed with sodium carbonate and a second insoluble product by acidifying a solution of the first product. He was convinced that his 'algin' was a nitrogen compound. In his later investigations of the 'algin', he realized that it behaved as an acid, i.e. forming salts with metals and liberating carbon dioxide from sodium carbonate, prompting him to rename it 'alginic acid'.

3.1.1 Types of alginates

The most important source of commercial alginates is brown algae. Alginate is the main constituent of brown algae and is found in the cell wall and intercellular regions.[3–6] However, only three types of brown algae are sufficiently abundant or suitable for commercial extraction of the alginic acid. In order of abundance, they are laminaria (British Isles, Norway, France, N. America, Japan), microcystis (USA), and ascophyllum (British Isles). The high viscosity alginate in commercial use has a molecular weight of about 150,000 and a degree of polymerization (DP) of about 750 but the average molecular weight of ordinary alginate is 15,000.[7,8]

Laminariales are the largest algae and most complex. They are composed of a lamina (frond), a stipe (stem) and a basal (roots). Plants of laminaria vary in length with age, reaching a maximum of 3 metres and since they present a large surface area to a turbulent environment, need to be firmly

anchored to the substratum. Marine algae in general may be said to be indifferent to the chemical composition of the substratum[8] in that unlike surface plants, which absorb their nutrients from the soil, they absorb minerals directly from the sea over their whole surface.[1,9] Harvesting is easy because most brown seaweed grow in shallow water. Table 3.1 gives the botanical sources of alginate used in the industry.

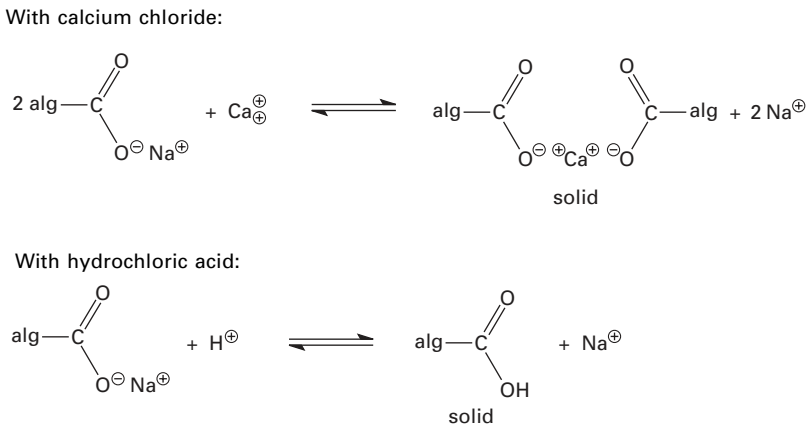
Table 3.1 Industrial source of alginate[1]

Genus	Species	Country	Marine location
Microcystis	*pyrifera*	USA	Fixed by holfast in deep water
Microcystis	*intergrifolia*		
Laminaria	*digitata*	Europe and Japan	Sulittoral
Laminaria	*saccharina*		
Laminaria	*flexicaulis*		
Laminaria	*stenphylla*		
Ascophyllum	*nodosum*	Europe	Littora
Nereocystis	*luetkeana*		
Fucus	*vesiculatosus*		
Fucus	*serratus*		
Fucus	*spiralis*		
Ecklonia	*maxima*	South Africa	Littora
Pelvetia	*canaliculata*		

3.1.2 Manufacturing process of alginate and alginate fibers

The manufacture of alginate fibers[10] consists of the following steps. Seaweed is collected, dried and milled. The powdered seaweed is treated with aqueous sodium carbonate and sodium hydroxide, which convert the alginate present to the sodium salt. The pigment and the cellulose present in the seaweed are not dissolved. The viscous solution of sodium alginate is purified by sedimentation then bleached and sterilized by the addition of sodium hypochlorite. The alginic acid is then precipitated by acidification, which is later washed and reconverted to the pure sodium salt. The sodium alginate salt is made into a thick paste, dried and milled to make sodium alginate powder. A dilute solution of sodium alginate is made, filtered, then spun by the viscose spinning method into a coagulation bath (wet spinning) containing certain polyvalent cation salts (Ca^{++}, Al^{+++}, etc.) or inorganic acid solution; about 0.02N hydrochloric acid, emulsified oil, and a small quantity of a cationic surface agent. The water soluble sodium alginate is thus precipitated in filament form as an alginic acid metal salt, e.g. calcium alginate or alginic acid. The filaments are drawn together, washed, lubricated, dried and wound

onto bobbins or cut (sometimes stretched to break the fibers by varying the relative feed rates which control the degree of stretch-breaking effect) to the required staple length suitable for non-woven products. The process is a chemical reaction and proceeds as follows in Fig. 3.1. As calcium or hydrogen ions are exchanged with sodium ion, the reaction proceeds until the sodium alginate is converted to calcium alginate or alginic acid.[11]

