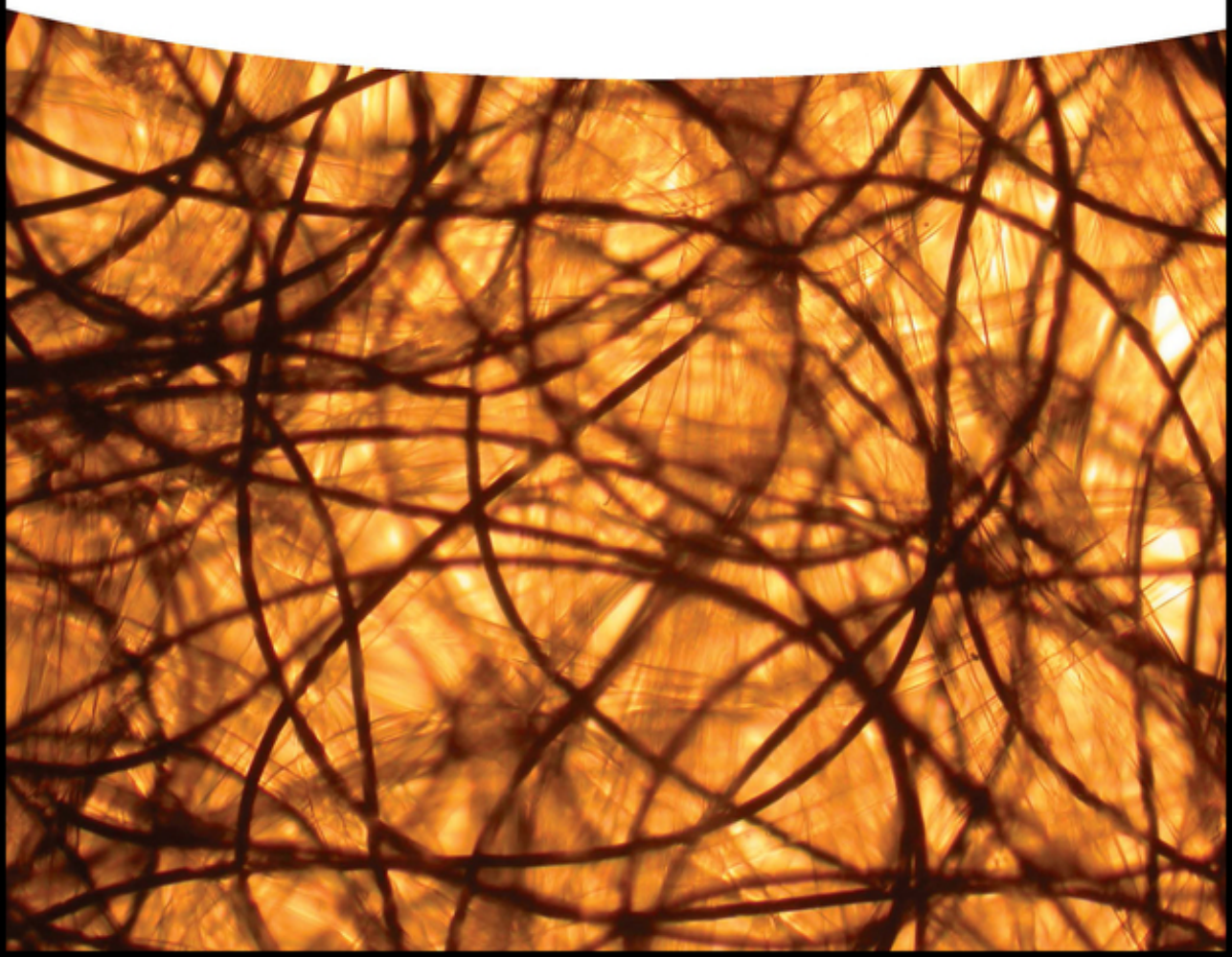


Yimin Qin

Alginate Fibers and Wound Dressings

Seaweed Derived Natural Therapy



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Yimin Qin

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Contents

Author Biography *xiii*

Preface *xv*

1	The Extraction of Alginate from Brown Seaweeds	1
1.1	Introduction	1
1.2	Global Distribution of Brown Seaweeds	2
1.3	The Extraction of Alginate from Brown Seaweeds	6
1.3.1	General Description of the Extraction Process	6
1.3.2	A Comparison of Alginic Acid Method and Calcium Alginate Method	9
1.3.3	Process Control	9
1.3.4	Key Process Parameters	10
1.3.4.1	Size Reduction of Raw Materials	10
1.3.4.2	Acid Treatment	10
1.3.4.3	Formaldehyde Treatment	12
1.3.4.4	Alkaline Extraction	12
1.3.4.5	Separation of Alginate from Insoluble Seaweed Residue	12
1.4	Ultrapure Alginate	14
1.5	Summary	15
	References	15
	Further Reading	17
2	Chemical, Physical, and Biological Properties of Alginic Materials	19
2.1	Introduction	19
2.2	The Chemical Structure of Alginic Acid	19
2.2.1	Early Studies and Basic Structural Feature	19
2.2.2	M/G Ratio and Distribution	20
2.2.3	C-5 Epimerization and Designer Alginate	21
2.2.4	Molecular Weight and Distribution	22
2.2.5	Chemical Stability	22
2.3	Physical Properties of Alginic Materials	24
2.4	Viscosity of Alginate Solutions	26
2.4.1	Effect of Molecular Weight on Solution Viscosity	26
2.4.2	Effect of Concentration on Solution Viscosity	27

