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Title: *Advances on Alginate use for spherification to encapsulate biomolecules.*

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Abstract: *Spherification methods to produce particles of millimetric size are detailed in this review, especially for encapsulation purpose and using alginate. Therefore, alginate properties and factors impacting its gelation, counting its structure and experimental conditions such as pH, temperature, crosslinker concentration, residence time and ionic strength, are largely discussed. Furthermore, the interest for using co-polymer in spherification is investigated. Thereby, alginate composite gels can enhance encapsulation efficiency, mechanical stability, barrier properties and thermal stability. The advantages and limitations of their use are discussed for each spherification process to improve the knowledge about alginate versatility. Alginate is still one of the most promising encapsulation materials.*

Keywords:

Alginate, Hydrocolloids, Spherification, Encapsulation, Composite, Coextrusion.

1 1. Introduction

2 Alginate is the salt of alginic acid, a natural polymer of uronic acids (mannuronic and
3 guluronic acids) extracted especially from brown marine algae (Blanco-Cabra et al., 2020;
4 Boyd & Chakrabarty, 1995; Günter et al., 2020) and also from some bacteria, such as
5 *Pseudomonas aeruginosa*.

6 The alginate gelation is one common way to produce beads or capsules. The term
7 spherification used in this review covers all the methods employed to design such particles of
8 millimetric size, ideally spherical. In this review, we consider spherification with the aim of
9 encapsulating different ingredients and active principles.

10 Alginate is Generally Recognized as Safe (GRAS), being nontoxic, nonantigenic,
11 satisfactorily biocompatible, and sufficiently biodegradable (Lee & Mooney, 2012). As a
12 result of its physicochemical properties, alginate is used for a large variety of technical
13 applications, as a coating material in textile industry (Misbah et al., 2019) or as a
14 disintegrating agent for tablets. Alginate is also commonly found in cosmetic (Adli et al.,
15 2020), pharmaceutical, medical (Shi et al., 2020) and food industries, as thickener and
16 stabilizer (Senturk Parreidt et al., 2018; C. Su et al., 2018; H. Zhang et al., 2019).

17 **Table 1**

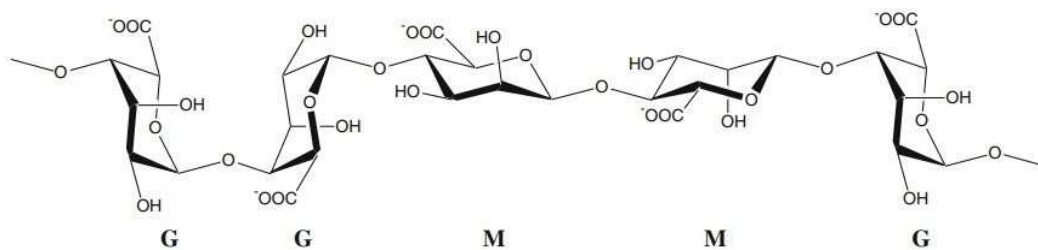
18 Alginates types and their applications

Code	Alginate types	Applications	References
E400	Alginic acid	Zero calorie ingredients for diet foods (biscuits, low-sugar marmalade, ice-creams).	Mancini & McHugh, 2013.
E401	Sodium alginate	Stabilizer and thickener in frostings,	Norton et al., 2010; Qin et
E402	Potassium alginate	puddings and processed fruits and fruit	al., 2018.
E403	Ammonium alginate	juices.	
E404	Calcium alginate	Matrix for encapsulation of volatiles constituents. Coating films to preserve frozen fish. Pearls from spherification process.	
E405	Propane-1,2 diol alginate	Stabilizer of emulsion in acidic environment (salad dressing). Stabilizer of foam in brewing industry.	Norton et al., 2010.

20 A major use of alginate today is the encapsulation technology through its biocompatibility and
21 capability to form a hydrogel through ionic cross-links with divalent cations, such as calcium
22 ions (B. B. Lee et al., 2016; Martău et al., 2019; Ramos et al., 2018).

23 1.1. Alginate molecular structure and its modification by processing methods

24 Alginate is formed by a chain of β -D-mannuronic acid (M units) and α -L-guluronic acid (G
25 units), linked via (1 \rightarrow 4) glycosidic linkage. The percentage of those units varies among algae
26 species (Rhein-Knudsen et al., 2017) and impacts alginate properties (Hecht & Srebnik,
27 2016).



28
29 **Fig. 1.** Structural characteristics of alginate. M: mannuronate residue; G: guluronate residue.

30 As polysaccharides properties are tightly related to their structures, the modification of
31 alginate structure has been widely explored. For that, alginate acid hydrolysis showed a uronic
32 acids release through an elimination reaction that led to molecular weight reduction (Haug,
33 Larsen, Smidsröd, et al., 1963; J. S. Yang et al., 2011). Chhatbar et al. (2009) studied the
34 effect of microwave-assisted acidic hydrolysis of alginate, and reported an acceleration of this
35 reaction with similar oligo-alginate properties than conventional acidic hydrolysis.

36 Alginate can also be enzymatically and thermally treated (Aida et al., 2010; Hartmann et al.,
37 2006; Kelishomi et al., 2016) to modify its structure and functional properties through the
38 molecular weight reduction or M/G ratio modification. The enrichment with G units results in
39 a rigid structure, when an enrichment with M units produces a flexible molecular structure
40 (Vold et al., 2006).

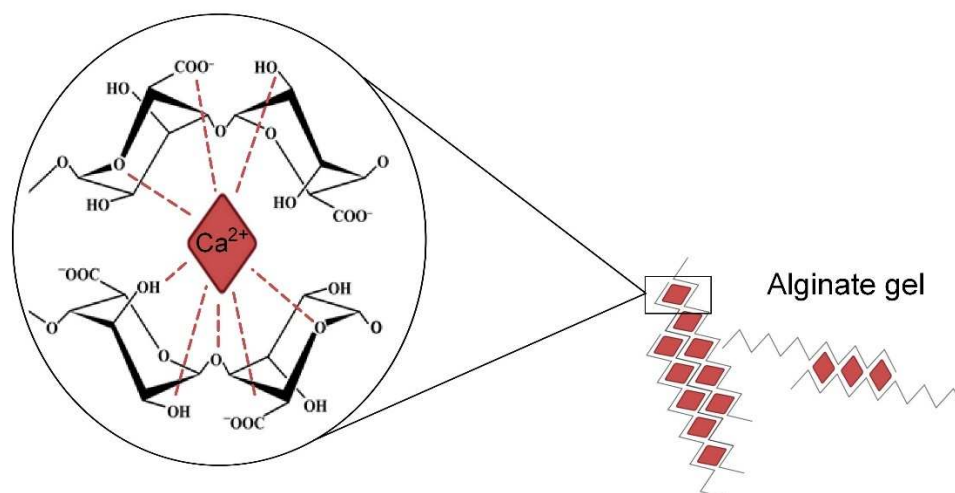
41 Ultrasounds treatment of alginate at different frequencies induce polymer structure
42 degradation, rearrangements and modifications of its molecular weight. A decrease of M/G
43 ratio has also been reported with changes of hydrophobic interactions making alginate treated
44 by 135 kHz having a stronger stiffness compared to the untreated polymer (Feng et al., 2017;
45 Taha et al., 2020).

46 In addition to their physicochemical properties, biological activities of oligo-alginate obtained
47 by alginate acidic hydrolysis have been investigated. Plant growth bio-stimulating activity
48 was demonstrated (Salachna, et al., 2018). Anti-allergic activity of a 13.3 kDa oligo-alginate
49 was reported after scission of an initial 1 605 kDa alginate polymer by a 3kGy alpha-
50 irradiation (Eu, et al 2008).

51 1.2. Ion-binding for alginate gelation

52 One of the most studied properties of alginate, is its ability to form hydrogels by cross-
53 linking with divalent or trivalent cations such as Ca^{2+} , Cu^{2+} , Sr^{2+} , Al^{3+} , for example. Those
54 cations present various affinities toward alginate, that result in hydrogels with different
55 structural and mechanical characteristics (Young modulus, gel morphology, etc) (Agulhon et
56 al., 2012; Kabir et al., 2020; Vinet & Zhedanov, 2011).

