

# 1 Superabsorbent polymers: a review on the characteristics and 2 applications of synthetic, polysaccharide-based, semi-synthetic and 3 ‘smart’ derivatives

4 Arn Mignon<sup>a,b</sup>, Nele De Belie<sup>a,\*</sup>, Peter Dubruel<sup>b</sup>, Sandra Van Vlierberghe<sup>b,\*</sup>

5  
6 <sup>a</sup> Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University,  
7 Technologiepark Zwijnaarde 904, B-9052 Ghent, Belgium.

8 [Arn.Mignon@ugent.be](mailto:Arn.Mignon@ugent.be), [Nele.DeBelie@ugent.be](mailto:Nele.DeBelie@ugent.be)

9  
10 <sup>b</sup> Polymer Chemistry & Biomaterials Research Group, Center of Macromolecular Chemistry,  
11 Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281, Building S4-  
12 bis, B-9000 Ghent, Belgium.

13 [Arn.mignon@ugent.be](mailto:Arn.mignon@ugent.be), [Peter.Dubruel@ugent.be](mailto:Peter.Dubruel@ugent.be), [Sandra.VanVlierberghe@ugent.be](mailto:Sandra.VanVlierberghe@ugent.be)

14  
15 \*Corresponding author: Sandra Van Vlierberghe  
16 Krijgslaan 281, S4 bis  
17 B-9000 Ghent, Belgium  
18 e-mail : [Sandra.VanVlierberghe@UGent.be](mailto:Sandra.VanVlierberghe@UGent.be)  
19 tel: 003292644508  
20

## 21 Abstract

22 The current review provides an overview of different types of superabsorbent polymers (SAPs) together  
23 with appropriate strategies elaborated to enable their synthesis. The main focus will be on  
24 polysaccharide-based, semi-synthetic and ‘smart’ SAPs along with their derivatives. SAPs have already  
25 shown their use in a plethora of applications including diapers, the biomedical field, agriculture, etc.  
26 The different polymer classification possibilities are discussed, as well as the classification of the  
27 constituting building blocks. The main part of SAPs still has a synthetic origin. However, as they are  
28 often not biocompatible, biodegradable or renewable, natural SAPs based on polysaccharides have  
29 gained increasing interest. Due to the low solubility of synthetic polymers, purification problems or the  
30 need for organic solvents, a trend has emerged towards combining polysaccharides with synthetic  
31 monomers to create semi-synthetic, hybrid SAPs for specialized applications with fine-tuned properties  
32 including wound dressings, fertilizers or self-healing concrete. These specialized, semi-synthetic SAPs  
33 offer strong potential for a series of applications in the future. However, future research in this respect  
34 is still needed to optimize homogeneity and to increase gel fractions. A final part of this review includes

35 'smart' SAPs such as SAPs with a T-, electro- and pH-sensitivity. These 'smart' SAPs are especially  
36 becoming useful for certain biomedical applications such as drug release for which an in vivo location  
37 can be targeted. The use of 'smart', semi-synthetic SAPs with fine-tuned characteristics combining the  
38 best characteristics of both synthetic and natural SAPs, offer the greatest potential for the future.

39

## 40 **Keywords**

41 Superabsorbent polymer

42 Smart polymer

43 Polysaccharide

44 Semi-synthetic

45

## 46 **Highlights**

47 • Polysaccharide-based SAPs sustainable alternative for conventional, synthetic SAPs

48 • Semi-synthetic SAPs with fine-tuned properties for specialized applications

49 • Smart SAPs particularly interesting for specific applications such as drug delivery

50

## 51 **Content**

52 Abstract ..... 1

53 Keywords ..... 2

54 Highlights ..... 2

55 1. Cornerstones associated with selecting the ideal SAP for a dedicated application ..... 4

56 2. Factors determining the absorption capacity of a SAP..... 4

57 3. Overview of polymer classification possibilities..... 5

58 3.1. Classification with respect to morphology ..... 5

59 3.2. Classification with respect to general building blocks ..... 6

60 3.3. Classification based on the cross-linking mechanism ..... 6

61 3.4. Classification based on the type of electrical charges present..... 6

62 4. Importance of SAPs..... 7

63 4.1. Comparative study on SAP and hydrogel publications ..... 7

64	4.2. Overview of SAP applications .....	8
65	5. Synthetic vs. polysaccharide-based natural SAPs .....	9
66	6. The composition, the origin and the use of synthetic SAPs .....	13
67	7. Natural SAPs based on different polysaccharides .....	13
68	7.1. Natural SAPs based on alginate and its derivatives .....	14
69	7.2. Natural SAPs based on chitosan and its derivatives .....	17
70	7.3. Natural SAPs based on agarose and its derivatives .....	18
71	7.4. Natural SAPs based on carrageenan and its derivatives .....	18
72	7.5. Natural SAPs based on cellulose and its derivatives .....	19
73	7.6. Natural SAPs based on starch and its derivatives .....	20
74	8. 'Smart' SAPs .....	23
75	8.1. Characteristics and applications of thermo-responsive SAPs .....	23
76	8.2. Characteristics and applications of pH-sensitive SAPs .....	24
77	8.3. Characteristics and applications of photo- and electro-sensitive SAPs .....	25
78	Conclusions and future perspectives .....	25
79	Acknowledgement .....	26
80	Data availability .....	26
81	References .....	27
82		
83		

## 1. Cornerstones associated with selecting the ideal SAP for a dedicated application

Superabsorbent polymer materials (SAPs) are cross-linked polymer networks constituted by water-soluble building blocks. SAPs are generally composed of ionic monomers and are characterized by a low cross-linking density, which results in a large fluid uptake capacity (up to 1000 times their own weight). Interestingly, these superabsorbent networks can absorb and retain aqueous solutions up to several hundred times their own weight [1-4], while even retaining it under pressure [1, 3]. A clear distinction can be made between hydrogels and SAPs. SAPs are generally composed of ionic monomers and possess a low cross-linking degree, which results in a larger fluid uptake capacity compared to conventional hydrogels (up to 10 times their own weight) [5, 6]. However, as both terminologies are often inappropriately used in literature, references with hydrogels will also be considered in the current review.

The ideal SAP needs to fulfill a number of requirements (depending on the application) including a high absorption capacity up to 1000 times its own weight, a tunable rate of absorption, a high absorbency when exposed to load, a high gel fraction after crosslinking (ranging from 85 to 95% [7, 8]), a low cost [9], excellent durability and stability upon swelling or during storage (shelf life of several years desired), non-toxicity and re-wetting capability (i.e. the ability to completely release the absorbed liquid as a function of time) [10]. To increase the strength and stability of the SAP, as an example for membrane shaped SAPs, the monomers are dissolved to enhance the mobility of the chains. The goal generally is not to meet all the above-mentioned criteria for one particular SAP, but rather to focus on those particular parameters which are useful for the targeted application. In the current manuscript, the focus is briefly placed on different parameters affecting the swelling capacity of SAPs, as further described in section 2. This parameter is generally of paramount importance for various applications. Other parameters such as the gel strength and gel stability are beyond the scope of the review. More details on gel strength or gel stability of different SAPs can be found in other reviews [7, 11-13].

After the absorption capacity, the different classifications in which SAPs can be subdivided will be presented in more detail.

## 2. Factors determining the absorption capacity of a SAP

One of the most important characteristics a SAP needs to show is a large water absorption capacity (i.e. the water absorbed by the SAP relative to the sample mass). The latter is determined by several factors. The osmotic pressure forces water into a polymer due to a higher ionic concentration inside the polymer compared to the surrounding solution because of the presence of charged and hydrophilic moieties onto the ionic monomers. The combination of these charged groups and additional polar moieties in a SAP

119 (hydroxyl, carbonyl or amine functionalities) attract water and induce hydrogen bonding. The amount  
120 of polar and/or ionic groups is directly proportional to the swelling capacity. Introducing a SAP into a  
121 solution with a lower ionic concentration will lead to a higher swelling capacity [14].

122 The **flexibility** on the other hand depends on the cross-link density. **A less dense network results in a**  
123 **more flexible material, but also in a higher absorption capacity.** Conversely, insufficient cross-linking  
124 can result in a material which partially dissolves, leading to a low gel fraction, when being introduced  
125 in an aqueous solution.

126 Raising the temperature of the water reduces the time required to reach equilibrium swelling [15].  
127 However, a higher temperature can also result in a reduced or increased swelling, depending on whether  
128 or not the SAP exhibits thermo-responsive behavior [15]. The latter will be discussed in the section  
129 covering ‘smart’ SAPs (section 8, *vide infra*).