2.4.3	Effect of Temperature on Solution Viscosity	28
2.4.4	Effect of Shear Rate on Solution Viscosity	28
2.4.5	Effect of Salt on Solution Viscosity	28
2.4.6	Effect of pH on Solution Viscosity	29
2.5	Polyelectrolyte Properties	29
2.6	The Ion-Exchange Properties of Alginate	29
2.7	Gelling Properties of Alginate	31
2.8	Film-Forming Properties	32
2.9	Fiber-Forming Properties	33
2.10	Bioactivities of Alginic Materials	33
2.10.1	Enzyme Inhibition Activities of Alginate	33
2.10.2	Biocompatibility and Cell Activities of Alginate	34
2.11	Summary	35
	References	35

3 Industrial Applications of Alginic Materials 39

3.1	Introduction	39
3.2	Functional Properties of Alginic Material	39
3.2.1	Alginate as a Thickening Agent	39
3.2.2	Alginate as a Gelling Agent	40
3.2.3	Alginate as a Film-Forming Agent	40
3.2.4	Alginate as a Stabilizer	41
3.2.5	Alginate for Encapsulation and Immobilization	41
3.3	Industrial Applications of Alginate	42
3.3.1	Food Ingredients	42
3.3.2	Medical and Pharmaceutical Uses	44
3.3.2.1	Dental Impression	44
3.3.2.2	Therapeutic Cell Entrapment	45
3.3.2.3	Controlled Release of Drugs	45
3.3.2.4	Alginate Oligoelectrolytes as a Mucin Polymer Network Modifier	45
3.3.2.5	Oligoguluronates as Modifiers of Cystic Fibrosis Mucus	45
3.3.3	Wound Dressings and Hemostatic Agent	46
3.3.4	Immobilization of Biocatalysts	46
3.3.5	Controlled Release of Active Agents	48
3.3.6	Textile Printing Paste	48
3.3.7	Sizing Agent for Paper	48
3.3.8	Coating for Welding Rods	49
3.3.9	Binders for Fish Feed	50
3.3.10	Biostimulants	50
3.4	Summary	50
	References	51

4 The Production of Fibers From Alginate 57

4.1	Introduction	57
4.2	The Properties of Alginate as a Fiber-Forming Polymer	58

4.3	Preparation of the Spinning Solutions	60
4.3.1	Molecular Weight of the Alginate Powder	60
4.3.2	Concentration of the Spinning Solution	61
4.3.3	Temperature of the Spinning Solution	61
4.3.4	pH of the Spinning Solution	61
4.4	The Production of Calcium Alginate Fibers	61
4.5	The Production of Calcium Sodium Alginate Fibers	65
4.6	The Production of Sodium Alginate Fibers	66
4.7	The Production of Alginic Acid Fibers	68
4.8	The Production of Zinc Alginate Fibers	69
4.9	The Production of Alginate Fibers Containing Pectin and Carboxymethyl Cellulose	69
4.10	The Production of Silver-Containing Alginate Fibers	71
4.11	The Production of Other Novel Alginate Fibers	73
4.12	Historical Development of Alginate Fibers	76
4.13	Summary	78
	References	78
5	Ion-Exchange and Gel-Forming Properties of Alginate Fibers	83
5.1	Introduction	83
5.2	Characterization Methods for Ion Exchange and Gel Forming Properties	83
5.3	Ion-Exchange Properties of Alginate Fibers	86
5.3.1	Ion-Exchange Between Calcium Alginate Fibers and Sodium Ions	86
5.3.2	Ion-Exchange Between Alginate Fibers and Zinc Ions	87
5.3.3	Ion-Exchange Between Alginate Fibers and Copper Ions	91
5.4	Gelling Properties of Alginate Fibers	94
5.5	Summary	98
	References	99
6	Applications of Alginate Fibers as Smart Woundcare Materials	101
6.1	Introduction	101
6.2	Functional Requirements of the Wound Dressings	103
6.3	Modern Advanced Wound Dressings	106
6.3.1	Chitin and Chitosan Fibers and Wound Dressings	107
6.3.2	Superabsorbent Cellulosic Fibers	108
6.3.3	Polyurethane Film and Foam	109
6.3.4	Hydrogels	110
6.3.5	Hydrocolloids	111
6.3.6	Activated Carbon	112
6.3.7	Low Adherent Dressings	113
6.3.8	Composite Wound Care Products	114
6.3.9	Antimicrobial Wound Dressings	116

6.3.10	Interactive Dressings	117
6.3.11	Tissue-Engineered “Skin Equivalents”	117
6.3.12	Cell-Containing Matrices	117
6.4	Applications of Alginate Fibers in Functional Wound Dressings	118
6.5	Development of Alginate Wound Dressings	119
6.6	Summary	121
	References	123
	Further Reading	124