57 For food or cosmetic application, Ca^{2+} is the most commonly used. So, in the literature,
58 calcium alginate gels are the most largely investigated. Gelation occurs in solution when
59 calcium ions replace sodium to cross-link two alginate chains and form a network (Vinet &
60 Zhedanov, 2011; Warsinger et al., 2015). Alginate gelation is commonly described as an
61 eggbox model formed by two antiparallel chains of polyuronates linked with Ca^{2+} binding
62 blocks as illustrated in fig.2 (Martău et al., 2019; Reynolds & Enquist, 2006). Stokke et al.
63 (2000) suggested a lateral association of G units in the eggbox structure.



64
65 **Fig. 2.** Alginate gel structure in presence of calcium ions (egg-box model) (Adapted from
66 Martău et al., 2019)

67 2. Spherification process

68 2.1. Gelation methods

69 Two main gelation methods can be presented: (i) the external gelation, also called diffusion
70 process (Bajpai et al., 2016; Rezvanain et al., 2017); and (ii) the internal gelation also called
71 pH-controlled gelation as pH determines gelation kinetics (Cao et al., 2020; Hernández-
72 González et al., 2020). These two methods are described below.

73 2.1.1. External gelation

74 The external gelation method leads to gel formation through diffusion of calcium ions in an
75 alginate solution (X. D. Liu et al., 2002). Alginate solution droplets are usually extruded into
76 a calcium bath; this method is called conventional or classical spherification. A solution
77 containing calcium ions can also be dropped into an alginate bath and this process is known as
78 inverse spherification.

79 Gel prepared by external gelation presents an inhomogeneous structure with low mechanical
80 properties, this is due to the presence of calcium ions mostly at the surface (Arriola et al.,
81 2019; McClements, 2017; Spadari et al., 2019; Q. Sun et al., 2018). A concentration gradient
82 of polymer/ions exists from beads surface to core (Sagdicoglu Celep et al., 2020). Several
83 researches focused on this feature to overcome it (Hernández-González et al., 2020; Puguan et
84 al., 2014), or to study bioactive substances delivery systems in food and medicine applications
85 (X. D. Liu et al., 2002; Mancini & McHugh, 2000).

86 2.1.2. Internal gelation

87 Internal gelation method is based on calcium release simultaneously into the all system under
88 controlled conditions. Usually calcium lactate is dissociated to initiate alginate gelation
89 (Strobel et al., 2020). Internal gelation allows a better control of gelation kinetics and
90 produces a homogeneous gel structure with pores. It is used for controlled delivery of active
91 compounds (Hernández-González et al., 2020). As an example, Strobel et al. (2020) reported
92 a significative enhance of fish oil stability after its encapsulation with internal gelation
93 method.

94 Javvaji et al. (2011) reported a novel light activated gelation method induced by photoacid
95 generation in an insoluble calcium salt dispersion. After 10min of UV-treatment, the released
96 H⁺ ions from the photoacid generator react with the calcium salt and release calcium ions that
97 cross linked with alginate to form a hydrogel.

98

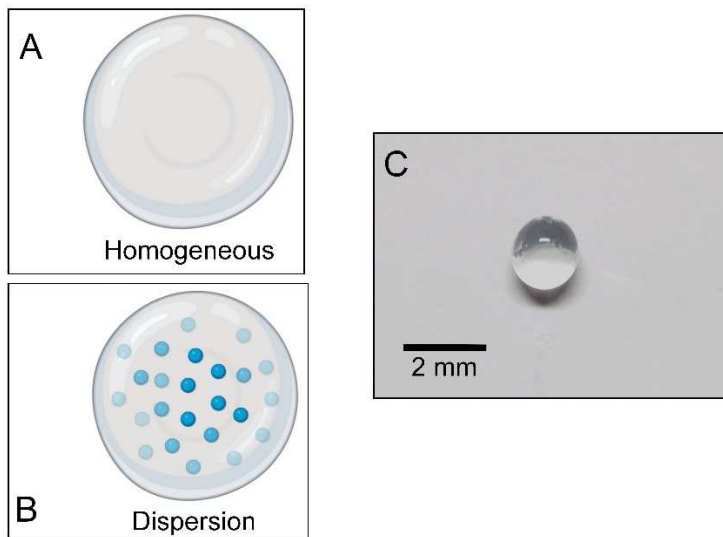
99 2.2. Spherification process using alginate

100 Encapsulation process permits to coat a substance for its preservation and/or addition of
101 functional properties. Several encapsulation methods involving alginate can give rise to
102 particles or capsules with several structural organizations. Thus, many parameters have to be
103 considered to choose the appropriate particle structure associated to an encapsulation method:
104 particle size, composition of encapsulated substance, stability of matrix and delivery features.
105 Besides, those methods have to be scaled up for industrial production (Ching et al., 2017).

106 2.2.1. Extrusion

107 2.2.1.1. Simple dripping

108 Simple extrusion process is the most commonly spread encapsulation way. The principle
109 consists in extrusion through a nozzle of an alginate solution or an emulsion containing
110 alginate. The formed droplets fall into a gelation bath containing an alginate crosslinker
111 (generally Ca^{2+}) under stirring. Following this basic principle, the process can be varied to
112 incorporate interesting components into alginate solution/emulsion in order to encapsulate it
113 and trap it into the matrix (Ching et al., 2017). Different structural organization can be
114 produced depending on the extruded solution. For instance, an alginate solution loaded with
115 the target compound tends to produce beads with homogenous microstructure Fig.3A. An
116 emulsion consisting in a lipidic phase dispersed in an aqueous phase of alginate results in
117 obtention of beads with a dispersed microstructure Fig.3B.



119 **Fig. 3.** Scheme of homogeneous structural organization for capsules (A), scheme of dispersed
120 structural organization for capsules (B) and a photograph of a homogenous capsule.

121 The beads shape depends on experimental conditions such as pH, calcium concentration and
122 temperature. However, beads sphericity is also determined by alginate solution viscosity and
123 fall distance between nozzle outlet and bath surface. The optimized fall distance to obtain
124 spherical beads has been determined in the range 7 to 10 cm knowing that droplets are formed
125 as a result of solution surface tension. This distance is necessary to the liquid to drag the
126 forces exerted by the gelling bath and overcome the impact to form a spherical bead. Also,
127 sphericity can be improved through surface active compounds addition (Blandino et al., 1999;
128 Ching et al., 2017)

129 Simple extrusion process allowed encapsulation of various compounds for delivery systems
130 and to increase their stability, including oils (Bannikova et al., 2018), essential oils
131 (Benavides et al., 2016; Gholamian et al., 2021), drugs (Hariyadi & Islam, 2020), probiotics
132 (Dehkordi et al., 2020; Praepanitchai et al., 2019), enzymes (Kurayama et al., 2020) and
133 proteins (Y. Su et al., 2019).

134 In order to produce particles of different sizes (from 20 μ m to 7mm), numerous encapsulation
135 processes have been derived from simple dripping process. Those methods differ generally by
136 the ways of formation and separation of alginate droplets. Usually, these methods are divided
137 into three groups: jet dispersion, spinning disk and atomization.

138 • Jet dispersion

139 The extruded polymer gel is split up following different methods. In this group, vibrating
140 nozzle (Pedrali et al., 2020), electrostatic atomization (Nikoo et al., 2018) and jet cutting
141 (Paulo et al., 2017) are commonly used. It is also possible to merge particular processes for
142 increased efficiency, as the vibrating electrostatic method for example (Pedrali et al., 2020).

143 • Spinning disk

144 Under centrifugal force, the alginate solution flow forms droplets due to the rotation of the
145 nozzle (or rotating disc). Spinning disk method is used to encapsulate flavor ingredients (Yin
146 & Cadwallader, 2018).