130 As already mentioned earlier, SAPs are often composed of ionic constituents. These ionic charges result  
131 from an acid-base balance. As a result, changing the pH of the aqueous environment can lead to  
132 (de)protonation of acidic or basic groups. An acidic (basic) monomer will mainly be (de)protonated  
133 below (above) its pKa, thereby leading to a reduced swelling capacity. When the pH is higher (lower)  
134 than the pKa, acids become negatively (base becomes positively) charged which results in an increased  
135 swelling due to an increased affinity for water. Additionally, the repulsion of the charges leads to an  
136 increased free volume, in which water can accumulate.

137 Exerting a mechanical force onto a swollen SAP will expel part of the water out of the SAP. The swelling  
138 capacity during application of such a force is referred to as the absorbency under load [16, 17].

139 Another parameter influencing the absorption capacity is the surface to volume ratio. Due to a higher  
140 surface to volume ratio, small particles swell faster compared to larger particles which is useful for  
141 example for osmosis desalination [18, 19]. **The swelling capacity is thus very depending on a multitude**  
142 **of parameters. The upcoming section will describe the different possible classifications to subdivide**  
143 **SAPs.**

144

### 145 **3. Overview of polymer classification possibilities**

146

147 Depending on the characteristics taken into consideration, SAPs can be subdivided into different  
148 categories:

#### 149 **3.1. Classification with respect to morphology**

150 SAPs can have a different morphological appearance in line with the envisaged application (Figure 1)  
151 including fibers [20, 21], powders [22, 23], granules [24, 25] or even sheets [1]. The original shape of a  
152 SAP should ideally not be altered by water uptake, which implies that the SAP should have enough  
153 strength to rule out any physical degradation whatsoever of the structure, even upon exposure to pressure

154 [10]. Powder and granule SAPs are often made through solution polymerization (again to enhance  
155 mobility) with a redox system, after which they are ground to the desired particle size [26, 27].  
156

### 157 3.2. Classification with respect to general building blocks

158 The main building blocks of a SAP (Figure 1) can either be synthetic (e.g. acrylates, acrylamide), natural  
159 or a combination thereof (cfr. semi-synthetic [28, 29]) . Synthetic SAPs are generally synthesized from  
160 petrochemically-based monomers such as acrylates or acrylamides [27, 30-32] while natural SAPs  
161 include polypeptides and polysaccharides [33, 34]. In case of semi-synthetic SAPs, natural and synthetic  
162 building blocks are generally combined to create a SAP exhibiting fine-tuned characteristics towards  
163 specialized applications [29, 35]. **This classification is the most general and widely used and will be**  
164 **mainly focused on throughout the upcoming paragraphs.** Some examples of semi-synthetic SAPs  
165 include methacrylated polysaccharides combined with acrylic monomers for application in mortar [6,  
166 36, 37], cationic guar gum/poly(acrylic acid) polyelectrolyte hydrogels or chitosan cross-linked  
167 poly(acrylic acid) hydrogels for drug release [38]. The synthesis of synthetic SAPs can lead to a lack of  
168 reaction control and high polydispersity, but these SAPs often have high mechanical strengths. Natural  
169 SAPs are readily available, are non-toxic and sustainable. The semi-synthetic SAPs can thus lead on the  
170 one hand to more sustainable and biocompatible SAPs than synthetic SAPs and on the other hand  
171 mechanically stronger SAPs than the pure natural SAPs.

172

### 173 3.3. Classification based on the cross-linking mechanism

174 This classification is especially interesting **with respect to** mechanical properties for a SAP. Physically  
175 and chemically cross-linked SAPs (Figure 1) can be distinguished, which are characterized by different  
176 association mechanisms connecting the constituting polymer chains. Physical bonds such as hydrogen  
177 bonds or molecular entanglements are weak (typically only several kJ/mol) compared to chemical (i.e.  
178 covalent) linkages ( $> 100$  kJ/mol). **An example of physically cross-linked SAPs includes the**  
179 **combination of sodium alginate with multivalent cations such as  $Ca^{2+}$  to create calcium alginate. This**  
180 **will be further discussed in detail in section 7.1. Natural SAPs based on alginate.** Chemical cross-linking  
181 results in strong covalent bonds (by linking with functionalized natural starting materials or synthetic  
182 cross-linkers, **often by free radical polymerization**, thereby creating networks).

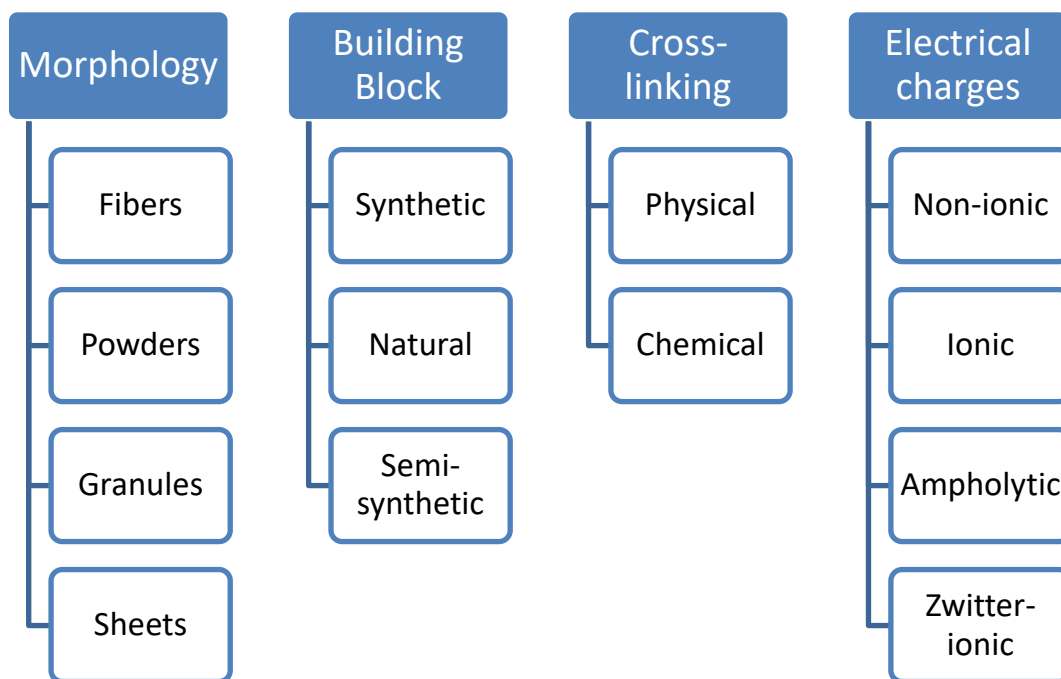
183

### 184 3.4. Classification based on the type of electrical charges present

185 Within this classification, four categories can be distinguished depending on the presence of electrical  
186 charges along the polymer backbone and/or side chains (Figure 1) [1]: (1) non-ionic—polymers  
187 possessing no charges (e.g. agarose); (2) ionic—SAPs with either anionic or cationic moieties (e.g.  
188 synthetic acrylates or alginate); (3) ampholytic—both acidic as well as basic functionalities are present;

189 (4) zwitter-ionic—SAPs containing both anionic and cationic groups with an overall net charge of zero.  
190 This classification is used in the context of **electro-sensitive** ‘smart’ SAPs.

191  
192



193  
194  
195

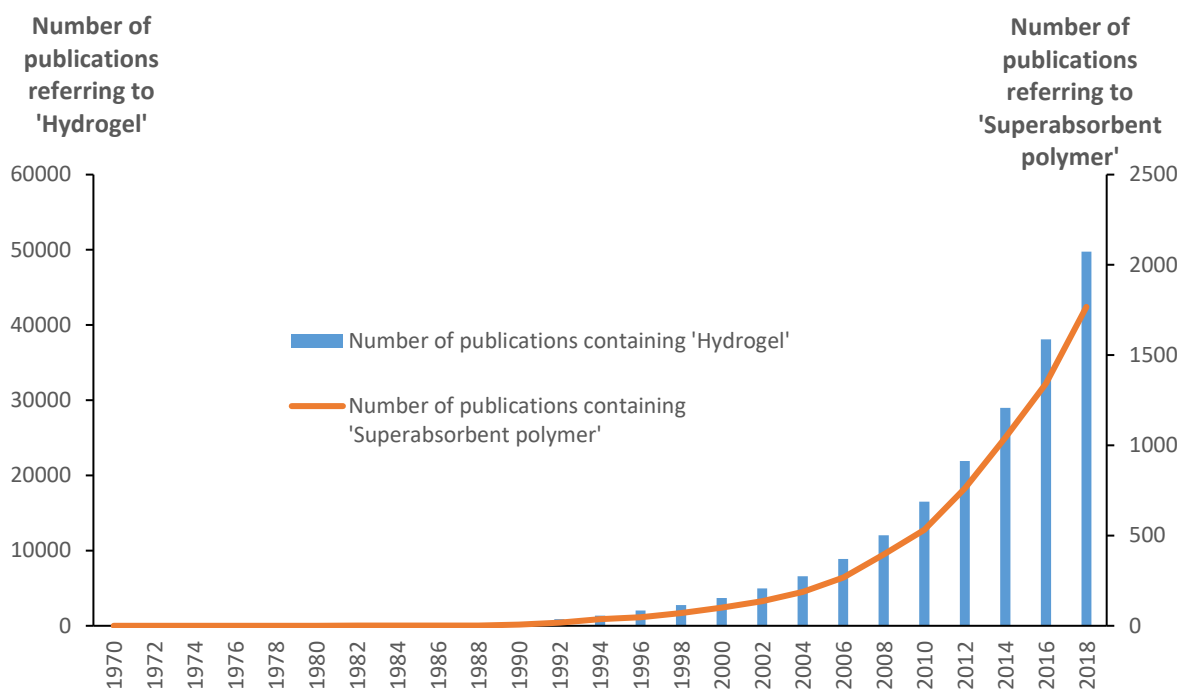
Figure 1: Subdivision of possible SAP classifications.