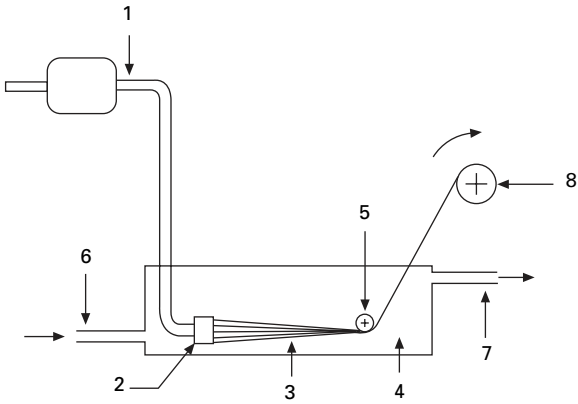


3.1 The precipitation process of sodium alginate/water solutions.

Speakman *et al.*[12] carried out the successful development of alginic acid fibers. One of their products was a green coarse monofilament of chromium alginate. Later they made multifilament yarns of calcium alginate, which were white in color and silk-like in appearance. Their ready solubility in weak alkaline solution, including soap, made it difficult to develop them as fibers for commercial use. A flow chart of the alginate manufacturing process has previously been described[11] and alginate can be wet spun in apparatus similar to those used for spinning regenerated cellulose fibers (Fig. 3.2).

There are many possible technical designs of wet-spinning processes. The precipitation (coagulation) bath can be situated horizontally or vertically (fiber moving upwards or downwards). Further manufacturing operations (drawing, washing, drying, etc.) can be realized continuously or periodically as separate operations.

The morphological structure of fibers is very sensitive to the composition and condition within the precipitating bath. A number of methods for producing conventional alginate fibers are described in literature.[13–15] Typical calcium alginate fibers may be prepared as follows: a 6.4% by weight aqueous sodium alginate solution is extruded through a jet containing 20 holes into a bath containing 5% salt of calcium chloride, a 0.2% acetic acid and 0.05% cetyl pyridinium chloride (cation active compound) at 40°C. By this process, it is possible to obtain alginate fibers which do not adhere to one another without



3.2 Scheme of a horizontal wet spinning system. 1. inlet of the spinning dope; 2. spinneret; 3. spinning line; 4. coagulation bath; 5. take-godet; 6. and 7. inlet and outlet of the spinning bath.

addition of emulsified oil to the bath. The threads produced are 37% stretched by passing them over godets and reeled into skeins. They are then washed in a 0.1% solution of calcium chloride at 80°C and then dried at room temperature and conditioned.

3.2 The chemical nature of alginate materials

3.2.1 Chemical structure and composition of alginates

The molecular structure of alginates may be considered from three different though interrelated points of view. There is the chemical structure which describes the nature and sequence of constituent units, the conformations which describe the arrangement in space and the intermolecular interactions. These are discussed in this section.

Alginate is a natural occurring polymer and is the major matrix polysaccharide in brown seaweed. It occurs as an insoluble complex of potassium, sodium, calcium and magnesium.[16] Dillon and McGuinness[17] suggested that alginic acid was a polymer of mannuronic acid. In addition Lunde, Heen and Oy[18] suggested that alginic acid had a pyranose structure. This view was supported by Hirst, Jones and Jones's[19] study of methylated alginic acid. Research work by Fischer and Dorfel[20] showed that guluronic acid was also present in alginic acid. Alginic acid consists of two uronic acids, β-D-mannuronic acid and α-L–guluronic acid. Work carried out on the acetylation of alginic acid[17] confirmed that the pyranose structure was correct and closely related to the cellulosic type structures. Similar to cellulose, alginic acid has a long linear chain structure consisting of a large number of pyranose rings turned through 180° to each other and linked by a $\beta(1 \rightarrow 4)$

glycosidic bridge.[21] The importance difference between these two polymers is the side groups attached to C5. Cellulose has a hydroxymethyl group ($-CH_2OH$) whereas alginic acid has a carboxyl group (–COOH).

In 1967 Haug *et al.*[22] showed by free boundary electrophoresis that both heterogeneous and homogenous acid hydrolysis led to a splitting of the alginic acid molecule into chemically different fragments. It was found that alginic acid was a block copolymer containing long sequences of an alternating structure of both mannuronic acid and guluronic acid residues. The arrangement of the polymannuronic acid chain is similar to that found in cellulose in which the individual pyranose rings lie at a very small angle to the polymer chain in a zig-zag formation. The corresponding angle in polyguluronic acid is larger and in an alternating sequence, the repeating unit alternates between the two angles. For convenience the three blocks in the chain can be represented as:

$$—[GG]_m—[MM]_n—[MG]_p—$$

The values of n, m and p are not necessarily constant within a polymer chain.

The conformation seems to be stabilized by the formation of intramolecular hydrogen bonds between the hydroxyl group on C3 of one unit and the ring oxygen atom of the next unit in the chain. The molecular chains are bonded into sheets by means of hydrogen bonds formed between the hydroxyl of the carboxyl group and the oxygen atom on C3 in the pyranose ring in parallel chains and between the axial hydroxyl group on C2 and the oxygen atom of the carboxyl group in anti-parallel chains.[23]

The physico-chemical and biological properties are dependent on the relative proportions of these blocks and their average lengths. The carboxylic acid group in the unit makes it more reactive than cellulose and contributes to its solubility in alkaline conditions and with some sequestering agents. The ratio of mannuronic to guluronic units in an alginate molecule is referred to as M/G ratio. The M/G ratios indicate, indirectly, the proportions of the blocks within an alginate molecule, which in turn give rise to the specific properties of that alginate molecule.