147 • Atomization

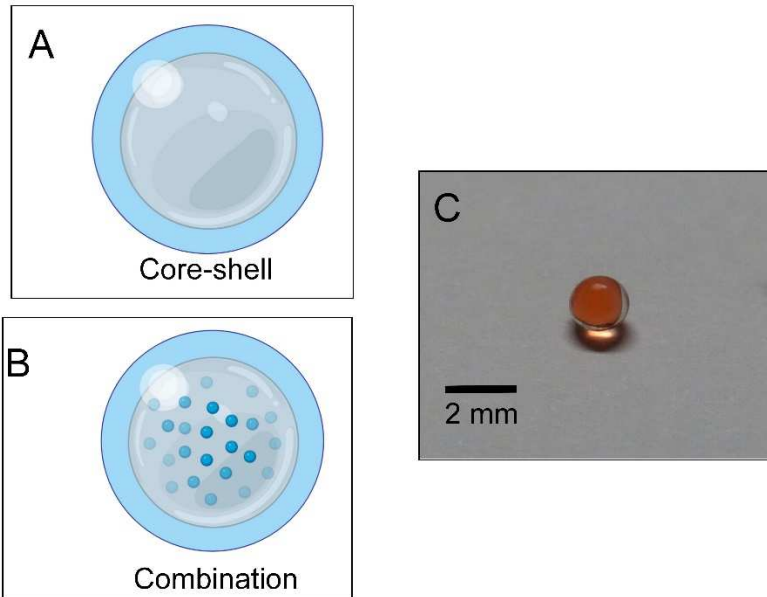
148 Another extrusion method is atomization. The process basis is the extrusion of pressurized
149 polymer solution through a nozzle while injecting pressurized air, atomized particles fall then

150 into a gelling bath. Atomization can be applied for lipid encapsulation for example (Strasdat
151 & Bunjes, 2013).

152 2.2.2. Coextrusion

153 Coextrusion, also called annular jet method, is an encapsulation technique which allows to
154 obtain core-shell capsules as shown in Fig.4A. Alginate solution and solutions containing the
155 substances to encapsulate are simultaneously injected through a coaxial nozzle, which permits
156 to obtain an annular jet formed by two concentric jets. The outer material represents the shell
157 material, *i.e.* alginate solution, and the inner contains the solution with the target substance.
158 The jet is then separated into droplets and collected in a gelling bath. As for the simple
159 dripping process, different separative methods are possible: vibration, electrostatic forces,
160 spinning disk or simple dropping into crosslinker solution (Oxley, 2012a).

161 In addition to the previously mentioned factors that impact beads size, a couple of factors are
162 specific to coextrusion process to reach a given shape of core-shell capsules. For instance,
163 nozzles sizes (internal/external) affect capsules size. Slow flow rate tends to produce larger
164 capsules (drop by drop system) than capsules produced at high flow rate (Lucía et al., 2017;
165 Oxley, 2012a).



167 **Fig. 4.** Scheme of a core-shell structural organization for capsules (A), scheme of a
168 combination structural organization for capsules (B) and a photograph of a core-shell capsule.
169 Coextrusion technology allows production of capsules with a huge payload (over 90%) and a
170 large range of capsules size can be obtained with a diameter from few microns to a several
171 millimeters. The process is easily scaled-up for industrial use (Oxley, 2012a; Wang et al.,

172 2013). For example, Lucia et al (2017) worked on the production of almonds essential oil
173 liquid-core capsules obtained by coextrusion process (Lucía et al., 2017). Silva et al (2018)
174 studied the encapsulation of *Lactobacillus acidophilus* and compared the simple dripping
175 method to the coextrusion technique. An additional protective function was observed for
176 beads produced by coextrusion and especially for capsules obtained with a composite shell
177 made of an alginate/shellac matrix (Silva et al., 2018).

178 3. Factors influencing alginate gelation and spherification

179 3.1. Molecular weight of alginate

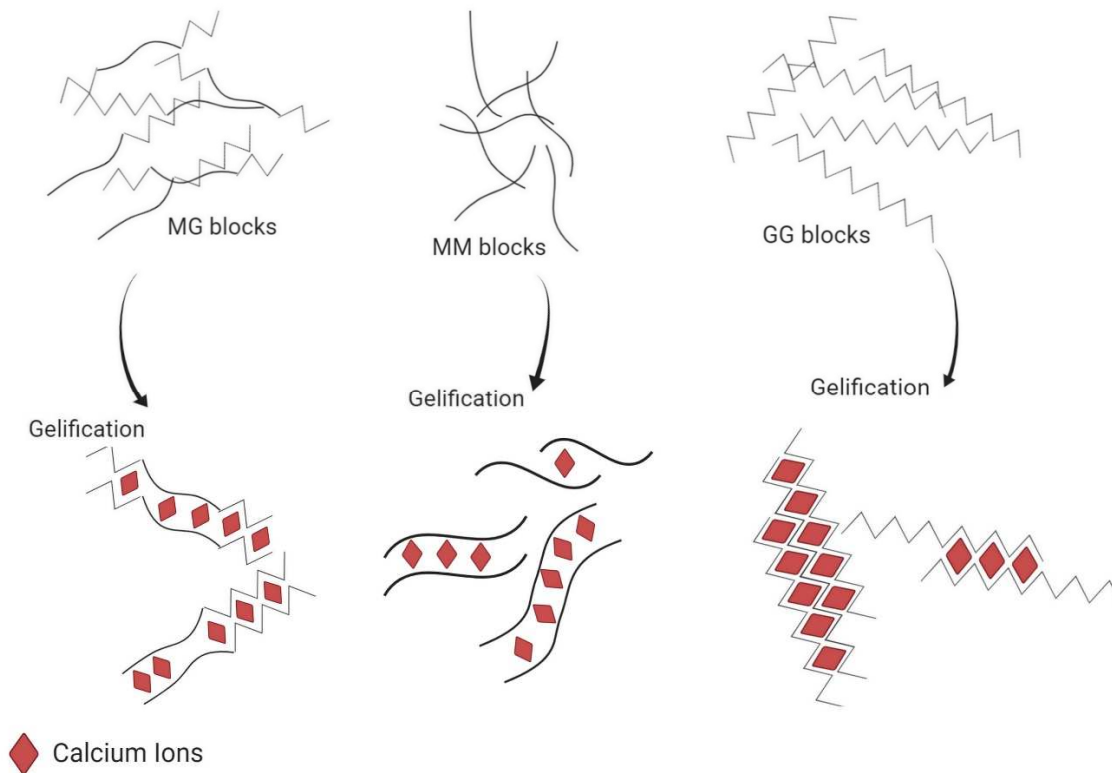
180 Generally, high molecular weight of alginate due to long polymeric chains results in a larger
181 number of Ca-binding sites then tighter crosslinking in the gel (Hu et al., 2020). These
182 interactions impact gelation process and produce a high viscosity gels, so that low molecular
183 weight alginate weight alginate ($1,43 \times 10^5$ g mol⁻¹) viscosity is 2.4 times lower than higher
184 molecular weight alginate ($3,5 \times 10^5$ g mol⁻¹) viscosity (0.05 Pa.s versus 0.12 Pa.s) in the same
185 experimental conditions.

186 Gelation kinetics are also faster with increasing alginate molecular weight (Fernández Farrés
187 & Norton, 2014). Moreover, similar conclusions have been found after acidic treatment of
188 high molecular weight alginate so that low molecular weight alginate obtained produced low
189 viscosity gels (Haug, Larsen, Smidsröd, et al., 1963; Jiao et al., 2019).

190 Effects of other novel processing methods have been studied. Such as high-pressure
191 homogenization also called dynamic high pressure that caused a reduction of alginate
192 molecular weight and viscosity under 300 MPa and after 5 cycles when a minimal viscosity
193 plateau was observed (Harte & Venegas, 2009).

194 3.2. M/ G ratio and distribution of G, M and GM units along the alginate chains

195 Alginate gelation is dependent of the percentage of G and M units, as a consequence of a
196 higher degree of hindered rotation around the glycosidic linking. Because of this
197 configuration, cross linking between alginate Ca²⁺ is mostly due to G units (Braccini et al.,
198 1999; Feng et al., 2017; Jiao et al., 2019). M units moderate elasticity and lateral association
199 in alginate gelation. Gels formed with high percentage of M units are reported as soft and
200 elastic while those formed with high percentage of G units are described as compact and rigid
201 (Leirvåg, 2017). Beads produced with low molecular weight and high G content alginate are
202 the strongest, the biggest and best relevant to protect probiotics by encapsulation (Ramos et
203 al., 2018).