7 Absorption and Interactive Properties of Alginate Wound Dressings 125

7.1	Introduction	125
7.2	Characterization Methods	126
7.2.1	Test on Absorbency	126
7.2.2	Fiber Calcium and Sodium Contents	127
7.2.3	Gel Swelling	127
7.2.4	Wet Integrity	127
7.2.5	Wicking Behavior	127
7.2.6	Dry and Wet Strength	128
7.3	Absorption of Wound Fluid by Alginate-Based Wound Dressings	128
7.3.1	Absorption Mechanism of Alginate Wound Dressings	128
7.3.2	Absorbency of the Various Types of Alginate Wound Dressings	129
7.3.3	Fluid Retention Between Fibers and Inside Fibers	130
7.3.4	A Comparison of Absorption Properties Between Alginate Felt and Rope	131
7.3.5	Effect of Sterilization on the Absorption Properties of Alginate Dressings	131
7.3.6	Effect of Guluronate and Mannuronate Contents	132
7.3.7	Effect of Calcium and Sodium Contents	133
7.3.8	Effect of Nonwoven Structures	133
7.3.9	Effect of Adding CMC Into the Alginate Fibers	134
7.3.10	Wicking of Fluid	135
7.3.11	Dry and Wet Strength	137
7.4	Interactive Properties of Alginate Wound Dressings	138
7.4.1	Interactive Moisture Handling Properties of Alginate Wound Dressings	138
7.4.2	Biologically Interactive Properties of Alginate Wound Dressings	138
7.4.3	Enzyme Inhibition Properties of Alginate Wound Dressings	139
7.5	Summary	142
	References	143

8 Clinical Applications of Alginate Wound Dressings 145

8.1	Introduction	145
8.2	Biocompatibility and Bioactivities of Alginate Wound Dressings	145
8.3	Wound Healing Mechanisms of Alginate Wound Dressings	147

8.4	Clinical Applications of Alginate Wound Dressings	148
8.4.1	Applications of Alginate Wound Dressings in Pressure Ulcers	149
8.4.2	Applications of Alginate Wound Dressings in Leg Ulcers	149
8.4.3	Applications of Alginate Wound Dressings in Diabetic Foot Ulcers	151
8.4.4	Applications of Alginate Wound Dressings in Burn Wounds and Donor Sites	151
8.4.5	Applications of Alginate Wound Dressings as a Hemostatic Agent for Bleeding Wounds	154
8.4.6	Applications of Alginate Wound Dressings in Surgical Wounds	156
8.4.7	Applications of Alginate Wound Dressings in Nose Surgery	158
8.4.8	Applications of Alginate Wound Dressings in Anal Fistula Surgery	159
8.4.9	Applications of Alginate Wound Dressings in Cavity Wounds	160
8.4.10	Applications of Alginate-Based Composite Wound Dressings	160
8.5	Main Properties of Alginate Wound Dressings	160
8.5.1	Wound-Healing Promotion	161
8.5.2	The Hemostatic Properties of Alginate Wound Dressing	162
8.5.3	Pain Relief Properties of Alginate Wound Dressing	162
8.5.4	The Antimicrobial Properties of Alginate Wound Dressing	163
8.5.5	Alginate Wound Dressings as Cavity Filler	163
8.5.6	Cost-Effectiveness of Alginate Wound Dressings	163
8.6	Summary	163
	References	163

9 Functional Modifications of Alginate Fibers and Wound Dressings 169

9.1	Introduction	169
9.2	Chemical Modification of Alginic Acid	169
9.2.1	Chemical Modification of the Hydroxyl Groups	170
9.2.1.1	Oxidation	170
9.2.1.2	Reductive-Amination of Oxidized Alginate	171
9.2.1.3	Sulfation	172
9.2.1.4	Cyclodextrin-Linked Alginate	172
9.2.1.5	Acetylation of Alginate	172
9.2.1.6	Phosphorylation of Alginates	173
9.2.2	Chemical Modification of the Carboxyl Groups	173
9.2.2.1	Esterification	173
9.2.2.2	Amidation	174
9.2.3	Other Chemical Modifications	175
9.2.3.1	Organic Soluble Derivative of Alginate	175
9.2.3.2	Attachment of Cell Signaling Molecules	175
9.2.3.3	Covalent Cross-linking of Alginates	176
9.2.3.4	Graft Copolymerization of Alginates	177
9.3	Innovations in the Fiber-Making Process	178

9.3.1	The Production of Alginate Fibers Containing Metal Ions and Inorganic Compounds	179
9.3.2	The Production of Polyblend Fibers of Alginate and Other Polymers	180
9.3.3	The Production of Alginate Fibers Through Electrospinning	180
9.3.4	The Production of Alginate Fibers Containing Drugs	182
9.3.5	The Production of Alginate and Chitosan Composite Fibers	183
9.4	Summary	185
	References	186

10 Silver-Containing Alginate Fibers and Wound Dressings 193

10.1	Introduction	193
10.2	Antimicrobial Efficacy of Silver	194
10.3	Development of Silver-Containing Wound Dressings	195
10.4	Applications of Silver in Alginate Fibers and Wound Dressings	197
10.4.1	Types of Silver Compounds Used in Wound Dressings	197
10.4.2	Methods for Adding Silver to Wound Dressings	198
10.4.3	Examples of Silver-Containing Wound Dressings	199
10.4.3.1	Acticoat from Smith & Nephew	199
10.4.3.2	Silvercel from Johnson & Johnson	199
10.4.3.3	Aquacel Ag from ConvaTec	200
10.4.3.4	Contreet Foam from Coloplast	200
10.4.3.5	Silverlon from Argentum Medical	200
10.4.3.6	SilvaSorb from Medline	200
10.4.3.7	Urgotul SSD from Laboratoires URGO	200
10.4.3.8	Actisorb Silver 220 from Johnson & Johnson	200
10.4.3.9	Microbisan from Lendell Manufacturing Inc.	201
10.4.4	Differences Between Silver-Containing Wound Dressings	201
10.4.4.1	Different Silver Compounds	201
10.4.4.2	Different Contact Areas	202
10.4.4.3	Different Absorption Capacities	202
10.5	Preparation of Silver-Containing Alginate Fibers and Wound Dressings	203
10.5.1	The Addition of Silver Into Alginate Fibers Through Chemical Reaction	203
10.5.2	The Addition of Silver Into Alginate Fibers Through Blending	203
10.6	Release of Silver Ions from Silver-Containing Alginate Fibers	204
10.7	The Antimicrobial Effect of Silver-Containing Alginate Fibers and Wound Dressings	205
10.8	Properties and Applications of Silver-Containing Alginate Wound Dressings	206
10.8.1	Wound Healing Properties of Silver	206
10.8.2	The Release of Silver from Silver-Containing Wound Dressings	206
10.9	Test Methods for Assessing the Antimicrobial Properties of the Silver Dressing	208