3.2.2 Chemical properties of alginic acid

For short periods of time, alginate is unaffected by acids and alkalis at room temperatures. On heating to 80°C and at pH values above 9, depolymerization occurs and unsaturated derivatives are formed. At pH values below 2 the rate of hydrolysis depends on the dissociation of the carboxyl groups on the alginate monomers. Acid hydrolysis of alginate occurs in both strong and weak acids, but at a slower rate than most neutral polysaccharides. Alginate salts are soluble between pH 5–10 at room temperature, however, outside this pH range, degradation is considerable.[23]

Univalent metals such as sodium and potassium give salts of alginic acid which are soluble in water and form smooth solutions having good flow properties. Soluble alginates are easily and quickly dissolved in soft water with the aid of a stirrer. Hard water may result in precipitation of insoluble alginate salts. The addition of divalent cations to an alginic solution reduces the solubility of the polymer resulting in precipitation or, if the concentration and molecular weight are sufficiently high, gelation. The gel is not thermally reversible but can be re-dissolved by ion-exchange of the divalent for a monovalent cation. The salts of univalent metals (except silver) are soluble in water since no cross-links are formed.

Some salts and derivatives of alginates and their special features are shown in Table 3.2. The most important and useful property of alginic acid is the ability to form water insoluble salts by reaction with multivalent metal ions. The insoluble alginic acid in water is easily brought into solution by neutralization with sodium hydroxide to form a highly ionised salt. The alginate poly-ion therefore carries a negative charge, which reacts with positive

Table 3.2 Salts and derivatives of alginic acid[1]

Compound	Solvent	Special properties
Sodium alginate	Water	Available in a wide range of grades
Potassium alginate	Water	–
Magnesium alginate	Water	–
Ammonium alginate	Water	Low ash content
Calcium alginate	Calcium chelating agents	Gel formation
Aluminium alginate	Ammonium solution	–
Copper alginate	Ammonium solution	–
Zinc alginate	Ammonia and ammonium salts	–
Silver alginate	Ammonium solution	Darkens on exposure to light
Triethanolamine alginate	Water and 75% ethanol	Forms soft films
Propylene glycol alginate	Water and acidic solutions	–
Alginic acid acetate	Water	–
Alginic acid sulphate	Water	Low molecular weight ester have blood anticoagulant properties
Alginic acid amide	Hot water	Forms gel on cooling

ions. In general, alginates are insoluble in non-aqueous solvents, but some amine salts of alginate are soluble in non-aqueous solvents. Pure organic solvents have no effect on alginates.[11] The insolubility of polyvalent metal ion salts is due to association with two or more carboxyl groups on different chains; the molecule loses its freedom of movement and a close linked network structure is formed.

In the process of precipitation, the polyvalent metal alginate tends to become aligned when extruded through orifices and can be obtained in the form of fibers. If the precipitated alginate is not subjected to extrusion, the polyvalent metal alginate precipitate forms a gel, in which a large amount of water is held in the insoluble precipitate (hydrocolloid gel).

Alginate gels are randomly cross-linked networks with short extended segments in between metal ion junctions. The exact nature of the gel junction is not clear but evidence suggests that the association of the chains occurs by stacking with polyvalent ions packed between chains. Unlike the dilute solution properties where isolated molecules are considered, gelling is concerned with the interaction between alginate chains.[11] Ion binding and gelling are closely linked properties of alginate and are important in understanding its behavior. Calcium ion chelation to alginate chains has been investigated by circular dichroism (c.d.) and by equilibrium dialysis in the presence of various concentrations of sodium chloride.[24] These results together with the work on X-ray diffraction of alginate led to the theory of an 'egg box' structure where a cooperative interchain binding the calcium alginate gel is formed. Ion selectivities, in exchange reactions between monovalent and divalent metal ions, have been investigated by Haug and Smidsrod.[25,26] Interaction between alkaline earth metal ions such as calcium and magnesium show that the extent of exchange increased as the content of guluronic acid residues increased. Guluronic acid rich alginates (low M/G ratios) therefore have a higher Ca^{++} binding activity than mannuronic acid rich alginate.[5,25,27,28] A strong auto-cooperative binding of Ca^{++} ion occurs between the chains in the gel state. Compared to other acidic polysaccharides, this property of guluronic acid is unique. Work on the ion selectivity of polyuronides led to the speculation that the divalent ions, especially Ca^{++} are bound at two or more points on the uronic acid monomer.[1]

3.2.3 Properties of alginate solutions

The viscosity of a particular molecular weight of alginate solution is affected by temperature and concentration.[7] The viscosity of salt alginate solutions decreases with increasing temperature and this effect is reversible unless temperatures are so high as to cause partial depolymerization of the molecules which then results in a viscosity decrease. In addition the viscosity of sodium alginate is pH sensitive. It is constant in the pH range 5–10. Below 4.5, a

significant increase in viscosity occurs and below pH 3, insoluble alginic acid is precipitated. The concentration of sodium alginate affects its flow properties and for a 2.5% medium-viscosity sodium alginate solution (w/v) the behaviour is pseudoplastic at high shear rates, 10–10,000 sec^{-1}, whereas a 0.5 % (w/v) solution of the same sodium alginate can behave in a Newtonian manner at low shear rates. Pseudoplastic behavior[29] at this concentration is typically only seen at high shear rates, 1000–10,000 sec^{-1} The addition of increasing amounts of non-aqueous water miscible solvents such as glycol, acetone, etc. to alginate solution results in viscosity increases and eventual precipitation.