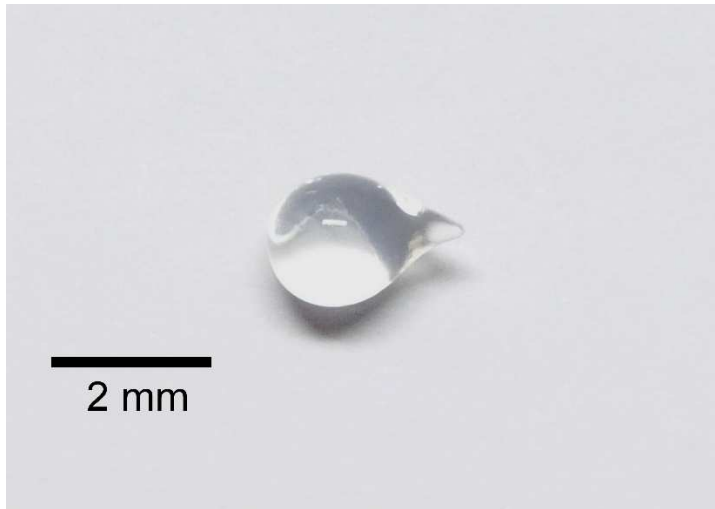
204

205 **Fig. 5.** Effect of calcium on the MG, MM and GG alginate units.

206 3.3. Alginate Concentration

207 Gelation can be impacted by alginate concentration. Fernández Farrés *et al.* (2013) found that
 208 higher concentration of the biopolymer, in the range of 1% to 4% (w/w), induced higher
 209 viscosity, elasticity rupture strength and gel hardness. As expected, higher concentration of
 210 alginate molecules increased the number of cross-linking interactions with calcium ions and
 211 reinforced gel structure (Fernández Farrés *et al.*, 2013). However, excessive concentration of
 212 alginate reduced binding opportunities by decreasing Ca^{2+} diffusion through the matrix (J.
 213 Yang *et al.*, 2020). Nevertheless, for moderate changes in alginate concentration from 1.3 to
 214 1.7% [w/w], Hu *et al.* (2020) did not notice significant variations of alginate beads structure.

215 In the case of beads processing, alginate concentration has also an impact on beads shape in
 216 alginate extrusion process, alginate beads tend to be more spherical when viscosity increases.
 217 The result of a bead made with the appropriate viscosity can be found in Fig.3C.
 218 Nevertheless, when viscosity is too high, beads are drop-shaped as shown in Fig.6 (Z. Q. Li *et al.*, 2013).
 219



220

221 **Fig. 6.** Example of a drop-shaped alginate bead.

222 3.4. Concentration of calcium ions

223 An increase of Ca^{2+} concentration results in an increase of cross-linking gelation rate. Faster
224 diffusion of calcium ions in gels lead to higher gel viscosity, elasticity, and stability (J. Li et
225 al., 2016). The calcium versus carboxyl group concentrations ratio is called the R value and
226 describes effect of Ca^{2+} on alginate gelation and it is defined as follows:

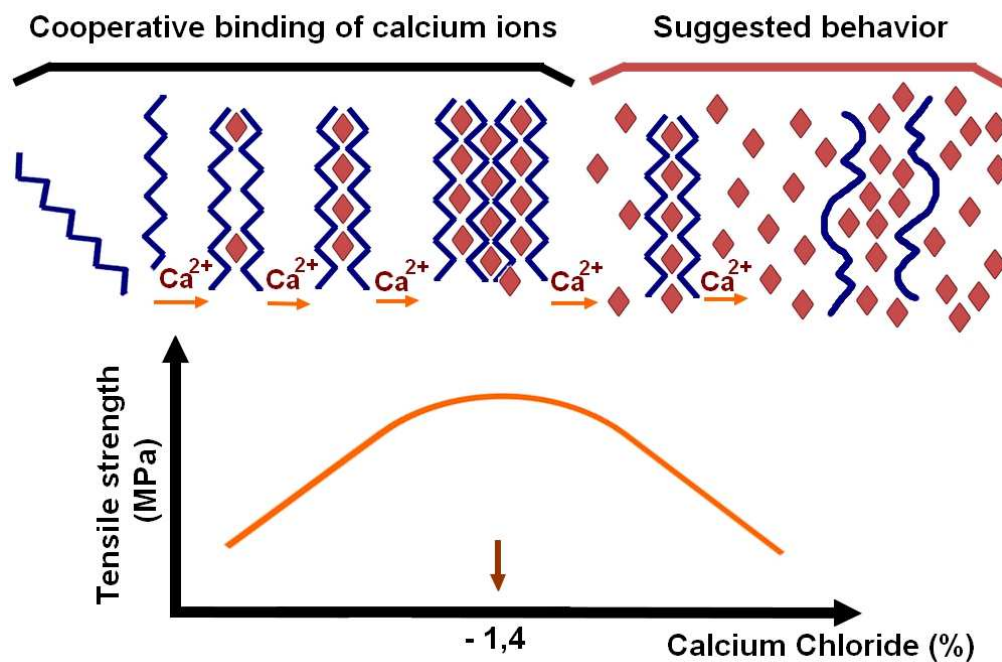
227

$$R = [\text{Ca}^{2+}]/[\text{COO}^-]$$

228 Alginate crosslinking with calcium ions can be described in three steps: (i) the mono-
229 complexation at $R < 0.25$, (ii) dimerization at $0.25 < R < 0.55$ resulting in formation of the egg-
230 box model; and (iii) third step occurs at $R > 0.55$ and results in the lateral association of the
231 polymer chains forming intra of inter-clusters (Y. Fang et al., 2007).

232 Higher viscosity and maximum tensile stress of alginate gel are reached at around 1.4% (w/w)
233 of $[\text{CaCl}_2]$ for alginate concentration equaled to 127mM. Ca^{++} saturation of alginate chains
234 can explain that maximum tensile stress occurred (Cuadros et al., 2012). At high calcium
235 concentration calcium ions induce excessive positive charges that will segregate alginate
236 chains leading to the gel disintegration. The mechanism between alginate structure and
237 calcium chloride concentration is illustrated in Fig. 7.

238 It should be noted that, while producing alginate beads, a high calcium concentration also
239 affects beads sphericity which tends to be less spherical at high calcium concentrations
240 (Cuadros et al., 2012).



241
 242 **Fig. 7.** Scheme representing the mechanism of strengthening and weakening of the alginate
 243 gel as a function of the concentration of calcium chloride (Adapted from Cuadros et al., 2012)

244 3.5. Residence Time

245 The time during which alginate is into contact with calcium ions in gelation bath is called
 246 residence time. When alginate drops are exposed to calcium, ions migrate from surface to
 247 core. Required residence time for reticulation (t_{gel}) can be calculated using Fick's second law
 248 which can be expressed as:

$$249 \quad \frac{C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

250 Where C is alginate concentration (mol/m^3), t is time (s), D is diffusion substance coefficient
 251 (m^2/s) and x is the position (m).

252 Fick's second law can be approximated as:

$$253 \quad \frac{C}{t_{gel}} \approx D \frac{C}{L^2}$$

254 Where C represents alginate concentration (mol/m^3), L is a characteristic length given by the
 255 bead radius (m), and D the diffusion coefficient of calcium chloride in water: $10^{-9}m^2/s$
 256 (Evageliou et al., 2000). It has been demonstrated that after a residence time of 30 min,

257 samples exposed to different calcium concentrations showed similar behaviors (Cuadros *et al.*
258 (2012). Residence time seems to have no effect on beads sphericity (Hartmann *et al.*, 2006).