- 10.9.1 Zone of Inhibition 208
- 10.9.2 Challenge Testing 208
- 10.9.3 Microbial Transmission Test 209
- 10.10 *In Vitro* and *In Vivo* Findings of the Clinical Benefits of Silver in Wound Healing 210
- 10.11 Local and Systemic Toxicity of Silver in Wound Healing 211
- 10.12 Clinical Efficacy of the Silver-Containing Dressings 212
- 10.13 Summary 213
- References 213

A Appendix A: List of Silver Containing Wound Dressings 217

B Appendix B: Answers to Commonly Asked Questions About Alginate Wound Dressings 221

- B.1 What Are Alginic Acid, Sodium Alginate, and Calcium Alginate? 221
- B.2 What Do M and G Mean With Alginate Fibers and Wound Dressings? 221
- B.3 What Are the Differences Between Alginate Wound Dressing and Calcium Alginate Wound Dressing? 222
- B.4 How Can Calcium Alginate Dressing Form Hydrogel on Contact With Wound Exudate? 223
- B.5 What Role Does Alginate Wound Dressings Play in “Moist Healing”? 223
- B.6 What Are the Main Applications of Alginate Wound Dressings? 223
- B.7 What Is the Absorption Mechanism of Alginate Wound Dressing? 226
- B.8 What Is the Reason That Calcium Alginate Fibers Do Not Gel in Pure Water? 226
- B.9 What Are the Differences Between the Absorption of Wound Exudate by Cotton Gauze and Alginate Wound Dressings? 227
- B.10 What Are the Differences Between High G and High M Alginate Fibers When They Are Applied on Exuding Wounds? 227
- B.11 Can Sodium Alginate Be Absorbed by the Body When Calcium Alginate Fibers Are Converted Into Sodium Alginate Upon Contact With Wound Exudate? 228
- B.12 Alginate Wound Dressings Are Divided Into Wet Integral and Wet Dispersible, What Does These Two Types Mean? 228
- B.13 How Can Alginate Wound Dressings Reduce Pain? 229
- B.14 Are There Any Inappropriate Consequences for the Residue Alginate Fibers Left on the Wound Surface? 229
- B.15 Are There Any Differences Between the Alginate Wound Dressings Under Different Brands? 229
- B.16 In the Manufacturing Processes, What Do Nip Rolling, Needle Punching, and Freeze Drying Mean? 230
- B.17 Can Alginate Wound Dressings Be Used in Combination With Topical Medicines Such as Anti-inflammatory Drugs Like Iodine? 230

- B.18 Can Alginate Wound Dressings Be Used on Infected Wounds? 230
- B.19 Can Alginate Wound Dressings Be Cut Into Pieces Before Being Applied to Wounds? 231
- B.20 What Should Be Done When Alginate Wound Dressings Adhere to the Wound Surface? 231
- B.21 Some Patients Experience Granulation Edema When Applied With Alginate Wound Dressings, Is This Related to the Release of Calcium Ions by the Dressing? 231
- B.22 What Are the Clinical Efficacy of Alginate Wound Dressings When Used for Pressure Sore Wounds? 231
- B.23 What Are the Clinical Efficacy of Alginate Wound Dressings When Used for Leg Ulcer Wounds? 231
- B.24 What Are the Clinical Efficacy of Alginate Wound Dressings When Used for Diabetic Foot Ulcer Wounds? 232
- B.25 What Are the Clinical Efficacy of Alginate Wound Dressings When Used for Burn Wounds? 232
- B.26 What Are the Clinical Efficacy of Alginate Wound Dressings When Used for Anal Fistula Wounds? 232
- B.27 Does Alginate Wound Dressing Possess Hemostatic Properties? 232
- B.28 Where Are the Seaweeds Used in the Production of Alginate Wound Dressings Come From? 233

Index 235

Author Biography

Dr. Yimin Qin studied for his PhD at the University of Leeds between 1986 and 1990. After spending three years at Heriot-Watt University working on his postdoctoral project, he became the R&D manager at Advanced Medical Solutions Plc in Cheshire, UK, where he led a team of scientists and developed a number of high performance fibers and wound dressings from alginate, chitosan, and other natural polymers. He then went to study for an MBA at Manchester Business School and, after graduation, took up the position of Fibers Product Manager at SSL International, working on advanced silver containing antimicrobial alginate fibers and wound dressings. In 2002, Dr. Qin went back to China and taught at Jiaying University in Zhejiang Province. In 2015, he was appointed as the director of the State Key Laboratory of Bioactive Seaweed Substances at Qingdao Brightmoon Seaweed Group, where his main research interests focused on the extraction, purification, modification, and applications of alginate and other novel bioactive seaweed substances.