3.3 Physical properties of alginate-based materials

3.3.1 Structure property relationships

The modulus of calcium alginate materials is directly proportional to the level of cross-linking in the system. Microscopical work[24] has shown that structural differences can be seen on alginate gels by varying the type of the metal ion used in gel formation. The modulus is also dependent on the type of divalent metal used, and increases with increasing affinity of the polyuronate for the divalent metal:

$$Pb^{++} > Cu^{++} > Cd^{++} > Zn^{++}, Ni^{++}, Co^{++} > Mn^{++}$$

The stiffness of the molecular chain of alginates has been compared with other polysaccharides by Smidsrod *et al.*[26] Alginates are found to be stiffer than the similar polymers like carboxymethylcellulose (Brucker *et al.*[30] and Smidsrod *et al.*[26]). The stiffness is also dependent upon polymer composition and L-guluronic acid rich alginates posses a more rigid chain conformation than D-mannuronic acid rich alginates. The molecular stiffness of the three types of alginate blocks in solution decreases in the order:

$$(G)_n > (M)_n > (MG)_n.$$

Unlike calcium polyguluronate, calcium polymannuronate does not form gels with any significant rigidity. The number and strength of the gel network junctions has a marked effect on the modulus of rigidity of the resulting fibers. In nature alginate occurs in brown algae as a mixed salt in which Ca^{++} ions provide gel strength to the alginate for support issues.[1] The most obvious difference observed between polymannuronate rich gel and polyguluronate rich gels is that the polymannuronate type forms voluminous, turbid slurries of aggregates whereas polyguluronate gels form rigid, transparent gels of high modulus. Gel formation has been associated with the occurrence of L-guluronic units in alginates. Alginate gels of the $(MG)_n$ type have been observed to have a low but measurable gel rigidity.[1] The modulus of rigidity indicates that alginate gels are typical viscoelastic gels.

3.3.2 Alginate fibers

Useful polymeric fibers tend to have certain things in common at both the molecular and macromolecular scale. Even though fiber uses may vary tremendously the basic tenet for useful textile fibers is that that long-chain molecules lie in a somewhat parallel arrangement along the fiber length and lateral forces to hold the molecules together and give cohesion to the fiber structure. Additionally some measure of freedom of molecular movement is often a bonus as this gives fiber extensibility and accessibility for moisture absorption and uptake of other chemicals, for example dyestuffs.[28] Alginic acid possesses a high degree of polymerization, is a linear polymer and has very reactive groups at close and regular intervals along the length of its constituent molecules. This allows hydrogen bonding and van der Waal's forces to occur and thus alginic acid is a potential fiber forming material. The functionality of the alginate chains also means that it is possible to strengthen the lateral force in the fiber by the introduction of cross-links between two active groups with a suitable agent.[12] Furthermore cross-links formed by using formaldehyde-based reagents can improve the fiber's water resistant properties by progressively decreasing hydroxyl content of the system. The promise of such an alginate system has meant that many attempts have been made to spin fibers from other alginate salts in the hope of obtaining fibers that would be suitable for normal textile use. Some metallic alginates are sufficiently resistant to alkalis and laundering conditions. In this group are beryllium, chromium and aluminium. Beryllium alginate is toxic and brittle while chromium alginate is green in colour, which in addition to issues of chromium itself, limits restricts commercial applications.[12]

As a fiber, alginates, e.g., calcium alginate can be stretched to give a high degree of orientation and to enhance fiber crystallinity as shown by sharply defined X-ray diffraction patterns. In comparison to other natural fibers, however, the degree of orientation and crystallinity of alginate is lower than in cellulose even after stretching. This is due to cross-linking of the chains by the metal ions which takes place in the chemical coagulation bath immediately as the fibers are extruded through the spinneret. Hence, the cross-linking which is vital to gel formation also decreases molecular rearrangements and thus normal stretching less effective than in conventional wet spun fiber systems. Indeed, experience has shown that 30% stretch is about the maximum before breakage occurs.[29] However, improvements can be obtained by drying the filaments under tension since they can then contract in only one direction, and straightening of the chain molecules will tend to take place. This is aided by high temperature and the presence of water, a plasticizer which allows the breaking, and reformation of bonds.

Alkali resistant alginates (beryllium and chromium) have few ionic bonds but considerable coordinate links, which are more stable. These links decrease extensibility but increase tenacity of the fibers.

Chamberlain *et al*. found that there is a relationship between metal content and tensile strength and that a 10% metal content gave the highest fiber strength. Moussavi[2] reviewed the physical properties of alginate produced by other workers and the results are summarized in Table 3.3.

Table 3.3 Physical properties of alginate fibers quoted by different workers

Type of alginate	Tenacity (cN tex^{-1})	Extension at break (%)	Density (g cm^{-3})	Reference
Calcium	15.4	14.5	–	31
Calcium	10.1	11.6	–	32
Calcium	18.3	14.0	1.78	33
Calcium	18.3	6.0	1.77	34
Calcium	12.8	14.0	1.75	35
Calcium	12.8	12.6	1.68	2
Zinc	20.4	10.0	1.77	2

When the metal content is kept constant, the tensile properties of alginate fibers are largely affected by the moisture content. Calcium alginate yarns have a dry strength comparable to that of viscose rayon (18–39 cN tex^{-1}), but their wet strength is low (< 3 cN tex^{-1}). Their extensibility is sufficiently high to meet most textile requirements both in use and in processing.[35] The variation in physical properties with moisture content is shown in Table 3.4.