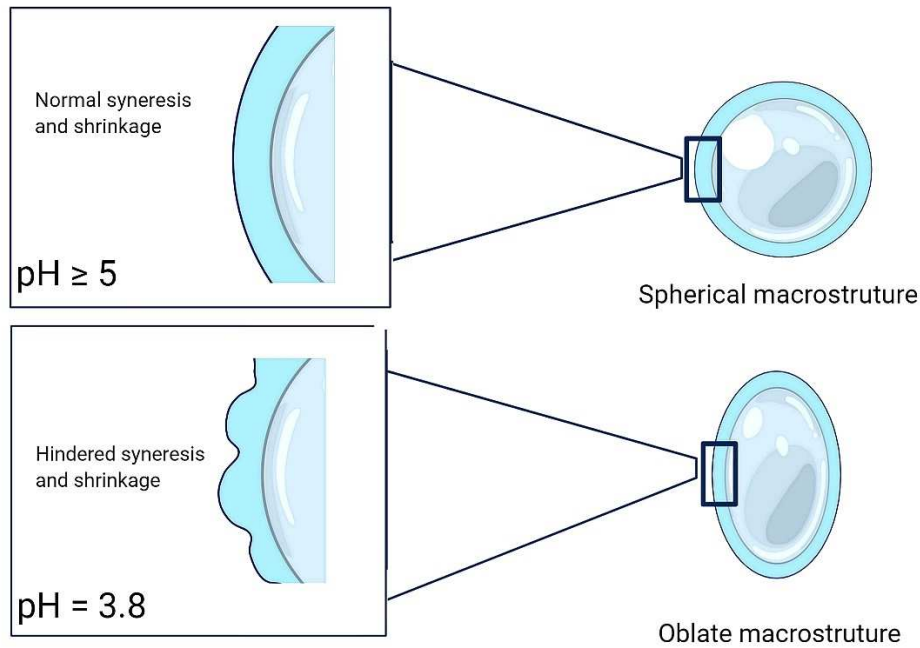
259 3.6. pH

260 pH impacts alginate water solubility and ion-binding as it determines the electrostatic charges
261 of G and M units. M and G units have pKa of 3.38 and 3.65, respectively. Alginate polymer
262 residues have pKa value usually estimated around 3.4 (Park *et al.*, 2019). Alginate composed
263 of a high content of MG-sequences are more soluble at low pH and precipitate at pH around
264 2.6 and 2.7 while high G units content alginate precipitate at pH around 3.25 (Haug, Larsen,
265 Samuelsson, *et al.*, 1963; Sonogo *et al.*, 2016; Zazzali *et al.*, 2019). At higher pH values
266 (below pH = 10.5) glycosidic bonds of alginate gel start to weaken and break leading to
267 structural degradation (Zazzali *et al.*, 2019).

268 The microstructure of the alginate gel has been largely studied and it has been established that
269 gel obtained at pH = 3.8 has a denser and interconnected microstructure due to stronger chains
270 interactions. This phenomenon leads to less syneresis and shrinkage of the gel. Gels produced
271 $\text{pH} \geq 5$ present lower interconnectivity in their microstructure and lower density, then
272 allowing syneresis and shrinkage (Augst *et al.*, 2006; Jeong *et al.*, 2020; Moe *et al.*, 1992;
273 Topuz *et al.*, 2012).

274 During preparation of alginate beads, interfacial tension is impacted by pH, lower pH values
275 result in lower interfacial tension. pH also influences beads shape, beads produced in low pH
276 gelation bath tend to be oblate, particularly in low alginate and ions concentrations, while
277 those produced at $\text{pH} > 4$ tend to be spherical (Chuang *et al.*, 2017; Sonogo *et al.*, 2016;
278 Zazzali *et al.*, 2019).

279



280

281 **Fig. 8.** Macrostructure of alginate beads synthesized at pH= 3.8 and pH ≥ 5.

282 3.7. Temperature

283 Gelation temperature has an impact on alginate gel microstructure. High temperature seems to
 284 enhance and facilitate calcium ions penetration through alginate network while low
 285 temperature slows down diffusion and gelation process. Low temperature led to more ordered
 286 and regular network and higher temperature produced a denser network with lower young's
 287 modulus (Jeong et al., 2020). At physiological gelation temperature around 36-40°C, an
 288 alginate gel with high young's modulus was produced (Leo et al., 1990; Oates & Ledward,
 289 1990).

290 Jeong et al. (2020) reported that an increase in gelation temperature led to lower alginate
 291 viscosity and reduced beads size. Gelation temperature seems also to influence beads
 292 sphericity that increased with higher gelation temperature. Besides, a high beads rupture
 293 strength was reported at low gelation temperature (5°C) (Cerciello et al., 2017; Y. Gu et al.,
 294 2018; Sanchez-Ballester et al., 2019; Vu et al., 2017). If the gels are stable at range 0 to
 295 100°C, more G units content increase alginate gels thermal stability (Hartmann et al., 2006).
 296 Above 100°C the structure began to depolymerize and at 180°C the gel was totally
 297 destructured (Aida et al., 2010).

298 3.8. Ionic strength

299 Gelation is impacted by solution ionic strength. Low ionic strength allows gel formation, but
 300 high level of monovalent salts competed with calcium ions for carboxyl alginate groups
 301 resulting in an instable and weak system. Van Leusden et al. (2017) reported a structural
 302 alteration of alginate beads exposed to high NaCl concentration. This modification might be
 303 due to a decrease of electrostatic attractive interactions into the system and/or increase in
 304 beads pore size resulting in the release of the encapsulated compounds (Jiao et al., 2019).
 305 Apparently, salts ions dislocated some Ca²⁺ leading to gel disintegration. The extent of
 306 network destructure increased with higher salts concentration (Jiao et al., 2019).

307 3.9. Shear rate

308 Jiao et al. (2019) reported the influence of shear rate on the gelation method described as “*in*
 309 *situ* addition of calcium”, to favor homogenous gelation by avoiding disadvantages of
 310 external gelation. Shear rate had an impact on gelation kinetics: when shear was applied at the
 311 beginning of gelation process, the onset time of gelation was higher and gel particles were
 312 faster formed (Hernández-González et al., 2020; Jiao et al., 2019; Puguán et al., 2014).
 313 However, gel viscosity decreased with increasing shear rate applied demonstrating the
 314 relation between shear rate and gel rheology (Mancini & McHugh, 2000).

315
 316 In conclusion for factors influencing alginate gelation and spherification, Table 2 summarizes
 317 the effect of the principal parameters on alginate beads gelation. We choose to present the
 318 clearer effect for an efficient production of alginate bead with desired properties. Some
 319 parameters have not been enough studied to appear in our summarized Table 2 and factors as
 320 pH has an effect depending on application.

321 **Table 2**
 322 Effects of increased factors influencing alginate gelation and spherification.

Enhanced Parameters	Effects of gel formation				Effects on beads formation			
	Viscosity	Compactness	Network stability	Ca ²⁺ penetration kinetics	size	strongness	sphericity	rupture strength
	Alginate structure							
↗Molecular weight	↗	↗	↗	↘	↘	↗	↗↘	↗
↗M/G ratio	↘	↘	↘	-	-	↘	-	↗
	Experimental environment							
↗ [alginate]	↗	↗	↗	↘		↗	↗↘	
↗ [Ca ²⁺]	↗	↗	-	↗	-	-	↘	
↗Temperature	Optimum at 36-40°C	↘	↘	↗	↘	-	↗	↘

323 4. Composite Alginate gels

324 Composite gels with alginate and other polymers have been studied for multiple purposes and
325 in many fields, such as encapsulation, packaging films, or edible films. This interest results
326 from the ambition to modify gel mechanical properties (Poncelet et al., 1992), brings new
327 characteristics and extends its use. Polysaccharides and proteins are the main components
328 used for copolymerization. Depending on copolymer nature mixed with alginate, gelation
329 process varies as described below.