Preface

Alginate is a natural polysaccharide extracted from brown seaweeds. In the medical textile industry, alginate fibers have been used for the production of high-performance wound dressings due to their high absorption properties and good biocompatibility. In recent years, as more and more efforts are made to use alginate fibers in conventional textiles and industrial textiles, many types of functional alginate fibers have been developed by using ion exchange, polymer blending, and other novel processing technologies. These fibers combine the properties of alginate and various types of additives, making them useful in a large variety of specialized applications.

Technically, calcium alginate fibers can be readily made by first dissolving sodium alginate powder in water and then extruding the solution through a spinneret into an aqueous calcium chloride bath. In addition to this type of conventional alginate fiber, functional alginate fibers can be made with a number of novel processing methods. Because it is a polymeric acid, alginate fibers can be used as carriers to deliver zinc, copper, silver, and other bioactive metal ions for wound care and other novel applications. In addition, since both the dope preparation and coagulation processes are carried out in aqueous solutions at a neutral pH, many bioactive materials, such as drug and enzyme, can be combined into the alginate fibers without losing their bioactivities.

Alginate fibers have many unique properties that are highly useful for functional textile materials and medical textile products. For example, they possess ion-exchange and gel forming properties when in contact with body fluid, in addition to other excellent performance characteristics such as hemostatic, antimicrobial, wound healing promotion, skin whitening, and many other unique bioactivities. These novel properties are highly applicable to medical textile materials such as functional wound dressings, functional face mask materials, hygiene products for women and children, and incontinence products for adults.

Historically, the most successful application of alginate fibers has been functional wound dressings made from alginate fibers through nonwoven processing. These high performance dressings have been widely applied to a wide variety of chronic exuding wounds, where the high absorption is achieved via strong hydrophilic gel formation, which limits wound secretions and minimizes bacterial contamination. In addition, alginate wound dressings can help maintain a physiologically moist

microenvironment that promotes healing and the formation of granulation tissue. Upon wound healing and dressing change, these novel wound dressings can be rinsed away with saline irrigation, so removal of the dressing does not interfere with healing granulation tissue. This makes dressing changes virtually painless, a performance highly beneficial to patients with acute or chronic wounds.

This book offers a general introduction to the sources of alginate and the production methods for alginate fibers and wound dressings, in addition to the novel properties and applications of these functional materials in wound management. Taking into consideration the latest results of clinical research conducted around the world, this book summarizes the unique properties of alginate wound dressings, including their “gel blocking” properties and the ability to promote wound healing, facilitate hemostasis, reduce pain, suppress bacteria growth, and lower treatment costs in the treatment of a wide range of wounds including leg ulcers, burn wounds, pressure sores, surgical wounds, and many other types of wounds with high levels of exudate.

Because alginate fibers and wound dressings cover a large field with a diversified range of specialist knowledge, it is inevitable that this book will not be able to offer precise explanations in all areas, and the author appreciates critical feedback in such cases.

30th June 2023

Yimin Qin
Jiaxing University

1

The Extraction of Alginate from Brown Seaweeds

1.1 Introduction

Alginic acid is an anionic polysaccharide distributed widely in the cell walls of brown seaweeds, where it exists in the cell walls and extracellular matrix in the form of a mixed salt of sodium, calcium, magnesium, strontium, and barium alginate. The British chemist E C C Stanford first described the extraction of alginic acid from brown seaweed in a patent dated 12 January 1881 [28]. In the following years, Stanford carried out the initial studies on the chemical nature of alginic acid, which he named “algin.” [29] Due to the protein components in the seaweed extract, Stanford initially believed that alginic acid contained nitrogen.

Brown seaweeds are distributed in many parts of the world, and following Stanford's initial work, many other scientists around the world made further studies on this novel biomaterial. In 1926, Atsuki and Tomoda [2] and Schmidt and Vocke [27] reported that uronic acid was a constituent of alginic acid. Shortly after these two studies, other scientists found D-mannuronic acid in the hydrolysate of alginate [3, 17, 19–21].

The chemical nature of alginate was further clarified in 1955, when Fischer and Dorfel found that in addition to D-mannuronic acid, the hydrolysates of alginic acid also contained L-guluronic acid [6]. This finding is important to illustrate the nature of alginic acid as a copolymer composed of two types of monomers, i.e. D-mannuronic acid (M) and L-guluronic acid (G). Figure 1.1 shows the chemical structure of these two monomers.

It is now widely known that as a natural copolymer, the proportions of D-mannuronic acid and L-guluronic acid vary widely for alginate extracted from different types of brown seaweeds, resulting in variations of the physical properties of alginate-based materials. As a polymeric acid, alginic acid can form salt with various types of metal ions to form alginate salt, with alginate being a term commonly used as a general description for the various types of alginic acid based salts, as well as all the derivatives of alginic acid and alginic acid itself. These seaweed-derived polymeric materials have thickening, gelling, emulsifying, film, and fiber-forming properties that are widely utilized in many diversified industries.

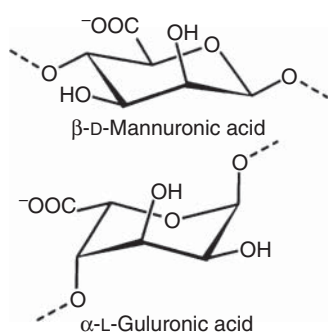


Figure 1.1 The chemical structures of β-D-mannuronic acid and α-L-guluronic acid.