#### 196 **4. Importance of SAPs**

197 Both the industrial and academic research and the commercial relevance of SAPs have grown over the  
198 years. The upcoming subsections will describe these developments in more detail.

##### 199 **4.1. Comparative study on SAP and hydrogel publications**

200 Throughout the last 20 years, SAP research has shown a growing tendency. The latter is evident based  
201 on the amount of published research articles covering ‘hydrogel’ or ‘superabsorbent polymer’ in their  
202 abstract which increased gradually over time (see Figure 2). Nowadays, this trend should be placed into  
203 further perspective as in earlier times, the terminology ‘hydrogel’ and ‘SAP’ has often been used  
204 irrespective of the swelling potential. More recently, differentiation between both has become more  
205 pronounced based on the extreme difference in swelling capacity enabling proper identification of both  
206 material classes.



207  
 208 Figure 2: Cumulative number of publications containing the words ‘hydrogel’ or ‘superabsorbent  
 209 polymer’ in their abstract according to Web of Science as a function of the publication year.

#### 210 4.2. Overview of SAP applications

211 To date, SAPs have found their entry in a multitude of applications including diapers, sanitary napkins  
 212 [39, 40], for biomedical purposes (e.g. drug release [39, 41], and wound healing [39, 42, 43]), while  
 213 hydrogels are more often used for applications in which swelling is less preferred such as in tissue  
 214 engineering [39, 44] or (disposable) contact lenses [45, 46]. SAPs are also strongly used in the  
 215 agricultural sector as soil conditioners, nutrient carriers and water reservoirs (to conserve water in dry  
 216 areas) [4, 47-54]. Other applications include water purification and water-blocking tape. The latter is  
 217 composed of a non-woven textile covered with a binder and a SAP as a top layer [55-57]. For more  
 218 details on these strong developing agricultural applications of SAPs, the reader is referred to Guilherme  
 219 et al. [58]. Other applications include water purification and water-blocking tape. The latter is composed  
 220 of a non-woven textile covered with a binder and a SAP as a top layer [56, 57]. With respect to the latter,  
 221 the tape covers for example power transmission cables and retains water that would leach through the  
 222 plastic case present around the cable [59, 60]. Water-blocking tape has also been more recently used at  
 223 the different stages of oil production [61-63]. A final application receiving particular attention during  
 224 the last decade is the use of SAPs in mortar and concrete and especially for self-sealing and self-healing  
 225 of concrete cracks [6, 22, 36, 37, 64-69]. The cost estimation and life cycle assessment of these  
 226 superabsorbent polymers compared to other self-healing concrete mechanisms has been investigated  
 227 strongly in the past few years [9, 28, 70, 71].

228 As such, the field of SAPs is already crowded in a plethora of applications while potential retains in  
 229 many others. An overview of the different biomedical and non-biomedical applications using SAPs and



230 hydrogels is listed in Table 1. A whole range of different SAPs is used for the applications described in  
231 the current section. The following section will subdivide the SAPs according to their general building  
232 blocks and go into more detail on their respective advantages and disadvantages.

## 233 5. Synthetic vs. polysaccharide-based natural SAPs

234  
235 In addition to the classification based on the absence or the presence of charges (ionic, non-ionic,  
236 ampholytic or zwitter-ionic) or the cross-linking type (covalent versus physical) or the physical  
237 appearance (i.e. SAP morphology), the most important subdivision exists between synthetic, semi-  
238 natural or semi-synthetic and natural SAPs [10]. Typical monomers applied in synthetic SAP  
239 development include among other: acrylic acid (AA), acrylamide (AM), methacrylic acid (MAA),  
240 dimethylaminoethyl methacrylate (DMAEMA), dimethylaminopropyl methacrylamide (DMAPMA), 2-  
241 acrylamido-2-methylpropane sulfonic acid (AMPS), etc. (see Figure 5, upper panel, at the end of section  
242 7.6.). They can be introduced into a cross-linked (co)polymer network using a synthetic cross-linker  
243 such as N,N'-methylene bisacrylamide (MBA) (Figure 5). Semi-synthetic or semi-natural SAPs can be  
244 synthesized by the addition of a synthetic constituent to a natural, polymeric backbone through graft  
245 polymerization [3, 32, 72, 73]. In the latter case, the natural backbone is acting as a natural cross-linker  
246 for the synthetic monomers. Natural SAPs include polysaccharides and proteins. Proteins used for SAP  
247 applications are acylated [74] and are often grafted onto other polymers such as poly(acrylic acid) [30,  
248 75] to induce cell-interactive properties when targeting biomedical applications. The limited use of  
249 proteins as such for SAP applications resulted in the focus of the current review to be on polysaccharides.

250 Polysaccharides can be harvested from biosynthesis occurring in plants and animals. In recent research,  
251 polysaccharides produced by bacteria such as bacterial hyaluronan, gellan or xanthan have also been  
252 reported [76]. Currently used natural polymers for SAP include polysaccharides such as: alginate [36,  
253 76-79], chitosan [76, 80, 81], agar [82], carrageenan [83], dextrin [84], cellulose [51, 85], starch [85],  
254 gellan gum [76, 86] as well as proteins such as soybean, fish and collagen-based [10].

255 They have experienced a growing interest because of their designation as being biodegradable, readily  
256 available, biocompatible, non-toxic, renewable and sustainable. In addition, due to the increasing cost  
257 and finite nature of crude oil, natural polymers form a cost-effective and sustainable alternative [87, 88].  
258 Indeed, their renewability causes them to cause a lower environmental burden than synthetic SAPs [28].

259 Water-soluble polysaccharides carry functional groups such as alcohols, carboxylic acids and/or amines.  
260 These moieties can be used for cross-linking or grafting of other polymers. The upcoming section  
261 provides an overview of the origin, the composition and the application field of both synthetic as well  
262 as natural SAPs. The most often used natural polymers including alginate, chitosan, agarose,  $\kappa$ -  
263 carrageenan, cellulose and starch will be covered in greater detail. An overview of the different

264 advantages, disadvantages and recent examples of synthetic, natural and semi-synthetic SAPs can be  
265 found in Table 1. **The upcoming section will go into more detail on synthetic SAPs.**

Table 1: Advantages and disadvantages of the SAP types combined with the polymeric constituents and their applications.

SAP type	Advantages	Disadvantages	Material used	References	Application(s)
<b><u>Synthetic</u></b>	Abundant, multiple applications, high purity	Often not biocompatible, no cell adhesion, not biodegradable, not renewable, possible toxicity, lack of reaction control	Poly(acrylate)	[56, 89]	Hygiene product, water purification
			Poly(acrylic acid-co-acrylamide)	[26, 27, 50, 90]	Self-healing concrete, drug release, nutrient carrier
			Silicone	[46]	Contact lens
			Poly(2-hydroxyethyl methacrylate)	[91]	Ventricular catheter
			Poly(ethylene glycol)	[42, 65]	Wound healing, self-healing concrete
<b><u>Natural</u></b>	Renewable, biocompatible, biodegradable, decreased environmental impact, readily available, sustainable, proteins are cell adhesive	Extraction methods needed for the starting product, modifications required to create SAP <b>Shelf-life/sensitive storage conditions</b>	Starch	[4, 25, 39, 48]	Slow release fertilizer, soil conditioner, diaper
			Alginate-g-gelatin	[34, 92]	Tissue engineering, wound healing
			Alginate	[68, 93]	Self-healing concrete, wound healing
			Cellulose	[51, 94-96]	Personal care, water purification, water reservoir, tissue engineering
			Lignin	[97]	Water purification
			Gelatin	[57, 99, 100]	Water purification
			Chitosan	[39, 101]	Drug delivery, water purification
			Pectin	[53]	Drug delivery, wound healing
Guar gum		Nutrient carrier			