330 4.1. Polysaccharides as co-polymer

331 4.1.1. Pectin

332 Pectin is a biopolymer extracted from plant cell walls like citrus peel or apple pomace. B.
333 Zhang et al. (2019) reported that pectin gelation is enhanced by addition of guluronic units.
334 Encapsulation in alginate-pectin gel exhibited a significant reduction of anthocyanins
335 degradation (Guo et al., 2018; B. Zhang et al., 2019). A lower energy consumption has also
336 been demonstrated in jelly candy manufacturing using alginate-pectin cold gelation instead of
337 traditional heating process (de Avelar & Efrain, 2020). In the medical field, alginate-pectin
338 hydrogel presented great improvement of mechanical properties, water absorption, thermal
339 stability, and drug release for wound dressing application (Oh et al., 2020; Rezvanain et al.,
340 2017). In food industry, pectin-alginate-gelatin composite gels showed promising results for
341 probiotics encapsulation, by increasing stability of encapsulated bacteria (Vaziri et al., 2018).

342 4.1.2. Gums

343 4.1.2.1. Guar gum

344 Guar gum is extracted from guar beans (*Cyamopsis tetragonoloba*). It is composed of a linear
345 chain of (1-4)- β -D-mannopyranose linked with β -galactopyranosyl groups. Guar gum is water
346 soluble and usually used in coating. Guar gum is used as thickener of alginate-guar gum gel
347 (Mousavi et al., 2019; Rastegar & Atrash, 2020).

348 Gel made with alginate/guar gum was stronger at lower calcium level than pure alginate gel
349 and presented a high elasticity and rigidity due to a lower degree of porosity. It reduced
350 syneresis and shrinkage during storage. Guar gum addition to alginate enhanced network
351 stability in acidic conditions and thermal processing (Mousavi et al., 2019, 2020). Alginate-
352 guar gum gel exhibited an improved polyphenols and betacyanins encapsulation (Aguirre
353 Calvo et al., 2019), and enhanced preservation of antioxidant activity for encapsulated fatty
354 acids (Aguirre-Calvo et al., 2020).

355 4.1.2.2. Gum arabic

356 Also known as acacia gum, gum arabic is a natural polymer extracted from acacia trees and it
357 consists of β -D-galactopyranosyl units branched with side chains of L-rhamnose, D-galactose,
358 L-arabinose and D-glucuronic acid. This polymer is largely used in food, cosmetic and
359 pharmaceutical industries as thickening agent and stabilizer (Tsai et al., 2017). Interaction
360 between alginate and gum arabic has been recently studied by Sabet et al (2021). These
361 authors reported interactions between polymers at pH 7 and a stronger synergy at pH 4, due to
362 ionic interactions between respective negative and positive charges of alginate and gum
363 arabic. The ionic binding between alginate and gum arabic results in an increase of gel
364 viscosity and viscoelasticity (Sabet et al., 2021).

365 The alginate/gum arabic composite exhibited great results in drug encapsulation. Moreover,
366 Nayak et al (2012) reported an encapsulation efficiency of $86.02 \pm 2.97\%$.

367 4.1.2.3. Other gums

368 Other gums such as galbanum gum or basil seed gum have been investigated recently for
369 different applications, especially in food packaging field. Addition of gum to alginate matrix
370 brings a real advantage in terms of barrier function against gas, water, oil transport (Hamedi et
371 al., 2017; Mousavi et al., 2020).

372 4.1.3. Chitosan

373 Chitosan is a linear polysaccharide extracted from crustaceans' shells chitin. It is a nontoxic
374 biopolymer formed by D-glucosamine and N-acetyl glucosamine units. Chitosan is used in
375 numerous field due to its numerous properties, *i.e.* antioxidant, lipid binding, anti-
376 inflammatory and antimicrobial effects (Kulig et al., 2016).

377 Chitosan gel viscosity increases with pH. The strongest alginate-chitosan gels were obtained
378 with increasing pH and chitosan weight percentage, but considerable viscoelasticity and
379 maximum encapsulation capability were obtained at neutral pH (Afzal et al., 2018).

380 Combining alginate and chitosan improves mechanical and chemical gel properties and favors
381 thermal resistance. Chitosan has been largely investigated in coating alginate capsules, due to
382 its positive charges that lead to an ionic complexation with negative charges of alginate. This
383 complexation allows chitosan solubilization into a non-acetic acid or hydrochloric solutions.
384 Thereby, coating with chitosan enhanced capsules membrane thickness and their protective
385 abilities (Fernandes et al., 2020; Raeisi et al., 2020; Taqieddin & Amiji, 2004).

386 Composites exhibited great results for globulin preservation during thermal treatment (Kulig
387 et al., 2016; Romo et al., 2020). De Prisco et al (2015) reported a better stress tolerance to
388 food processing for probiotics encapsulated with alginate-chitosan composites.
389 Alginate/chitosan composites have been examined for oil co-encapsulation or
390 microencapsulation to protect oil from oxidation, capsules showed good oxidative stability
391 and oxidation products were lower for chitosan/alginate compared to non-encapsulated oil.
392 Results also showed an effective oil vehicle for nutraceuticals (Atencio et al., 2020; Hamed et
393 al., 2020). Microwave treatments have also been considered for drugs controlled-release
394 alginate/chitosan microbeads. Depending on experimental conditions, microwave treatments
395 could induce cross-linkage or breakdown. Thus, Wong et al. (2002) reported a retarded drugs
396 release from alginate/chitosan beads treated at 80 W for 10 minutes as a consequence of
397 enhanced alginate/chitosan cross-linking.

398 4.1.4. Carrageenan

399 Carrageenan is a sulphated polygalactan that can be obtain from red seaweeds, it contains 15
400 to 54% charged sulphate ester groups. This polysaccharide is formed by D-galactose and 3,6-
401 anhydro-galactose linked by α -1,3 and β -1, 4-glycosidic bonds. There are various
402 carrageenan types: λ , κ , ι , ϵ , μ . The classification depends on the sulphate ester groups number
403 and position (Necas & Bartosikova, 2013). Alginate/carrageen composite have been largely
404 investigated in edible films formulation for food and non-food applications; good barrier and
405 protection properties have been reported (Tavassoli-Kafrani et al., 2016).
406 Combination of κ -carrageenan and alginate enhances gel rigidity and mechanical stability.
407 Carrageenan/alginate composite gel appeared more transparent than conventional alginate gel
408 with a compact and smooth surface. Addition of carrageenan tends also to improve thermal
409 properties, elastic modulus, gel water content, and swelling which is induced by sulphate
410 groups from carrageenan molecules. Beads formed with carrageenan/alginate composite had a
411 larger diameter than alginate beads (L. Li et al., 2019; Mohamadnia et al., 2008).
412 The pH-dependent properties allowed use of carrageenan/alginate complex in a pH-
413 responsive beads for insulin encapsulation. In this study, protection against acidic condition
414 and controlled release were investigated (Lim et al., 2017). Good protection was observed at
415 pH=1.2 and progressive release with good kinetics was noticed at pH=7.4. This point made
416 composite carrageenan/alginate beads promising encapsulation matrix for oral insulin intake.
417 L.Gu et al (2021) worked on immunoglobulin encapsulation for controlled release and

418 reported high encapsulation efficiency. Composite exhibited a denser internal microstructure
419 and a good protection in acidic gastric conditions (L. Gu et al., 2021).

420 4.1.5. Starch

421 One of the most abundant and cheap natural polysaccharides is starch. Starch contains
422 amylose and amylopectin with linkage of α -D-glucopyranose molecules. Starch is largely
423 used in hydrogel production, due to its free hydroxyl groups. Starch works in synergy with
424 alginate. Water absorption capacity and encapsulation efficiency are improved. For instance,
425 López Córdoba et al. (2013) reported improvement of encapsulation efficiency from 55 to
426 65% of liquid extract of yerba mate (a high polyphenols tea-like beverage) (da Silva
427 Fernandes et al., 2019; López Córdoba et al., 2013). The synergy between starch and alginate
428 depends on chemical structures of both polymers, but also on processing conditions, such as
429 pH, ionic strength and salts concentration (da Silva Fernandes et al., 2019). Gelation of
430 alginate/starch composite occurs using different divalent cations (Mn^{2+} , Zn^{2+} , Ca^{2+} for
431 example), and characteristics of the composite gel vary from an ionic crosslinker to another
432 (da Silva Fernandes et al., 2019).