1.2 Global Distribution of Brown Seaweeds

Although alginic acid is present in several types of bacteria such as *Azotobacter vinelandii* and many species of *Pseudomonas* [7] and alginate can be successfully extracted from the biomass of the soil bacterium *A. vinelandii* ATCC 9046 cultivated on crude glycerol as an alternative carbon source [10], up to the present time, all commercially available alginates have been extracted from brown seaweeds, mainly *Laminaria hyperborea*, *Macrocystis pyrifera*, *Laminaria digitata*, *Ascophyllum nodosum*, *Saccharina japonica*, *Ecklonia maxima*, *Lessonia nigrescens*, and *Durvillaea antarctica*. The chemical composition of alginate extracted from different types of seaweeds varies according to seasonal and growth conditions, as well as within different parts of the plant [1, 13]. This variability in composition shows the biological role of alginate in seaweeds whose mechanical properties can be regulated partly by the variations in the M/G composition of alginate. For example, the brown seaweed *L. hyperborea* grows in very exposed coastal areas, where high mechanical rigidity is required in the stipe and holdfast, whereas high flexibility is needed in the leaves that float on streaming water. The stipe and holdfast contain alginate with a high content of L-guluronic acid, which is responsible for high gel strength, while the leaves contain alginate with a high content of D-mannuronic acid, which is related to softness and flexibility.

Figure 1.2 shows the distribution of the main species of wild brown seaweeds around the world. Globally, brown seaweeds, or Phaeophyceae, are a large group of multicellular algae that play an important role in the marine environment, both as a source of marine vegetables and for the habitats they form, which provide a natural environment for other marine organisms. For example, the brown seaweed *M. pyrifera* may reach 60 m in length and form prominent underwater forests. In the Sargasso Sea, the brown seaweed *Sargassum* creates unique habitats in a vast area of tropical water. In many parts of East Asia, the brown seaweed *S. japonica* is widely used as food for human consumption. Overall, there are about 1500–2000 species of brown seaweed in the world [11].

Figure 1.3 shows the main types of brown seaweeds used for alginate production. In 2015, the worldwide annual industrial production of alginate was estimated to be

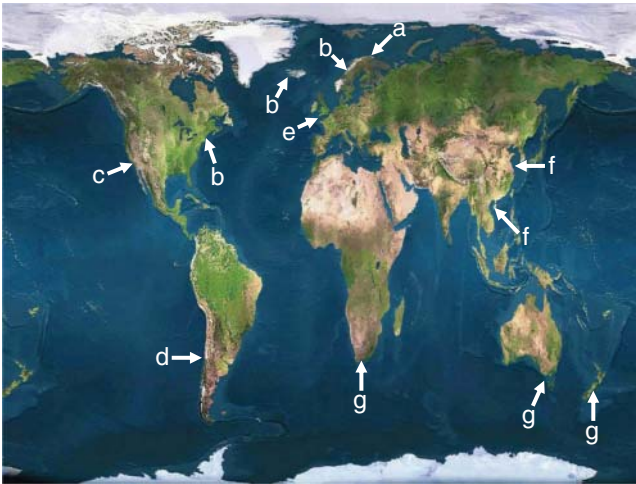


Figure 1.2 Distribution of wild brown seaweeds around the world, (a) *Laminaria hyperborea*; (b) *Ascophyllum nodosum*; (c) *Macrocystis pyrifera*; (d) *Lessonia nigrescens*; (e) *Laminaria digitata*; (f) *Saccharina japonica*; (g) *Ecklonia maxima*. Source: Adapted with permission from fig. 1.4, Qin [26].



Saccharina japonica



Ascophyllum nodosum



Laminaria hyperborea



Lessonia nigrescens



Macrocystis pyrifera



Lessonia flavicans



Ecklonia maxima



Durvillaea antarctica



Laminaria digitata

Figure 1.3 Main types of brown seaweeds used for alginate production. Source: Adapted with permission from fig. 1.2, Qin [25].

55 500 metric tons, utilizing 236 820 tons of dry brown seaweeds [26], which represents a small percentage of the biosynthesized material in naturally occurring wild brown seaweeds. It is estimated that the total quantity of wild seaweed stock on the Norwegian Sea coast is around 50–60 million tons, with 7 million tons washed to the shoreline annually. During the algae bloom in 2019, 20 million metric tons of brown seaweed, known as the Great Atlantic *Sargassum* Belt, stretched almost 9000 km. These naturally available seaweed biomasses are complemented by the cultivated seaweeds, and it is reasonable to assume that alginate is an unlimited and renewable resource even for a steadily growing industry.

The properties of alginate vary from one species to another, and the choice of which seaweeds to harvest and cultivate is based on both the availability of particular species and the properties of the alginate that they contain. For example, alginate extracted from *S. japonica* is not suitable for the production of food gel due to its high content of mannuronic acid. At present, the main commercial sources of wild brown seaweeds are species of *Ascophyllum*, *Durvillaea*, *Ecklonia*, *Laminaria*, *Lessonia*, *Macrocystis*, *Sargassum*, and *Turbinaria*. Of these, the most important are *Macrocystis*, *Laminaria*, and *Ascophyllum*.