<b><u>Semi-synthetic</u></b>	Advantages of both synthetic/natural, fine-tuned properties	Phase separation	Starch-poly(acrylamide)	[33]	Slow release fertilizer
		Loss of biodegradability	Acrylic acid/gelatin	[8]	Drug release
		Homogeneity	Carboxymethyl cellulose/acrylic acid	[102]	Water retention
			Chitin-acrylate	[31, 32]	Water retention, personal care
			Chitosan-poly(acrylic acid)	[38, 73]	Drug release, wound dressing
			Methacrylated alginate-acrylates	[28, 36, 70]	Self-healing concrete
			Methacrylated agarose/chitosan-DMAEMA	[37, 81]	Self-healing concrete
			Hydroxyethylacryl chitosan/sodium alginate	[103]	Drug release
			Alginate-poly(acrylic acid- co-acrylamide)		
			Carboxymethyl starch-g-polyacrylamide	[36, 104]	Wound healing, self-healing concrete
			Poly(acrylic acid)/nanofibrillated cellulose	[105]	Slow release fertilizer
			Cellulose/Polyethylenimine	[106]	Personal care, diapers
				[107]	CO <sub>2</sub> capture

## 268 **6. The composition, the origin and the use of synthetic SAPs**

269 **The majority of SAPs used nowadays have a synthetic origin.** The most often used monomers are based  
270 on acrylates or acrylamides [9, 27, 108]. **Free-radical polymerization of the vinyl monomers in the**  
271 **presence of a multifunctional cross-linker is the most used technique for the preparation of acrylic-based**  
272 **synthetic SAPs [7, 10].** Initiation of the reaction can be performed on the one hand through free-radical  
273 **azo- or peroxide-based thermal dissociative species or on the other hand through the use of a redox**  
274 **system [109].** A straightforward and often used process in this respect is the solution polymerization of  
275 **AA either in the presence or absence of its salts in an aqueous solution together with a water-soluble**  
276 **cross-linker such as N,N'-methylene bisacrylamide.** However, there is a lack of control over the reaction  
277 **as well as difficulty to handle a rubbery/solid reaction product and issues with the particle size**  
278 **distribution (cfr. polydispersity).** Additionally, the inhibitor is usually not removed due to technical  
279 **difficulties and cost-related issues associated with an industrial process [110].**

280 Synthetic SAPs can be used in a variety of biomedical applications including coatings for catheters [91,  
281 111], burn dressings [112, 113], drug delivery systems [7, 114] or other applications such as  
282 electrophoresis gels [115] and many more [116]. They can also be used for non-biomedical applications  
283 such as diapers, in water purification system[117], as water beads for plants [118] or as matrix for  
284 electronics [119]. More recent applications involve the use of SAPs based on AA and AM in concrete  
285 to mitigate autogenous shrinkage [120] or self-healing applications [28, 67]. AM-based SAPs have also  
286 found their entry in agricultural applications [121]. Poly(acrylate/acrylic acid) SAPs have been used for  
287 water conservation in sandy soil [108]. Cyclic acetal-based SAPs have been developed for applications  
288 requiring biodegradability [122].

289  
290 **However, despite being used for a variety of applications, synthetic SAPs are not renewable or**  
291 **sustainable and often not biodegradable.** Conversely, a more sustainable approach involves the use of  
292 **natural SAPs.** The upcoming paragraphs will describe in more detail the different polysaccharides used  
293 **to develop natural SAPs along with their derivatives to create semi-synthetic SAPs.**

## 295 **7. Natural SAPs based on different polysaccharides**

296 **The current section will deal with the various polysaccharides used in SAP applications being alginate,**  
297 **chitosan, agarose, carrageenan, cellulose and starch.** They each have their properties rendering them  
298 **useful for certain applications such as the water solubility of alginate, the thermo-sensitivity of chitosan**  
299 **or the abundance of cellulose and starch.** The following subsections focus on all these polysaccharides  
300 **and their derivatives in greater detail.**

## 301 7.1. Natural SAPs based on alginate and its derivatives

302

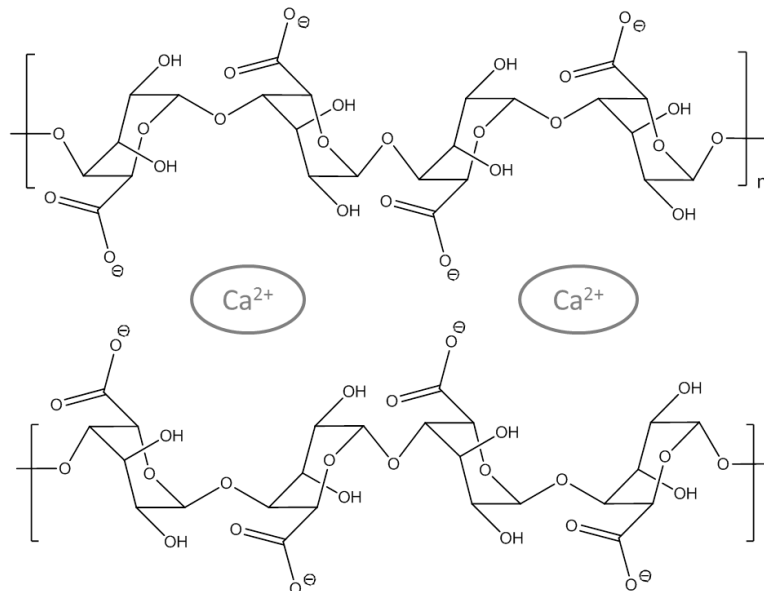
303 Sodium alginate (Figure 5) is a water-soluble, unbranched anionic polysaccharide extracted from the  
304 cell walls of brown algae (i.e. phaeophyceae) [77, 123]. The quality and amount of alginate depends on  
305 the type and age of the algae and the applied extraction method [76, 78]. It is a linear copolymer  
306 composed of  $\beta$ -D-mannuronate (M, pKa 3.4) and  $\alpha$ -L-guluronate (G, pKa 3.7), covalently linked in  
307 varying sequences and blocks and is commercially available as a sodium salt (NaAlg) [124, 125]. G-  
308 blocks are stiffer than M- or alternating GM-blocks because they are linked via their axial positions,  
309 instead of the equatorial links that are found in M-blocks. The exact composition of alginate chains  
310 varies with the source, the harvest location, the season and the part of the seaweed used. These factors  
311 also influence the gelling capacity and strength of the produced alginate. Typical molecular weights  
312 range between 50 and 100,000 kg/mol. Alginate contains carboxylic acid groups which become  
313 negatively charged in aqueous solutions possessing a pH above the pKa of the monosaccharide units,  
314 rendering them suitable to be applied in pH-sensitive SAPs, as discussed in the section covering ‘smart’  
315 SAPs (see section 1.8.3). This can be interesting for example for a controlled self-healing concrete with  
316 pH-responsive SAPs [68]. The total alginate production is estimated to be approximately 25,500 tonnes  
317 per year (of which 30% for the food industry) [126]. As such it is one of the most used polysaccharides.  
318 The two types of processing methods to manufacture alginate include the ‘acid precipitation method’  
319 and the ‘calcium precipitation method’. For the former, the polymer is typically extracted using 0.1 -  
320 0.2 M mineral acid (e.g. HCl). The insoluble alginic acid is then converted into soluble NaAlg through  
321 an aqueous alkali solution such as sodium hydroxide. Next, the extract is filtered to remove undesired  
322 solid material. Subsequently, the NaAlg can be obtained by evaporation. The latter method involves the  
323 addition of calcium chloride or an acid to precipitate calcium alginate or alginic acid respectively [127].  
324 Aqueous alginate solutions exhibit shear thinning while the viscosity depends on the polymer  
325 concentration, its molecular weight and the polymer composition [128, 129].