433 Addition of starch to alginate creates composite gels with variable porosity depending on
434 starch type, but starch addition provides a slower release of encapsulated substances (Feltre,
435 Almeida, et al., 2020; Okunlola & Adewusi, 2019). Starch type impacts gel water retention,
436 stability, and digestibility. Those features must be considered in the formulation of controlled
437 release beads. For instance, Hassan et al (2020) obtained promising results for gradual release
438 of nisin encapsulation (Feltre, Almeida, et al., 2020; Hassan et al., 2020).

439 Feltre, Sartori, et al (2019) recently reported an efficient encapsulation of oil with starch
440 incorporation in alginate systems, due to greater oil dispersion into oil/starch/alginate
441 emulsion. Beads formed by oil/starch/alginate emulsions containing equal proportions of
442 alginate and starch presented good results in terms of antioxidant activity preservation and
443 storage stability (Feltre, Sartori, et al., 2020). Similar results concerning encapsulated
444 component stability have been obtained by Jain et al (2020) for lycopene encapsulation with
445 an enhanced bioaccessibility. This could be promising for nutraceuticals and functional foods
446 application (Jain et al., 2020). As an example, alginate/starch/gelatin composite has been
447 recently investigated for encapsulation of β -carotene in oil/starch/alginate/gelatin emulsion.
448 The study demonstrated a great stability and oxidation reduction for encapsulated β -carotene
449 compared to β -carotene in free oil. Those results are very important to extend shelf-life of

450 components sensitive to oxidation during processing for food or drugs application (Guedes
451 Silva et al., 2021).

452 4.2. Proteins/ polypeptides as co-polymer

453 4.2.1. Whey Proteins

454 Under specific conditions, proteins can be used as cations source for alginate gel cross-
455 linking. Thus, alginate/proteins composite hydrogels are largely investigated and exhibited
456 great results in protein carriers with controlled release kinetics (Rahmani & Sheardown,
457 2018). Denatured whey protein isolates and alginate composite gels have shown great
458 thermal stability after 1 minute at 63 and 72°C and a good resistance to acidic conditions for
459 encapsulated probiotics by extrusion or spray-drying process (H. Liu et al., 2018;
460 Praepanitchai et al., 2019; Rajam et al., 2012). Dehkordi et al (2020) worked on an
461 alginate/whey protein isolate composite for probiotics encapsulation and reported a highest
462 survivability of *lactobacillus acidophilus* for an optimal matrix composed of 4.54% (w/v) of
463 alginate and 10% (w/v) of whey protein isolate (Dehkordi et al., 2020).

464 Recent studies showcased interest of protein addition in edible alginate films. Chkravartula et
465 al (2019) reported significant beneficial effects of whey protein on the physico-chemical,
466 rheological, mechanical and optical properties of edible packaging. Addition of whey proteins
467 to alginate decreased film viscosity and enhanced its hydrophobicity and reduced film water
468 absorption (Chakravartula et al., 2019).

469 4.2.2. Gelatin

470 Gelatin is largely studied in coacervation process, which is a spontaneous phase separation
471 between an insoluble complex and of another aqueous phase that occurs with pH change (de
472 Matos et al., 2018). Consequently, gelatin and alginate are pertinent materials for
473 encapsulation process by coacervation. Promising results have been obtained for essential oils
474 microencapsulation, especially with a 4% gelatin and high essential oils concentration matrix,
475 with a 73.7% encapsulation efficiency, and a good terpenes preservation (de Matos et al.,
476 2018; Heckert Bastos et al., 2020). Moreover, Y. Li et al (2019) reported a good effectiveness
477 of alginate/arabic gum /gelatin composite for preservation of encapsulated antioxidant
478 substances for oral delivery (Y. Li et al., 2019). Lemos et al (2017) also observed high
479 encapsulation efficiency in the production of buriti oil microcapsules through coacervation
480 (Lemos et al., 2017).

481 M. Lopes et al (2017) worked on probiotics encapsulation using an alginate/gelatin composite
482 matrix. Spherical and regular beads were obtained, and higher cells viability was reported at

483 1% w/v alginate and 0.1% w/v gelatin. Therefore, beads contained up to 10^5 CFU g^{-1} after 4
484 months of storage (M. Lopes et al., 2017).

485 **Table 3**

Co-polymers	Composition	Positive effect of co-polymer addition to alginate	Application	Refs
Pectin	α -D-galacturonic acid α -L-rhamnose	Encapsulated substance stability. Gel water absorption and thermal stability. Lower gel viscosity.	Probiotics encapsulation. Cold gelation for candy manufacturing.	Belscak-Cvitanovic et al., 2015; de Avelar & Efraim, 2020; Oh et al., 2020; Vaziri et al., 2018
Guar gum	β -D-mannopyranose β -galactopyranosyl	Strong gel Low porosity gel Network stability to heat and acidic conditions	Coating for food packaging Fatty acids encapsulation	Aguirre-Calvo et al., 2020; Mousavi et al., 2019; Rastegar & Atrash, 2020
Gum arabic	β -D-galactopyranosyl L-rhamnose D-galactose	High viscosity and viscoelasticity gel Encapsulation efficiency	Drugs encapsulation Radish juice liquid-core encapsulation	Nayak et al., 2012; Sabet et al., 2021; Tsai et al., 2017
Chitosan	D-glucosamine N-acetyl-glucosamine	Mechanical, chemical properties and thermal stability. Gel protective abilities and permeability	Protein encapsulation Omega-3 rich oil encapsulation Coating capsules	Fernandes et al., 2020; Hamed et al., 2020; Kulig et al., 2016; Romo et al., 2020
Carrageenan	D-galactose 3,6-anhydro-galactose	Gel rigidity and mechanical stability (elastic modulus). Water content, thermal properties, and swelling.	Immunoglobulins encapsulation Edible films for food application	L. Gu et al., 2021; L. Li et al., 2019; Necas & Bartosikova, 2013; Tavassoli-Kafrani et al., 2016
Starch	Amylose Amylopectin α -D-glucopyranose	Water absorption. Better oxidation stability Capsule digestibility	Spirulina encapsulation Edible films for food packaging Nisin or lycopene encapsulation	Feltre, Sartori, et al., 2020; Jain et al., 2020; Rajmohan & Bellmer, 2019; Wu et al., 2001
Whey protein	α -lactalbumin β -lactoglobulin Albumin Immunoglobulins	Gel antioxidant properties Active protection against visible light, heat, and acidic conditions	Films for food packaging Probiotics encapsulation	Chakravartula et al., 2019; Dehkordi et al., 2020; Oliveira Filho et al., 2019; Praepanitchai et al., 2019
Gelatin	Amino acids	Encapsulation efficiency Set up coacervation process	Essential oils encapsulation Probiotics encapsulation Antioxidant encapsulation	Heckert Bastos et al., 2020; Y. Li et al., 2019; S. Lopes et al., 2017

486 Co-polymers for alginate composite gels for encapsulation.

487

488 5. Other Encapsulation processes using alginate

489 5.1. Spray-drying

490 Spray-drying is known since the 1930's as one of the earliest encapsulation techniques due to
491 its simplicity of application and high productivity among many other advantages (Table 4) (Z.
492 Fang & Bhandari, 2012). The process principle is injection of a solution (emulsion or
493 dispersion with active compounds) through a simple nozzle or centrifugal wheel. The liquid is
494 then atomized into small droplets which fall and meet hot air in a drying chamber. After water
495 evaporation, particles fall to the bottom of the chamber and are collected in a powder form.

496 Spray-drying process is applied in many fields and several wall materials can be used.
497 Alginates exhibit good results for volatiles and emulsions encapsulation (Z. Fang & Bhandari,
498 2012; Rodríguez et al., 2016).

499 The efficiency of spray-drying process depends strongly on inlet air temperature, particularly
500 for thermolabile substance encapsulation, and can affect particles chemical and physical
501 properties in addition to core materials stability (X. Sun et al., 2020). In this perspective, X.
502 Sun et al (2020) studied the impact of inlet air temperature on spray-drying
503 microencapsulation of lipophilic carvacrol in an oil-in-water emulsion with alginate/pectin
504 composite shell material. They reported an optimum temperature for spray-drying
505 encapsulation between 100 and 130°C for carvacrol. However, even if a higher temperature
506 tends to increase encapsulation efficiency, it leads to reduce moisture content and retention
507 efficiency (X. Sun et al., 2020).