Table 3.4 Variation of physical properties with humidity[35]

Atmosphere	Tenacity (cN tex^{-1})	Elongation at break (%)
Dry	20.19	10
65% relative humidity	10.46	14
100% relative humidity (saturated)	2.66	26

In some cases it has been found that the physical properties of some alginate fibers change during storage. Calcium-based and alginic acid yarns deteriorate whereas chromium- and beryllium-based yarns improve rather than deteriorate during storage under standard conditions.[31]

3.3.3 Moisture properties of alginic acid-based fibers

Dry alginic acid and its salts,[7] when exposed to the air, will pick up moisture and attain equilibrium moisture content depending on the humidity of the atmosphere and this is similar to the behavior of cellulose, but the equilibrium moisture content is generally higher for the salts of alginic acid. Moisture

content over a wide humidity range was determined by Chamberlain *et al*.[31] although some difficulty was found in obtaining precise equilibrium uptake figures. Common alginate exists as an apparently dry solid even though it may contain up to 30% of water, and in a powder form readily forms clumps even in dry climates. Furthermore, insoluble alginate fibers when freshly precipitated from solutions retain large quantities of water, even when subjected to pressure. The amount of solvent (water) retained depends upon the composition of the salt and the concentration of the solutions from which it was precipitated. After drying, the insoluble alginate fibers will swell on absorption of water. Highly swelling insoluble alginates can be obtained using mixed salts of alkali metals.[7]

3.3.4 Thermal properties of alginic acid-based fibers

Very little published work has been carried out on the thermal properties of alginate fibers. On heating below 50°C highly polymerized alginic acid depolymerizes to give a stable low molecular weight alginic acid. Sodium alginate with a degree of polymerization of 500 can be stored, without observable change, for three years at temperatures between 10°C and 20°C. But at temperatures above 50°C, degradation of high molecular weight sodium alginate can occur. The presence of moisture increases the rate of degradation. Complete breakdown to uronic acids by heating is difficult, but can be achieved at low pH and breakdown of the polymer occurs with guluronic acid decomposing more rapidly than the mannuronic acid.[7] At temperatures from 50–200°C there is a breakdown of the uronic acid units. At temperatures above 200°C there is rapid degradation and roughly one molecule of carbon dioxide is evolved for every uronic acid unit decomposed.[36]

3.3.5 Biodegradation of alginate fibers

Biodegradable polymers and fibers are renewable resources that can be used for the manufacture of polymers and fibers and are clearly of interest with increasing environmental concerns and in the long term dwindling petroleum resources. Degradation of alginate is due to a variety of factors, which include light, water, atmospheric composition, fungi and microorganisms. Moisture content plays an important role in the degradation process due to microorganisms and bacteria. The mammalian digestive system is unable to degrade alginate[49] but when considered as a medical fiber, alginate is non-toxic, non-carcinogenic, biocompatible, sterilizable and offers cheap processing by nonwoven technologies. In general, it can be thought that the short-term degradation of textile materials is an undesirable property; however, this very property is useful for alginate products in disposable wound dressings.

3.4 Industrial applications of alginates

The UK was the only producer of alginate fiber until 1971. The fiber was made into soluble yarn, which would dissolve in the scouring process. It was also used to make fabric for supporting fine lace during manufacture, as a draw thread in knitting and a small proportion of alginate fiber was utilized in the medical field.[1]

In 1970 the soluble yarn market was taken over by polyvinyl alcohol thus leaving the medical field as the main outlet of alginate fibers other than fashion and fire resistant applications.[1] The current applications of alginates are shown in Table 3.5. The unique properties of alginate and its derivatives have found applications where thickening, suspending, emulsifying, stabilizing and gel formation is required. The properties of sodium alginate allow a solution thickening effect and certain emulsifying qualities by reducing the sedimentation rates of suspended solids. An example of this is propylene glycol alginate, which has both lipophilic and hydrophilic agent. It is used to thicken dyestuff paste for textile printing because of its high solution viscosity at low concentration and it is easily removed by washing. The monovalent alkali metal derivatives are soluble and stable at low pH values and are used to emulsify acidic solutions. Similarly, alginates and alginate derivatives are

Table 3.5 Applications of alginates

Industry	Product
Food	Ice cream, frozen desserts, milk shake mixes, chocolate milk, cream cheese, cake filling and topping, bakery jellies, margarine, baking, French dressings, salad dressing, syrup and topping, fish preservation, meat preservation, sausage casings, beer foam stabilization, soft drinks, synthetic foods, etc.
Pharmaceutical and cosmetics	Suspensions, jellies, ointments, emulsions and encapsulation, tablet disintegrating agent, tablet binder, tooth paste, shaving cream, hand cream and lotions, liquid shampoos, dental impression materials, moulding compounds, active compound in antibody formation, etc.
Paper	Surface sizing, coatings, adhesives.
Textile	Textile printing, spinning and weaving of temporary fibres from calcium alginate, wound dressings such as: bandages, adhesive strip, pads of various kinds, surgical sponges, tampons, theatre curtains, etc.
Rubber products	Latex creaming, latex thickening.
Other industrial uses	Fixation of ^{90}Sr and other divalent radioactive compounds in the bloodstream of mammals and seawater, paints, ceramics and refractory linings and moulds, insecticides, flocculants, liquid fertilizers, packaging, electrical insulating paper, anti-corrosion, etc.

used in pharmaceutical and textile industries for suspending and emulsifying groups so one molecule has the properties of an emulsifier and a thickener.