326

327 Interestingly, when NaAlg is combined with multivalent cations such as calcium ( $\text{Ca}^{2+}$ , originating from  
328 salts such as calcium chloride,  $\text{CaCl}_2$ ), a ionically cross-linked network is formed as the carboxylate  
329 moieties become coordinated by the cations, thereby becoming insoluble in water. The anionic groups  
330 will attract water into the structure, leading to SAP behavior. Helical chains are formed in the presence  
331 of calcium ions and arrange into the so-called ‘egg-box’ model, as illustrated in Figure 3 [130]. Another  
332 way to induce gel formation is by forming intermolecular hydrogen bonds by lowering the pH of the  
333 alginate solution below the pKa of both uronic acid groups. These gels are however more brittle  
334 compared to the ionic calcium alginate gels . **This increased brittleness is related to the presence of**  
335 **interconnected random aggregates compared to the calcium alginate.**

336

337 Alginate is often used for biomedical applications (e.g. controlled drug release, cell encapsulation, dental  
338 impression, wound dressing) [131-134] and in bioplastics (packaging, textiles, paper) [135]. It is also  
339 used in the food industry as a stabilizer, emulsifier and gelling agent [76, 78, 136]. When modified with  
340 propylene glycol, it can be used to bind edibles (e.g. microcrystalline cellulose [137], starch [138], etc.)  
341 under acidic conditions.  
342



343  
344 Figure 3: Calcium coordination of the egg box model of calcium alginate (-GMGM-) formed only by  
345 the G-blocks.  
346

347 Naturally based SAPs such as alginate also have certain disadvantages such as their low solubility, the  
348 need for purification through dialysis as well as scalability issues related to pilot installations. Therefore,  
349 there is a need to further modify these natural SAPs to create semi-synthetic SAPs. To ensure stability  
350 of processed, alginate-based materials or to further tune their physical properties, they are often modified  
351 in line with the desired application. An overview of commonly applied derivatization strategies  
352 elaborated for the polysaccharides, is given as a second part of the subsection of each polysaccharide,  
353 together with their respective applications. Care should be taken with respect to the derivatization of  
354 polysaccharides by incorporating monomers or grafts as this can also lead to modified biological  
355 properties. Indeed, depending on the envisaged application, biodegradability and toxicity of the  
356 modified SAPs should be investigated.

357 The hydroxyl groups of alginate can be modified by acetylation to increase the swelling potential of  
358 calcium gels [139], by phosphorylation which increases their resistance towards degradation [140] and  
359 by sulfation to ensure blood-compatibility and anticoagulant activity [141]. Its interaction with a cellular  
360 environment can be enhanced by the introduction of cell-signaling molecules [142-144]. To induce

361 hydrophobic or amphiphilic characteristics, hydrophobic moieties have already been attached onto the  
362 hydrophilic alginate backbone to prevent erosion in drug release applications [145-147].

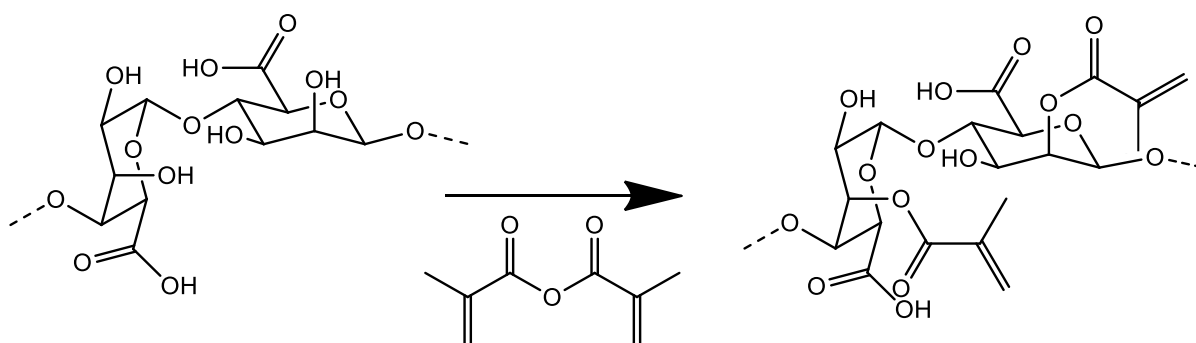
363 Graft polymerization can be used as an alternative method to change some characteristics of an alginate  
364 gel. A great variety of polymers have already been grafted onto alginate such as poly(acrylonitrile),  
365 poly(methyl acrylate), poly(methyl methacrylate), polyamides, itaconic acid and poly(acrylic acid-co-  
366 acrylamide) [148-152].

367 Poly(N-isopropyl acrylamide) (PNIPAAm) has already been grafted onto alginate using the carboxylic  
368 acid moieties by activating the acid with a carbodiimide followed by reaction with the amine group of  
369 PNIPAAm to introduce an amide linkage [153, 154]. Additional cross-linking with  $\text{Ca}^{2+}$  created a  
370 thermo-responsive polymer network as the lower critical solution temperature (LCST) behavior of  
371 PNIPAAm decreased the swelling capacity at temperatures exceeding the critical temperature.

372 Instead of physical cross-linking, which is associated with a limited stability, covalent cross-linking  
373 methods have also been established. For example, epichlorohydrin in a NaOH solution can be combined  
374 with ionically cross-linked alginate beads to induce covalent links between the hydroxyl groups present  
375 in alginate [155, 156]. Glutaraldehyde can also be used for the formation of acetal groups through  
376 reaction with the hydroxyl functionalities [157]. Another technique to develop covalently cross-linked  
377 alginate is by activating (with 2-chloromethyl-pyridine iodide) the acid moiety followed by subsequent  
378 reaction with a diamine to create amide-linked chains [148]. These approaches have resulted in a  
379 multitude of high-end applications such as beads for ion exchange chromatography to separate optical  
380 isomers of water-soluble  $\alpha$ -amino acids, cell encapsulation and controlled drug release [127].

381 A very straightforward but promising strategy to enable the development of a photo-crosslinked covalent  
382 network is the introduction of methacrylate moieties. For example, methacrylic anhydride (MAAH) can  
383 be used to enable simultaneous grafting onto and cross-linking of polysaccharides. This can be used for  
384 most polysaccharides (see Figure 5, bottom two rows where as an example one alcohol moiety is  
385 modified to a methacrylate) and will only be described as example here for alginate. Reaction of the  
386 hydroxyl groups from alginate with the anhydride will result in methacrylated alginate as displayed in  
387 Figure 4. These introduced double bond on the alginate backbone can subsequently be used in a free  
388 radical polymerization (with e.g. a redox initiator such as ammonium persulfate) in the presence of a  
389 whole range of monomers such as acrylic acid, acrylamide... [36, 158, 159]. Methacrylation can also  
390 be done by combining aminoethyl methacrylate to oxidized alginate by activating the carboxylate  
391 moieties using N-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide  
392 hydrochloride (EDC) [160].





393

394 Figure 4: Methacrylation of alginate using methacrylic anhydride. Activated double bonds are  
 395 incorporated in the alginate backbone to serve as a functional handle for subsequent free radical  
 396 polymerization.

## 397 7.2. Natural SAPs based on chitosan and its derivatives

398

399 Chitosan (Figure 5) is a linear polysaccharide composed of glucosamine building blocks. Glucosamine  
 400 is a so-called amino sugar as it has the same structure as glucose with the hydroxyl moiety at the C<sub>2</sub>-  
 401 position being replaced by an amine. Chitosan is made from chitin, which can be extracted from the  
 402 exoskeleton of invertebrates such as crabs and shrimps. It can also be found in the cell walls of fungi,  
 403 by partial deacetylation in an alkaline environment of N-acetyl amino groups or by enzymatic hydrolysis  
 404 in the presence of a chitin deacetylase. Since complete deacetylation is difficult to achieve, commercial  
 405 resources always report the degree of deacetylation (DDA). Chitin with a DDA higher than 50% is  
 406 considered as chitosan. A major disadvantage is that chitin is impossible to dissolve in most solvents  
 407 [161]. Chitosan, on the other hand, has a pK<sub>a</sub> value for the conjugated acid of 6.0 which results in  
 408 protonation in acidic environments and increases the solubility in acidic aqueous media [80, 162, 163].  
 409 This renders chitosan interesting to develop pH-responsive SAPs, which is further discussed in the  
 410 section tackling ‘smart’ SAPs (see section 1.8.3.).

411

412 Chitosan has many applications in the biomedical sector including among other as tissue engineering  
 413 scaffold, wound dressing, for hair treatment and drug delivery. It has also already been used for the  
 414 depollution of waste water and in the agricultural sector as a seed treatment, as biopesticide against  
 415 fungal infections and in winemaking as a preservative given its biocompatibility [99, 162, 164-166].

416 **Global chitosan production exceeds 118,000 tonnes annually [167].**

417 Amine moieties are more reactive than hydroxyl groups. Derivatizations described in literature thus  
 418 often take place through the amine functionality although some modifications do show hydroxyl  
 419 selectivity. N- or O-carboxymethylation, phosphorylation and alkylation are some of the derivatizations  
 420 which have already been described for chitosan [168, 169]. As an example, a carboxymethyl chitosan  
 421 grafted poly (acrylic acid) found its application in hemostatic wound dressings [73].

422 Chitosan can react with oxalic acid to deliver a hydrogel which is physically cross-linked via an  
423 ammonium-carboxylate complex which can adsorb copper(II) [170]. Hydroxybutyl chitosan can be  
424 created through reaction with 1,2-epoxybutane [171, 172].