508 Recently, Stobel et al. (2018) presented a new encapsulation process using spray-drying
509 technology and called the Cross-Linked Alginate Microcapsules process (CLAMs process). It
510 uses a calcium ions source which is insoluble at feed pH, but when solution is atomized the
511 base present in the matrix evaporates which drop its pH and allows calcium ions to solubilize
512 and react with alginate. The advantage of this process is to reduce the multi-step conventional
513 spray-drying process into a one-step operation (Jeoh et al., 2020; Strobel et al., 2018).

514 Stobel et al (2020) worked on fish oil encapsulation using the CLAMs process and reported
515 good results in term of shelf-life of encapsulated fish oil in a shell material made of modified
516 starch and alginate. Some promising enteric release properties were also observed for
517 gastrointestinal delivery of lipophilic bioactives (Strobel et al., 2020).

518 5.2. Spray-cooling

519 Also known as spray-congealing or prilling, spray-cooling is a process that allows atomization
520 of a liquid into small particles. The process is similar to spray-drying, the solution is injected
521 through a pressure nozzle, vibrating nozzle or a spinning disk into an atomization chamber.
522 Unlike spray-drying, the atomized liquid is cooled and hardened (Oxley, 2012b).

523 Encapsulation by spray-cooling allows encapsulation of actives ingredients dispersed into a
524 liquid matrix. Instead of spray-drying, encapsulation by spray-cooling allows encapsulation of
525 thermolabile substances (Oxley, 2012b). This process is used in food and nutraceutical
526 industry for preservation of flavor (Oxley, 2012b), vitamins (Chalella Mazzocato et al., 2019),
527 or other bioactive ingredients like probiotics (Dong et al., 2013).

528 5.3. Coacervation

529 Coacervation occurs in a colloidal system and leads to liquid/liquid phase separation between
530 a colloid-rich phase also known as coacervate phase and a solvent-rich diluted phase. The
531 coacervate phase can be composed of a single polyelectrolyte. In this case, it is called simple
532 coacervation. Complex coacervation occurs when the coacervate phase is composed of an
533 ionic complex of two opposite charges polyelectrolytes as for alginate complex coacervation
534 for encapsulation purposes. Solution pH strongly impacts coacervate formation, in addition to
535 polyelectrolytes concentrations and their mixing ratio, ionic strength and temperature (Gorji et
536 al., 2018; Thies, 2012).

537 Combination of proteins and alginate is often studied for delivery systems, and in many fields
538 such as food, cosmetic and pharmaceutical industries. Gorji et al (2018) worked on
539 characterization of alginate, beta-lactoglobulin and bovine serum albumin interactions in
540 solution. A protein-alginate ratio of 2:1 was used for this study. Being amphoteric proteins,
541 Beta-lactoglobulin and bovine serum albumin have an isoelectric point of 5.2 and 5,
542 respectively. They present positive charges at lower pH where alginate exhibit negative
543 charges at low pH. Therefore, complex coacervation occurred mainly at pH range between
544 ~1.6 and 4.2 where due to opposite charges of alginate and proteins (Gorji et al., 2018).

545 Another complex coacervation using gelatin and alginate has also been largely studied for
546 encapsulation. Alginate, negatively charged at low pH, can form a complex coacervate with
547 gelatin for essential oil encapsulation. Heckert Bastos et al. (2020) reported an optimum ratio
548 of 6:1 gelatin to sodium alginate and a pH of 4 for black pepper essential oil encapsulation
549 with an efficiency up to 82%. Similar efficiency result (74%) has been reported for citronella

550 essential oil encapsulation using 4% of gelatin and 10% of alginate. Microcapsules with a 434
551 μm diameter have been obtained with promising results for controlled release (de Matos et al.,
552 2018).

553 For olive oil encapsulation, microcapsules sizes increase with the increase of oil amount but
554 decreases with the increase of surfactant amount. Besides, FTIR spectra of free olive oil and
555 microencapsulated oil have shown same characteristics so that no interactions between oil and
556 alginate/gelatin composite have been exhibited (Devi et al., 2012).

557

Table 4

558

Advantages and limitations of principal encapsulation methods using alginate.

Methods	Advantages	Limitations	Refs
Extrusion	<ul style="list-style-type: none"> - Easy application and industrialization - Hydrophilic matrix - Encapsulation of a large variety of substances - Protection against oxidation - Long shelf-life - various capsules size 	<ul style="list-style-type: none"> - Low payload - Requirement of thermal treatment not compatible with heat-sensitive ingredients encapsulated -High porosity of microcapsules -Pure oil encapsulation in complicated 	Ching et al., 2017; Gouin, 2004.
Coextrusion	<ul style="list-style-type: none"> -Large payload -Slow-release kinetics compared to other methods -Large variety of core materials -Scaled up process -Additional protective barrier brought by the shell - Encapsulated material is surrounded by wall material 	<ul style="list-style-type: none"> - Risk of nozzles obstruction due to their small size - Process highly-dependent on core and shell fluid rates - Multifluidic technology expensive costs vs other methods -Difficulty to encapsulate extremely viscous matrix 	Gouin, 2004; Oxley, 2012a; Silva et al., 2018.
Spray-drying	<ul style="list-style-type: none"> -Inexpensive technology and availability of the equipment - Possibility to perform double or triple encapsulation - Good encapsulation efficiency - Good stability for storage -Quick process. -Low product volume for reduced transport cost 	<ul style="list-style-type: none"> - Limited shell materials choice - Exposition risk due to volatiles compounds at high temperature - Oxidation and degradation of thermolabile substances - Particles agglomeration - Particules size control 	Fang and Bhandari, 2012; Rodríguez et al., 2016; X. Sun et al., 2020.
Spray-cooling	<ul style="list-style-type: none"> -Inexpensive technology for encapsulation -Large possibility of materials -Fast release (depending on the main objective) -Controlled size and higher specific surface area vs particles spray-dried. 	<ul style="list-style-type: none"> - Weak protection on particles surfaces - High energy and cost required -Longer process time vs spray-drying - Handling and storage specific requirements 	Gouin, 2004; Liliana and Vladimir, 2013; Oxley, 2012b.
Complex coacervation	<ul style="list-style-type: none"> -High payload -Controlled release possibilities -Flexible regarding shell material -Large particles size range -No specific equipment required 	<ul style="list-style-type: none"> -Expensive process -Technique complexity - Low size range of capsules - Cohesion and adhesion of microcapsules. - Presence of solvents residues in spheres 	Bouquerand et al., 2012; Gouin, 2004; Ozkan et al., 2019; Saravanan and Rao, 2010;

559 6. Conclusion

560 Alginate is a widely used and investigated polymer for a large variety of technical
561 applications as thickener or stabilizer but also in spherification process for its gelation ability
562 to encapsulate sensible materials. It is Generally Recognized as Safe (GRAS), being nontoxic,
563 nonantigenic, satisfactorily biocompatible, and sufficiently biodegradable.

564 Alginate gelation depends on polymer chemical structure counting its molecular weight and
565 G/M units ratio and distribution along the alginate chain. Experimental environment greatly
566 influences alginate gelation including pH, temperature, polymer concentration, crosslinker
567 concentration, residence time and ionic strength.

568 Alginate has the advantage to be an encapsulation material adapted for most encapsulation
569 process especially spherification (extrusion and coextrusion) through its biocompatibility and
570 capability to form a hydrogel through ionic cross-links with divalent cations, such as calcium
571 ions. However, alginate has some limitations in certain applications. Therefore, alginate can
572 work in synergy with many polymers (e.g. polysaccharides and proteins). Thus, composite
573 alginate gels are widely studied recently in order to improve alginate encapsulation and
574 spherification properties, including encapsulation efficiency and payload, storage stability and
575 barrier properties.

576 Alginate is certainly one of the most promising encapsulation materials.

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