The polyelectrolyte and colloidal properties of alginates are used in the protective coatings of particles and granules (encapsulation) particularly in pharmaceutical and cosmetic industries. The action of alginate as a stabilizer is less well defined than other functions. Stabilization is assumed to depend on all the above-mentioned properties and prevents the formation of large ice crystals in many dairy products.[1] Alginates can form strong films and these can be used to coat textiles and paper with a grease resistant surface, e.g. greaseproof paper.

Gelation of sodium alginate on the addition of divalent salts is a property used frequently in the food industry. The calcium–sodium ion exchange properties of alginate are exploited to form gels of controlled strength. Calcium ions are usually introduced into the sodium alginate solution slowly and in a controlled manner, either by using a calcium salt of low solubility which has the necessary degree of ionization, selecting an appropriate pH to control the solubility of certain calcium salts or the use of a chelating agent to allow a slow release of calcium.[1]

The addition of low concentrations of sodium alginate to solutions of fertilizers and insecticides provides better adhesion to the soil and plant foliage, which in turn prolongs the effective life of the chemical. Alginate gel membranes can be used to desalinate and purify seawater and sewage effluent.[37] Sodium alginate can also 'fix' radioactive metal ions from seawater.[38] Another use of alginate is in the stabilisation of ocean bottom sediment. A recent innovation is the mixed gels of calcium alginate and gelatin.[31] These mixed gels have been reported to have a better range of controlled melting points than the respective gels alone, a property needed in the food industry. It has also been used to separate the oxidant and reductant in fuel cells.[39] The use of alginate to bind the components of solid rocket propellant has been described by Kaufman.[32]

3.5 Fabrication of alginates as useful flexible substrates in medical textile-based products

The type of use, the method of manufacture, the form and ways of disposal govern the choice of fibers used in the medical field. The fiber properties influence the final product through to the ultimate applications where the requirements may be absorbency, tenacity, flexibility and biodegradability.

In medical use one can consider alginate fibers as non-toxic, non-carcinogenic, non-allergenic, highly absorbent, haemostatic, of reasonable strength, biocompatible, capable of being sterilized, manipulatable to incorporate medicants and using cheap nonwoven technology to process it.

The incorporation of biological agents into the fiber used for nonwoven

wound dressings provides a means for directly introducing such agents to the wound without a separate application and with no additional discomfort to the patient. In this regard, it may be used to introduce various therapeutic drugs for absorption through the skin or to diagnose topical skin reactivity to various agents. A recent discovery about alginate is their activity in antibody formation, antiviral properties [39] and hypocholesterolemic activity[40,41] where the alginate was found to be the active ingredient and not just a suspender. The pharmaceutical and medical industries have known about the ^{43}Ca and ^{90}Sr fixation properties of alginate for many years.[36,42,43] Alginate has been shown to be effective in reducing the absorption of ^{90}Sr from human intestines.[44,45]

Nonwoven alginate fabrics have attracted attention as disposable textiles especially in wound dressings. Shorter production cycles, high flexibility and versatility and low production cost are some of the claimed advantages. An ideal nonwoven wound dressing for medical textile must be haemostatic, have good integrity, good absorbency and excellent retention properties. The dressing must form a soft, moist, non-adherent, hydrocolloid gel upon contact with any fluid. A haemostatic action ensures that on contact with blood, calcium ions are released and exchanged for sodium ions and these interact with blood clotting cascade mechanism resulting in clot formation. High absorbency improves the efficiency of exudate uptake together with its associated toxins and other undesirable matter. A high retention capacity means that blood is retained within the dressing when it is removed from the wound and dripping of blood is minimized. Good integrity ensures that the fabric has sufficient strength when being handled. It must be flexible to provide conformability to all wound surfaces. The material must also be permeable to gases to allow sufficient oxygenation of tissues so as to promote natural healing while allowing wound gases to escape, thus preventing the wound from becoming malodorous.[46,47]

Calcium alginate is insoluble in water and therefore slow in its haemostatic action. Partial replacement of calcium ions by sodium ions (popularly known as 'conversion')[48] makes the fabric more soluble and also increases the haemostatic action.[49] Suitable medicaments are also incorporated into the fiber.[46,47] These include those which aid wound recovery like antibacterial and angiogenesis promoting agents. Popular antibacterial medicament agents such as chlorhexidine are acetate or gluconate salts prepared by treating the fiber with an aqueous solution of the medicament or its salt. Hyaluronic acid (HA) is normally employed as a sodium salt and is an active agent in wound healing and angiogenesis.[46,47]