425

### 426 **7.3. Natural SAPs based on agarose and its derivatives**

427 Agar, which is extracted from red algae (i.e. rhodophyta), was initially discovered in the 17<sup>th</sup> century in  
428 Japan and is used for its gelling properties [76, 173]. Agar is made of two components including agarose  
429 and agarpectin. Agarose (Figure 5) is constituted from  $\beta$ -D-galactopyranose and 3,6-anhydro-L-  
430 galactopyranose. It only contains hydroxyl functionalities. Agarpectin on the other hand consists of the  
431 same building blocks as agarose, but contains additional anionic groups such as sulfate or pyruvate. Due  
432 to cooperative hydrogen bonds, a gel can be formed by double helices. Because of the slow organization  
433 of these double helices, physical agarose gels exhibit syneresis behavior during which water is expelled  
434 from the gel as a function of time. Agarose gels are often used for gel electrophoresis of DNA, RNA,  
435 plasmids and chromosomes and in the food industry as a vegetarian gelatin substitute. They are also  
436 used in the pharmaceutical sector as sustained release devices, for the production of intricate casts used  
437 in dentistry and for dye making [174]. The yearly production of agar is estimated to be 10,600 tons/year  
438 [175].

439 The main difference between agarose and alginate lies in the presence of carboxylic acid moieties in  
440 alginate. Therefore, only the derivatization of the hydroxyl groups described above can also be used for  
441 agarose. Additionally, an important functionalization of agarose involves the possibility to use 1,3-  
442 dibromo-2-propanol to produce covalently cross-linked beads, which can be introduced in separation  
443 technology [176]. Further functionalization is often performed depending on the envisaged application.  
444 Agarose beads have already been epoxidized with epichlorohydrin followed by reaction with ethylene  
445 diamine or cysteine to create a support for enzyme immobilization [177]. Other researchers covalently  
446 cross-linked either alginate or chitosan with agarose using carbonyldiimidazole to study the effect of  
447 charges on neural tissue scaffolds [178].

### 448 **7.4. Natural SAPs based on carrageenan and its derivatives**

449 Carrageenan is refined from the cell walls of red algae (i.e. rhodophyta). To enable extraction, an alcohol  
450 precipitation method is used, which is versatile for every type of seaweed, but comes together with a  
451 major investment. A second technique is 'gel press technology'. Due to its lower cost, it has started to  
452 completely replace the first method. However, this latter technique is only useful to produce  $\kappa$ -  
453 carrageenan (Figure 5), which is a disadvantage for other carrageenan types. Carrageenan is composed  
454 of repeating units of  $\beta$ -D-galactopyranose and  $\alpha$ -D-galactopyranose [179]. It is especially used in the  
455 pharmaceutical and food industry as emulsifier, stabilizer or thickeners [83, 180]. Its yearly production  
456 amounts around 60,000 tons/year [175].

457 There exist a series of chemical modifications to modulate the physico-chemical properties of  
458 carrageenan. For splitting the ι-carrageenan chain, the Smith periodate degradation can be used [181].  
459 K-carrageenan containing hydroxyalkyl groups has already been developed to create a gel with a  
460 decreased syneresis and therefore, a broader industrial scope [182]. The association of κ-carrageenan  
461 with CaCl<sub>2</sub> changes the swelling capacity of the gel [183]. Another often used derivatization type  
462 characteristic for these polysaccharides is alkalization. Different types of carrageenan can undergo  
463 cyclization when using a concentrated 1M sodium hydroxide solution at a temperature of 80°C. The  
464 latter improves the gelling properties as reflected by their strength [184-186]. By using alkaline  
465 hydrolysis or microwave irradiation, carrageenan gels have already been ‘cross-linked’ with  
466 poly(acrylamide) [187-189], acrylic acid [190] and methyl methacrylate [191]. In addition, a  
467 copolymerization with acrylic acid and 2-acrylamido-2-methylpropane-sulfonic acid has already been  
468 performed as well [192]. The latter hydrogels are especially very promising for the industrial  
469 immobilization of enzymes [193]. More specifically, by precipitating calcium phosphate into a κ-  
470 carrageenan matrix, porous nanocomposites could be prepared which are useful for bone tissue  
471 engineering [194]. Other derivatizations performed earlier include acetylation, oversulfatation and  
472 phosphorylation of κ-carrageenan [195, 196]. These modifications can enhance the antioxidant activity  
473 of carrageenan [197]. Synthetic κ-seleno-carrageenan may inhibit the proliferation of breast cancer cells  
474 [198]. Alternatively, an *O*-maleoyl derivative of κ-carrageenan could be manifested by the reaction of  
475 tetrabutylammonium salt of the anionic carrageenan fragments with maleic anhydride, 4-  
476 dimethylaminopyridine and tributylamine under homogeneous conditions in *N,N*-dimethylformamide  
477 [199]. As indicated by the many highlighted examples, the derivatization of carrageenan is very  
478 versatile[200].

#### 479 **7.5. Natural SAPs based on cellulose and its derivatives**

480 Cellulose (Figure 5) is considered as the most abundant organic compound which is derived from  
481 biomass [96]. In addition to its main origin being wood, other sources include plant fibers (leaf, stalk,  
482 fruit or the rigid structure), marine animals, algae... [201]. Total production of primary cellulose sources  
483 was estimated at 1200-1500 million tons/year in 2011 [202]. It is a linear homopolysaccharide composed  
484 of β-1,4-anhydro-D-glucose units [203]. The hydroxyl groups present can lead to strong hydrogen  
485 bonding. It shows a multi-scale microfibrillated structure which is useful for many of its applications.  
486 Additionally, it is characterized by hierarchical crystalline and amorphous regions and shows a highly  
487 cohesive nature. Some of its main applications can be found in paper, textile and the material industry.  
488 Interestingly, cellulose in combination with carboxymethylcellulose has already resulted in promising  
489 SAPs with biomedical applications enabling the controlled release of bovine serum albumin [204].  
490 Nano-fibrillated cellulose (NFC) has already been combined with acrylic acid during the UV-initiated  
491 polymerization to improve the swelling properties of poly(acrylic acid) to become applied in agriculture

492 or for sanitary purposes [106]. SAPs based on cellulose nanofibrils and chitosan-graft-poly(acrylic acid)  
493 could potentially be used for the drug release properties of solutes [205].

494

495 Pristine (CNC) and surfactant-modified cellulose nanocrystals (s-CNC) have already been used to  
496 investigate the barrier and migration properties of PLA nano-biocomposites [206]. Cellulose has also  
497 been modified with poly(ethyleneimine), ethylenediaminetetraacetic dianhydride, perfluoro-  
498 octadecanoic acid or thiols to enable the selective removal of metals [107, 207-210]. Cellulose has also  
499 already been modified with quaternary ammonium groups to actively remove reactive red dyes [211].  
500 **Maleylated cellulose-g-poly(acrylic acid) has already been useful for its application in agriculture [212].**  
501 Cellulose esterification has been performed by condensation of the carboxylic acid, acid anhydrides or  
502 acyl chlorides with a cellulosic alcohol group [210]. These have been used for drug delivery applications  
503 [213]. Ethylcellulose blended with or grafted with responsive polymers were used as coating materials  
504 to prepare coated particles with drug cores [214].