Macrocystis pyrifera grows best in calm, deep waters with temperatures of 15 °C or less. It is sensitive to water temperature and does not withstand a rise above 20 °C. It grows on rocky bottoms where its holdfast can become established and can be found as large underwater forests, with plants rising to and growing along the surface, at times up to 20 m in length.

Laminaria species are harvested principally in Norway, Scotland, Ireland, and France. *L. hyperborea* grows on rocky seabeds, usually at depths from 2 to 15 m. In Norway, where this type of seaweed is particularly abundant, fresh seaweed is harvested with specially designed equipment before being used for alginate production. *L. digitata* is found on either side of the low water mark and is usually harvested by hand when the plants are exposed at low tide. It is collected in France, Norway, and Scotland but the quantities are small in comparison with *L. hyperborea*. In France, it is harvested using small boats with a hydraulic arm fitted with a hook device at the end, which is lowered into the bed of *L. digitata* and rotated so that the weed wraps around it. The arm is then raised to the surface, bringing the seaweed with it.

Ascophyllum nodosum grows in the intertidal zone. It has been harvested by hand in Scotland and Ireland for more than a century. A mechanized harvesting technique was developed in Norway, whereby the seaweeds are cut and then pumped through a large diameter pipe into a net bag on a shallow-draught water jet-propelled vessel. The operation is carried out at high tide, and the bags can be left floating for later collection.

Other types of brown seaweeds for alginate production include *Lessonia*, *Ecklonia*, and *Durvillaea* species. *Lessonia* is collected in Chile, where it is cast up after storms. This particular species of brown seaweed has been popular in the alginate industry for the production of food-grade alginate due to its relatively high content of guluronic acid. *Lessonia trabeculata* grows in the sublittoral at a depth of 1–20 m. It has a very thick holdfast and stands up underwater, rather like *L. hyperborea*. Figure 1.4 shows an illustration of the brown seaweed *L. trabeculata*.



Figure 1.4 An illustration of the brown seaweed *Lessonia trabeculata*.

Ecklonia cava grows in deep water up to 20 m and is harvested by divers in both Japan and Korea. *Eisenia bicyclis* grows in a similar location and is collected along with *Ecklonia* in Japan. *Ecklonia* that has been cast up by storms is collected in Korea and South Africa. In Korea, it is used by the local alginate producer. The Korean industry also uses waste *Undaria* that is unsuitable for food uses, just as the Japanese industry uses similar waste from *S. japonica* seaweeds.

The alginate obtained from *Sargassum* and *Turbinaria* has a poor viscosity, so these species are used only when the above colder water species are not available. The Indian alginate industry is based on *Sargassum* that grows in the south, for example, along the coasts of Kerala and Tamil Nadu states. The species that grow in the north give a low-viscosity alginate, unsuitable for the main Indian market of textile printing. *Turbinaria* is used only when supplies of *Sargassum* are unavailable. The Philippines has large resources of *Sargassum*, but this is exported mainly to Japan for use in animal feeds and fertilizers.

Sargassum species are found worldwide in both the eulittoral and upper sublittoral zones. They exhibit a wide variety of shapes and forms. The alginate content is usually low, and the quality of the alginate is poor. For alginate extraction, they are regarded as the raw material of last resort.

None of the common seaweeds for alginate production are cultivated. They cannot be grown by vegetative means but must go through a reproductive cycle involving an alternation of generations. For alginate production, this makes cultivated brown seaweeds too expensive when compared to the costs of harvesting and transporting wild seaweeds. The only exception is *S. japonica* (formerly known as *Laminaria japonica*), which is now widely cultivated in China for food but is also used for alginate production. Since its initial development in the 1950s, the cultivation of *S. japonica* has been very successful in China, reaching about eight million tons of wet seaweed annually, of which about two-thirds is used as food and the rest is available for alginate production. Figure 1.5 shows an illustration of the cultivation of brown seaweed, *S. japonica*.



Figure 1.5 An illustration of the cultivation of brown seaweed, *Saccharina japonica*.

1.3 The Extraction of Alginate from Brown Seaweeds

1.3.1 General Description of the Extraction Process

Figure 1.6 shows an illustration of the wet and dry structures of brown seaweed, where alginic acid is the main structural component, accounting for up to 40% of the dry seaweed biomass. Alginate exists mainly in the intercellular mucilage and algal cell wall as a water-insoluble mixture of calcium, magnesium, potassium, and sodium salts, which provide the mechanical strength and flexibility of the seaweed as a marine bio-organism. In addition, as a hydrophilic biopolymer, alginate



Figure 1.6 An illustration of the wet and dry structure of brown seaweed.

acts as a water reservoir, preventing dehydration when part of the seaweed is exposed to air. In general, the biological role and morphophysiological properties of alginate in brown seaweeds are similar to those of cellulose and pectin in terrestrial plants.

For the commercial extraction of alginate from brown seaweeds, F C Thornley first established a business based on using alginate as a binder for anthracite dust in 1923, and when that was not successful, he moved to San Diego. By 1927, his company was producing alginate for use in sealing cans. After some difficulties, the company changed its name to Kelp Products Corp., and in 1929, it was reorganized as Kelco Company.