There are various types of nonwoven wound dressings comprising the alginates discussed in literature.[50–55] Sorbsan (from the Maersk company) surgical dressing is a carded web of laid calcium alginate fibers and this is presented as a loose fiber 'rope' for cavity packing, or a ribbon for narrow

wounds or sinuses; in addition flat nonwoven pads can be applied to large open wounds. Kaltostat (from ConvaTec) is a haemostatic wound dressing comprising a carded and needle-tacked web of alginate fibers and the dressing is used on surface wounds. In both cases these materials in the presence of body fluids containing sodium ions, the fibers absorb liquid and swell and calcium ions in the fibers are partially replaced by sodium ions. The dressings then appear gel-like in appearance and these structures provide micro-environments that are believed to facilitate wound healing. The swelling properties of both Sorbsan and Kaltostat products have recently been discussed by Yimin Qin[86] in which he describes how high (M) alginate fibers exchange ions more easily than high (G) fibers. In addition, high (M) fibers have better gelling abilities than those of high (G) fibers, although the gelling ability and absorption capacity for high (G) fibers can be improved by the introduction of sodium ions into the substrate.

In another development, dried tow is crimped, staple cut and converted to nonwoven fabric by conventional carding, cross-lapping and needle punching techniques.[56] A highly absorbent nonwoven fabric has been produced by Mahoney.[57] Staple alginate fibers are processed to provide a mat and fibers in the mat are entangled by means of barbed needles. The number of layers in the mat depends upon the desired basis weight. David Tong[58] has described a process of producing a web of dry alginate fiber material suitable for making medical or surgical dressings. It is a continuous method of producing a unitary dried nonwoven web of non-bonded alginate fibers from a spinning dope containing an aqueous solution of a soluble alginate salt. A nonwoven alginate fabric has been prepared by spreading a tow of calcium alginate filaments in a flow of water and overfeeding the spread of filaments onto a water-pervious support so that the filaments cross over each other. When dried the filaments become bonded to each other at their points of contact.[59] A wound dressing of alginate staple fibers of good integrity and capable of been lifted from a wound in one single piece and having little or no residue is claimed by Susan M. Cole.[60] The integrity is imparted by subjecting the nonwoven web to a hydroentanglement process.

Mahoney *et al.*[61] have described a process of producing a nonwoven fabric from crimped and staple cut alginate fibers. The web from a conventional card is built up by the sequential laying of layers of fibers, over one another, until a web of the desired weight is achieved. The layers are joined together at a plurality of points throughout by needle punching and an embossed pattern produced on at least one of the major external surfaces of the fabric by calendaring. A detectable X-ray strip may be incorporated between the webs.

When the basis weight of a nonwoven dressing is lower than 60 g m^{-2}, reinforcing fibers of greater strength such as staple rayon are incorporated by blending with alginate fibers during web formation. The finished dressing

is packaged in a hermetically sealed envelope and sterilized with either ethylene oxide or by gamma-irradiation.

Modifications of alginate to either improve or introduce novel functional properties in the last few years are detailed in literature.[62–69] Much attention has been focused on absorption, retention properties, non-immunogenic, bioerodible implantation composition and incorporation of medicants to assist the natural haemostatic property of the fiber. In this regard, Mahoney *et al.*[70] claim to have improved the absorbency of alginate fiber by 120 times its own weight. Blending of alginate with carboxymethyl cellulose with the object of improving the swelling and reducing the brittleness of alginate fibers has been attempted.[62] Gilding has patented a porous fibrous material alginate which comprises of either zinc, copper, silver, cerium, manganese, cobalt cations and/or any cation which is an enzyme co-factor, the cation provides exchangeable ions which have wound healing properties and increased absorbency.[71]

Interesting developments have occurred in the fabrication of water soluble alginate fibers.[54] Continuous filaments of a water-soluble alginate can be obtained by extruding an aqueous spinning solution of water-soluble alginate into a coagulating bath of a large quantity of a hydrophilic organic non-solvent in which the sodium alginate is insoluble. The prompt displacement of the water in the dope with the non-solvent produces the fibers. Water-soluble alginates that may be used include, salts from sodium, lithium, potassium, magnesium or ammonium and organic amine salts and organic esters. It may contain different types of salt structures in the molecule, and can be used singly or as a mixture of two or more of the above. Sodium alginate is often preferred since it provides fibers of a high mechanical strength. The potassium salt or propylene glycol ester maybe used together with the sodium alginate. The aqueous dope may contain 5–10% by weight of the water-soluble alginate. When the concentration is too small, neither coagulation nor formation of alginate filaments takes place. The coagulation medium is an organic solvent that is water miscible but is also a non-solvent for the water soluble alginate. The water in the fiber is displaced by the organic solvent to allow fiber formation. Typical organic non-solvents used are methanol, ethanol or isopropanol, acetone, dioxane, ethylene glycol monomethyl ether, dimethyl sulphoxide, dimethylformamide, dimethylacetamide, acetonitrile, methylethyl ketone or phenol. Among these, acetone is often chosen as it provides fibers of a reasonably high mechanical strength. These organic non-solvents may also be used singly or as a mixture.

The coagulating bath inevitably contains water after an aqueous dope is extruded into it. The build-up of water should be controlled and ideally be in as small amount as possible and never above 20%. This can be achieved by connecting the coagulation bath to a circulation system in which the non-solvent is dried by dehydration equipment and in addition more dehydrated

solvent can be added from another reservoir to supply the bath with the dehydrated non-solvent continuously. The bath is maintained at a temperature between 20–100°C depending upon the non-solvent used or other extrusion conditions. After the fibers are formed in the coagulating bath, they may be immersed in a second dehydrating non-solvent, and then either heated or air-dried.