#### 505 **7.6. Natural SAPs based on starch and its derivatives**

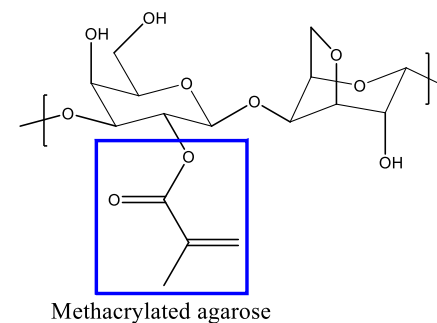
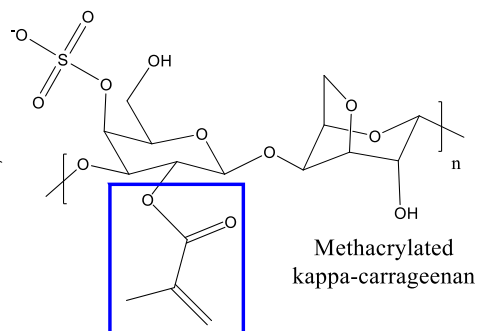
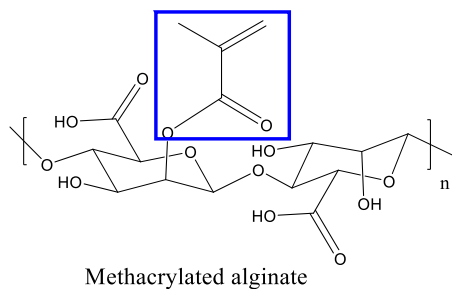
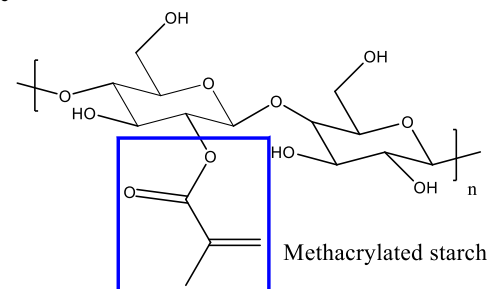
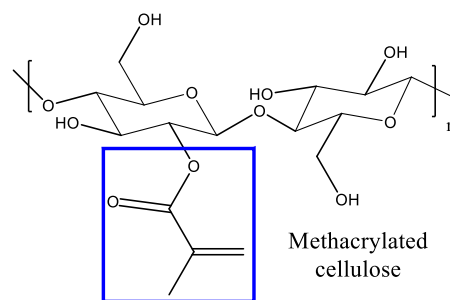
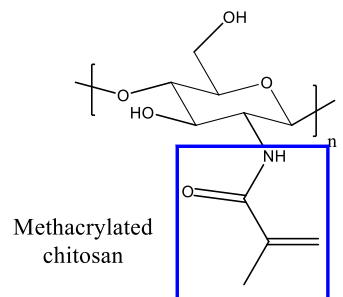
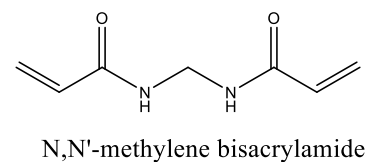
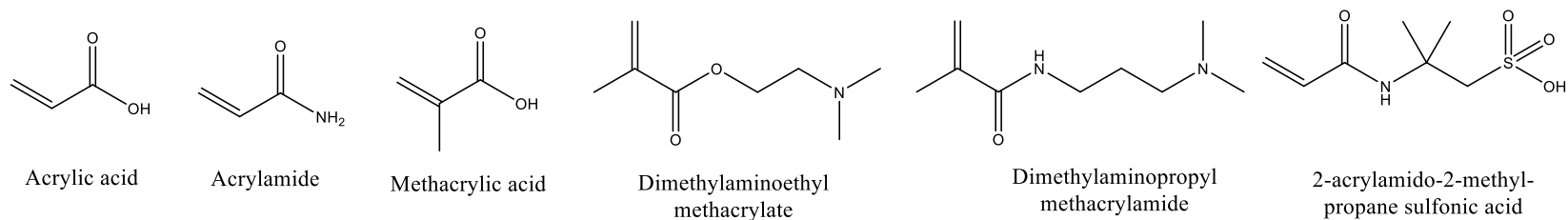
506 In addition to cellulose, starch (Figure 5) is the second most abundant biomass found in nature and is  
507 derived from plant roots, stalks and crop seeds. The main sources are maize, wheat and potatoes [215].  
508 It is composed of glucose units connected by glycosidic bonds, consisting of linear and helical amylose  
509 and branched amylopectin. It has industrial applications for the manufacturing of alcohols and biofuels.  
510 It can also be useful as thickening or gluing agent (e.g. adhesive in the papermaking process). The  
511 worldwide production of starch amounts 75 million tons [216]. The amylose/amylopectin ratio has a  
512 large influence on the properties of the starch. A larger amount of amylopectin increases the viscosity  
513 thereby reducing the mobility of the chains. An increasing amylose content leads to a stronger grafting  
514 efficiency and higher swelling capacity [217]. Double-coated polymers constituting ethyl cellulose as  
515 inner coating and a starch-based SAP as outer coating have already been developed as slow-release  
516 fertilizers to improve the fertilizer effectiveness [25].

517

518 Starch has already been applied (industrial, Free-Flow (*FF*)) as particle stabilizer for oil-in-water  
519 emulsions and modified with carboxymethyl cellulose to create new biodegradable composites for a  
520 plethora of applications [218]. Natural rubber has for example, been improved by grafting with modified  
521 cassava starch to enable controlled urea release or oil absorption [219, 220]. Metals can also be captured  
522 by starch-graft-acrylic acid/montmorillonite or starch-g-poly(acrylic acid)/sodium humate SAPs [221].  
523 Starch-graft-poly(acrylamide) SAPs can be used for soil conditioning applications to retain soil moisture  
524 [222]. **Carboxymethyl starch-g-polyacrylamide found its use as slow release fertilizers [105].**

525

526 The description of the different polysaccharides used for SAP development as well as their derivatives  
527 indicate the importance of executing further research towards the use of natural SAPs. Despite having  
528 many advantages towards the targeted applications, even semi-synthetic SAPs can often result in  
529 challenges to be tackled such as low gel fraction or limited homogeneity. Further research on these semi-  
530 synthetic SAPs is still needed as these become interesting for specialized applications such as drug  
531 release, where environmental stimuli are needed to create fine-tuned SAP properties.



532

533

534

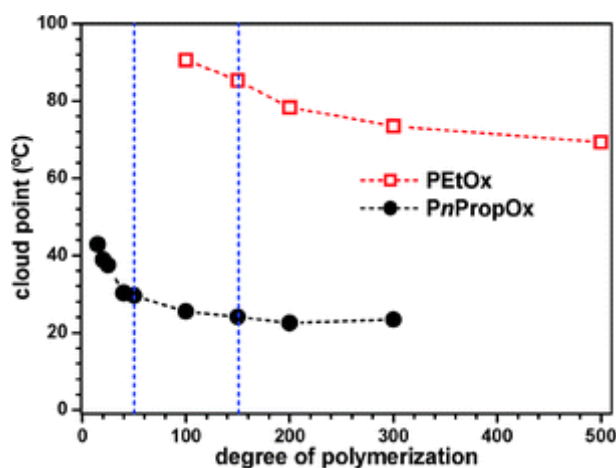
Figure 5: Chemical structure of the most common synthetic monomers (upper panel), the most used synthetic cross-linker (center) and methacrylated polysaccharides of which alcohol moieties can be modified into a methacrylate (lower panel). The latter can act as natural cross-linkers.

## 535 8. 'Smart' SAPs

536 Some SAPs undergo distinct physical changes upon small environmental variations [121]. These  
537 interesting, so-called 'smart' polymers [223] have the ability to sense environmental stimuli [224]  
538 including changes in pH [38, 81, 225-227], temperature [227-229], light [230, 231], pressure [232, 233],  
539 etc. A multitude of applications including drug release, is concomitant with the extensive use of pH-  
540 sensitive, 'smart' SAPs [227, 234]. The aim generally is to create a system which releases bioactive  
541 components at a rate precisely matching physiological needs at the correct time point and/or appropriate  
542 site. To achieve this, the system needs to 'sense' a signal caused by a disease or injury and respond  
543 accordingly [227]. The most used 'smart' hydrogel systems will be discussed herein.

### 544 8.1. Characteristics and applications of thermo-responsive SAPs

545  
546 One of the most often used type of 'smart' SAP have a temperature-responsiveness [235, 236]. Thermo-  
547 responsive SAPs can have either a lower critical solution temperature (LCST) below which all  
548 components are miscible or an upper critical solution temperature (UCST) where materials are able to  
549 dissolve above a certain temperature. Some thermo-responsive SAPs are based on chitosan, cellulose,  
550 xyloglucan, poly(N-vinylcaprolactam) ... [229]. Some synthetic examples include poly(N-isopropyl  
551 acrylamide), poly(2-oxazoline) (Figure 6) and poly(N,N-diethyl acrylamide) [227, 237]. Chitosan is also  
552 thermo-responsive and has already been used for neural tissue engineering and skin regeneration [238,  
553 239]. At a temperature below the LCST, the hydrophilic segments interact with water and the polymer  
554 starts to absorb the surrounding water. When the temperature increases, the gel starts to shrink and forces  
555 the absorbed liquid out, as the hydrophobic interactions increase. **This effect is often referred to as**  
556 **negative temperature sensitivity** [240]. An interpenetrating network of poly(acrylic acid) and  
557 poly(acrylamide) shows an increased swelling upon increasing the temperature and can thus be  
558 considered as a positive temperature sensitive polymer [241]. Thermo-responsivity also occurs in natural  
559 SAPs. A thermo-sensitive pectin-based SAP has already been used for oral drug delivery [101].

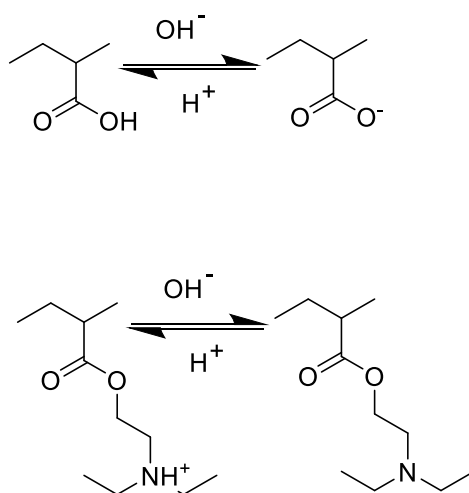


560

561 Figure 6: Cloud point as a function of chain length for poly(ethyloxazoline) and poly(n-  
562 propyloxazoline) [237].