Prior to the establishment of Kelco, there were a few companies established in the United Kingdom following the discovery of alginate by Stanford in 1881, such as British Algin Company Ltd. (1885), Blandola Ltd. (1908), Liverpool Borax Ltd. (1909). In 1934, Cefoil Ltd. was established to extract alginate from seaweeds in order to make fibers for military uses [18, 31]. World War II stimulated the alginate industry when production units were set up in Scotland and California using local seaweed resources of wrack and kelp. After the war, other production units followed suit and were constructed close to natural seaweed beds in the United States, Norway, France, the United Kingdom, Japan, and, more recently, China. The raw materials are mainly *M. pyrifera* in California, *L. hyperborea* in Norway, *L. digitata* in France, and *A. nodosum* in Scotland. In China, the kelp *S. japonica* was introduced from Japan and has been successfully cultivated on a large scale, usually grown on ropes along the Pacific coast.

Yields of alginate from different types of brown seaweeds vary greatly [24]. It has been reported that the yields of alginate as a percentage of dry seaweed biomass are, respectively, 18–45% for *M. pyrifera* [8, 30], 16–36% for *L. digitata* [4, 16], 14–21% for *L. hyperborea* [4], 17–25% for *S. japonica* [12], 16–34% for *Saccharina latissima* [16], 13–29% for *L. trabeculata* [5], 24–28% for *Ecklonia arborea* [9], 45–55% for *Durvillaea potatorum* [15, 23] and 12–16% for *A. nodosum* [22].

Figure 1.7 shows a process flow chart for the extraction of alginate from brown seaweeds. During the extraction process, the goal is to obtain dry, powdered sodium alginate. The natural calcium and magnesium salts of alginic acid in the seaweed biomass do not dissolve in water, while the sodium salt does. Therefore, the rationale behind the extraction of alginate from the seaweed is to convert all the alginate salts to sodium salts and dissolve them in water. After removing the seaweed residue by filtration, alginic acid can be recovered from the aqueous solution.

During the extraction process, once the alginate component of seaweed is in the aqueous extraction medium, there are two different ways to recover it. The first is to add acid to the extraction solution to convert sodium alginate into alginic acid, which does not dissolve in water and hence can be separated from the water. The alginic acid separates as a soft gel, and some of the water must be removed from this. After this has been done, alcohol is added to the alginic acid, followed by sodium carbonate, which converts the alginic acid into sodium alginate. Since sodium alginate does not dissolve in the mixture of alcohol and water, it can be separated from the mixture, dried, and milled to an appropriate particle size.

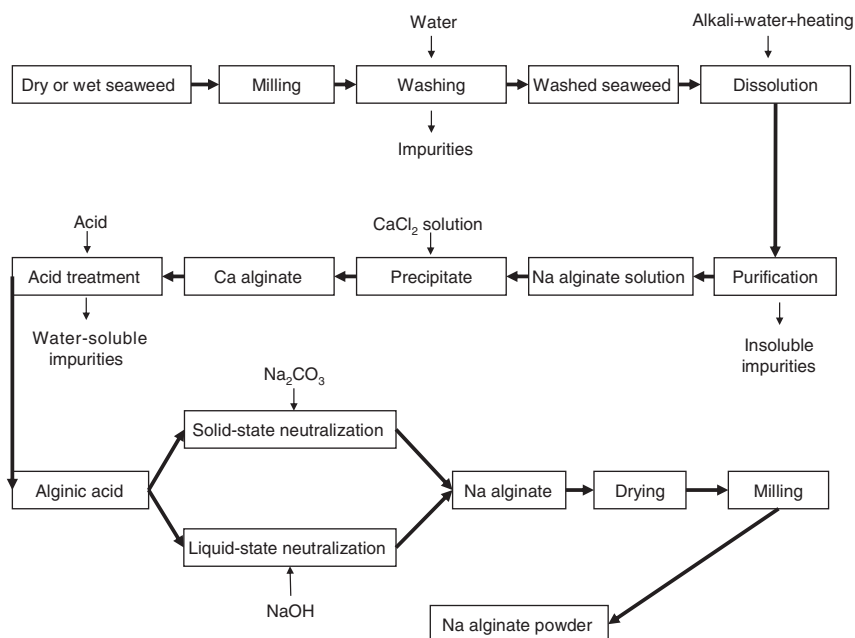


Figure 1.7 Process flow chart for the extraction of alginate from brown seaweeds.

Source: Adapted with permission from fig. 3.4, Qin [26].

The second method of recovering sodium alginate from the initial extraction solution is to add a calcium salt, which results in the formation of water-insoluble calcium alginate that can be separated from the aqueous medium. In order to further purify the alginate material, acid is added to convert it into alginic acid before adding sodium carbonate to convert alginic acid to sodium alginate, which is extruded into pellets that are then dried and milled.

These two processes are straightforward, and the chemistry is simple, i.e. convert the water-insoluble alginate salts in the seaweed into soluble sodium alginate and precipitate it either in the form of alginic acid or calcium alginate so that alginate can be separated from the extract solution. The difficulties lie in handling the materials encountered in the process. In order to extract alginate, the seaweed biomass should be broken into pieces and stirred with a solution of an alkali, usually sodium carbonate. Over a period of time, alginate dissolves as sodium alginate to produce a thick slurry, which also contains parts of the seaweed that do not dissolve, mainly cellulose. The solution is often too viscous to be filtered and must be diluted with a very large quantity of water before it passes through a filter cloth. However, the pieces of undissolved residue are very fine and can quickly clog the filter cloth. Therefore, before filtration is started, a filter aid, such as diatomaceous earth, must be added, which holds most of the fine particles away from the surface of the filter cloth and facilitates filtration. Since the filter aid is expensive and in order to reduce the quantity of filter aid needed, some processors force air into the extract as it is being diluted with water, where fine air bubbles attach themselves to the particles of