3.6 Alginates in bioengineering

Research papers, comprehensive as well as specialized reviews, have been published on some important aspects of tissue and cell immobilization technology. There are also specialized monograms, and conference proceedings pertaining to this field, which have excited microbiologists and bioengineers.[72] Of interest in this chapter is an overview of alginate in the field, as it would be extremely difficult to include and cover every report on all the aspects of tissue and cell entrapments due to paucity of space, but clearly this is an area being actively pursued.

Rapid advances in the field have lead to the development of novel materials, in which different types of cells and tissues are encapsulated or combined with a variety of biopolymers in an attempt to restore, maintain, or improve tissues or organ function. The cell, or the biological component of the cell–biomaterial combination, secretes special chemicals or hormones while the biomaterial component protects the cell from immune attacks while at the same time being biocompatible with the host tissue. These encapsulated live cells, organelles or tissues have led to the production of artificial organs suitable for implantation in mammalian bodies.[73–77] In this class of biomaterials, alginate is becoming increasingly popular as a culture medium for many types of cell and tissue entrapment because of the requirement for mild conditions and the simplicity of the procedures used. For clarification purposes a transplant is regarded as the tissue or organ transferred from one body or body part to another whilst an implant is an inserted or embedded object or device by surgical means, e.g. a drug capsule or a pacemaker.[78]

Lim's[79] patent claims to have encapsulated tissue or individual cells in a manner that they remain viable and in a protected state within a membrane permeable to nutrients, ions, oxygen and other materials needed to both maintain the tissue and support its normal metabolic functions, but impermeable to bacteria, lymphocytes and large proteins of the type responsible for immunochemical reactions resulting in rejection. In their patent, Skjak-Breaek *et al.*[80] have reviewed prior problems associated with encapsulated implant rejection and described a method of encapsulating cells in an alginate containing a high content of guluronic acid residue that would solve the problem. Their claim is that their microencapsulation provide transplant or implant *in vivo* which is non-immunogenic and non-fibroblast inducing. Further attempts to

improve implant acceptance by the host body is described by Cochrum *et al.*[81] In their patent they describe a method of preparing a multiple layer coating of biological tissue and cells for transplantation by multiple application of sodium alginate gelled with divalent cations. This gives a transplant with distinct structure where biological tissue or cell core is covered with the first layer alginate coat surrounded by an intermediate halo layer which is then covered by the outer coating. A subsequent patent[82] describes a transplant with a core of a viable, physiologically active cells and non-fibrogenic coating of metal alginate having a high mannuronate to guluronate molar ratio and free from fibrogenic amounts of fucose, sulphate, phloroglucinol and protein moieties. They claim the coating has permeability sufficiently low and thickness sufficiently large to protect the tissue cell from host immunological agents after transplantation, but thin enough to be permitting diffusion of sufficient nutrients and cell products. Shah[83] claims to have macroencapsulated somatic cells using ultrapurified sodium alginate and polysulfone hollow fibers. He used a high guluronate, low endotoxin, low divalent metal toxin contents and low protein impurities. The islet cells prior to being encapsulated were purified to reduce the bioburden of microorganism including viruses. Encapsulation was done in RPMI 1640 tissue culture fluid containing the necessary nutritional supplements and ATP source of energy. The open ends of the fiber were covered with a porous membrane. To further improve biocompatibility, the outer wall of the polysulfone was lightly gelled with alginate gel and sulfonic group to inhibit complement activation. He claims that such gelled, encapsulated fiber does not affect diffusion of glucose or insulin across the hollow fibers. These organic non-solvents may also be used singly or as a mixture.

Recent studies in the area of sustained drug release are by Chi and Woo[84] and by Steiner *et al.*[85] Chi and Woo describe a carrier made of sodium alginate/xanthan gum and gel hydration accelerator, which is a mixture of hydoxypropyl metylcellulose and propylene glycol alginate. It is claimed that the carrier provides a constant drug level in blood for 24 hours or more owing to the fact that the drug release rate follows zero order kinetics and does not significantly vary with the degree of gastrointestinal motility due to rapid gel hydration without forming a non-gelated core. Steiner *et al.* describe a drug delivery to the pulmonary system, which is achieved by encapsulation of the drug in alginate among other biomaterials into microparticles having a size between 2 and 5μm.[85] They claim that the microparticles formed release drug at a pH of 6.4 to 8.0 and that they have been modified to target specific cell types and to effect release only after reaching them. Of interest to this work is the engineering of an alginate encapsulation that can be recognized by the body as a normal part of the physiology and to precisely trigger healing and reconstruction processes. This will be achieved by designing receptor sites onto the material matrix or scaffold where cellular

recognition and cell–cell signalling will be expected to trigger biological processes.

The use of alginate in textile scaffolds has certain specialized uses. Flexibility provides versatility and thus alginate fiber systems are ideal for encouraging cells to recreate the tissue geometry in three dimensions. Scaffolds may be knitted, woven, nonwoven, braided, embroidered or a combination of these techniques. They may be modified to meet the different cell requirements by, say, altering the fiber diameter, length or even the extreme step of modifying the polymer.

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