## 563 8.2. Characteristics and applications of pH-sensitive SAPs

564  
565 Due to the formation of ions at specific pH-values, the reactive groups in the polymer networks of pH-  
566 sensitive hydrogels (e.g. carboxylic acid, sulfonic acid or amine functionalities) either repel or attract  
567 one another. The latter behavior thus depends on the acidity or the basicity of the aqueous environment.  
568 Some pH-sensitive SAPs are based on poly (acrylic acid), poly(vinylpyridine) or poly(vinylimidazole)  
569 [229]. Electrostatic repulsions between charged conjugates of acidic or basic moieties lead to additional  
570 ionization, which implies that the  $pK_a$  of a polymer is more spread over a pH-range rather than being  
571 characterized by a single value characteristic for the individual monomers. Identical charges repel one  
572 another thereby creating more free volume in which a higher amount of water can be absorbed which  
573 results in a higher swelling capacity. Acid moieties are negatively charged above their  $pK_a$ , while this  
574 is the case for basic moieties below their  $pK_a$  (Figure 7). By combining various synthetic and natural  
575 pH-responsive polymers, very specialized applications can be targeted. An example is the use of pH-  
576 reponsive SAPs based on poly(acrylic acid-co-acrylamide) SAPs, methacrylated alginate and acid  
577 monomers or methacrylated polysaccharides with amine-based monomers for self-healing of cracks in  
578 concrete [37, 67, 68, 81]. Starch-poly(sodium acrylate-co-acrylamide) [43], acryloyl ester of 5-[4-  
579 (hydroxy phenyl) azo] salicylic acid (HPAS) [234] has been used as a drug delivery system. Poly(acrylic  
580 acid) based nanoparticles can be used for cancer therapy as drug delivery agent [242].



581  
582 Figure 7: pH-dependent ionization of poly(acrylic acid) (top) and poly(*N,N'*-diethylaminoethyl  
583 methacrylate) (bottom).

584



### 585 **8.3. Characteristics and applications of photo- and electro-sensitive SAPs**

586  
587 Light-sensitivity of SAPs is very interesting as this property can influence the solubility of the polymer  
588 to which the respective group is attached. The stimulus can be delivered directly with high accuracy and  
589 ease of control via laser. An interesting example of a UV-responsive hydrogel is a network containing  
590 leucocyanide moieties [243]. Dissociation of the molecule into a cyano anion and a triphenyl methyl  
591 cation occurs upon irradiation (488 nm with an intensity varying between 0 and 150 mW). This leads to  
592 an increased water affinity and electrostatic repulsion of the ionic groups and thus an increased swelling  
593 capacity. An opposite effect can occur when incorporating a visible light-sensitive chromophore, such  
594 as chlorophyllin sodium copper salt into a temperature-sensitive hydrogel such as poly(N-isopropyl  
595 acrylamide) [244]. As the chromophore absorbs the light, it disperses the energy as heat due to radiation-  
596 less transitions, thereby increasing the hydrogel temperature which results in a decreased swelling due  
597 to the negative temperature sensitivity of poly(N-isopropyl acrylamide).

598 Electro-responsive hydrogels are similar to pH-responsive hydrogels as in both cases the sensitivity is  
599 related to the presence of ionic groups. An electrical or chemical potential can be created accordingly  
600 as ionic groups are attracted by oppositely charged electrodes. Depending on the charges of the ions and  
601 the electrodes, this can lead to either an increased or a reduced swelling degree for example using sodium  
602 alginate-g-poly(acrylic acid) [227, 245]. Some light or electro-sensitive SAPs are based on  
603 poly(acrylamide), poly(ethyloxazoline), polythiophene [229]...

### 604 **Conclusions and future perspectives**

605 The present review reports on the potential of polysaccharides to become applied (possibly in  
606 combination with synthetic building blocks such as monomers and cross-linkers) as superabsorbent  
607 polymers (SAPs). Both synthetic and polysaccharide-based SAPs have already been used for a  
608 multiplicity of applications such as diapers, the biomedical field, agriculture, etc. With respect to cost-  
609 effectiveness and sustainability, the natural SAPs are of particular interest. They are renewable  
610 (decreased environmental impact compared to synthetic SAPs), biodegradable, readily available,  
611 biocompatible, non-toxic and function thus as a sustainable alternative for synthetic SAPs. Furthermore,  
612 they carry different functionalities which can be modified to render them more suited for the envisaged  
613 application or to covalently couple them to synthetic monomers to create so-called semi-synthetic SAPs.  
614 These semi-synthetic SAPs have gained increasing interest in recent years as they create fine-tuned  
615 properties for specialized applications. The combination of different polysaccharides with synthetic  
616 monomers offers a versatile range of inherent physical properties and concomitant possibilities and is  
617 an approach which will be further exploited throughout the upcoming years. Finally, 'smart' SAPs are  
618 often useful for biomedical applications such as drug release as they can target a certain *in vivo* location  
619 exerting particular characteristics triggering the release of the encapsulated/coupled drug.

620 In future work, the focus should be on more sustainable, biodegradable natural SAPs to avoid an increase  
621 of the current plastic soup with a huge environmental impact (e.g. oceans). Additionally, ‘smart’ SAPs  
622 will be needed to target specialized applications for which fine-tuned properties are necessary.  
623 Combining synthetic monomers with polymers of bio-based origin will also improve the sustainability  
624 of synthetic SAPs. As synthetic SAPs are still used in a major part of current applications, ‘smart’ semi-  
625 synthetic SAPs require additional research efforts in the upcoming years.

## 626 **Acknowledgement**

627 A. Mignon would like to thank the FWO (Research Foundation Flanders) for project funding  
628 (3G019012, Effect of tunable hydrogels on concrete microstructure, moisture properties, sealing and  
629 self-healing of cracks. and 12Z2918N, Co-extrusion electrospinning as novel tool for the next generation  
630 wound dressings: taking ultimate control over the dressing mechanical and release properties.). S. Van  
631 Vlierberghe would like to acknowledge FWO (G0A2816, G005616N, G0F0516N) for financial support  
632 under the form of research grants.

633

## 634 **Data availability**

635 The raw data required to reproduce these findings are available to download from [to be added]. The  
636 processed data required to reproduce these findings are available to download from [to be added].

## 637 **References**

- 638 [1] M.J. Zohuriaan-Mehr, H. Omidian, S. Doroudiani, K. Kabiri, Advances in non-hygienic applications  
639 of superabsorbent hydrogel materials, *J Mater Sci* 45(21) (2010) 5711-5735.
- 640 [2] S.G. Abd Alla, M. Sen, A.W.M. El-Naggar, Swelling and mechanical properties of superabsorbent  
641 hydrogels based on Tara gum/acrylic acid synthesized by gamma radiation, *Carbohydrate Polymers*  
642 89(2) (2012) 478-485.
- 643 [3] Y. Yu, L. Liu, Y. Kong, E. Zhang, Y. Liu, Synthesis and properties of N-maleyl chitosan-cross-  
644 linked poly (acrylic acid-co-acrylamide) superabsorbents, *Journal of Polymers and the Environment*  
645 19(4) (2011) 926-934.
- 646 [4] X. Xiao, L. Yu, F. Xie, X. Bao, H. Liu, Z. Ji, L. Chen, One-step method to prepare starch-based  
647 superabsorbent polymer for slow release of fertilizer, *Chemical Engineering Journal* 309 (2017) 607-  
648 616.
- 649 [5] F.L. Buchholz, A.T. Graham, *Modern superabsorbent polymer technology*, John Wiley & Sons, Inc,  
650 605 Third Ave, New York, NY 10016, USA, 1998. 279 (1998).
- 651 [6] A. Mignon, D. Snoeck, P. Dubruel, S. Van Vlierberghe, N. De Belie, Crack Mitigation in Concrete:  
652 Superabsorbent Polymers as Key to Success?, *Materials* 10(3) (2017) 237.
- 653 [7] E.M. Ahmed, Hydrogel: Preparation, characterization, and applications: A review, *Journal of*  
654 *advanced research* 6(2) (2015) 105-121.
- 655 [8] S.M.H. Bukhari, S. Khan, M. Rehanullah, N.M. Ranjha, Synthesis and characterization of chemically  
656 cross-linked acrylic acid/gelatin hydrogels: effect of pH and composition on swelling and drug release,  
657 *International Journal of Polymer Science* 2015 (2015) 15.
- 658 [9] A. Mignon, Effect of pH-responsive superabsorbent polymers on the self-sealing and self-healing of  
659 cracks in concrete. PhD, Ghent University, 2016.
- 660 [10] K.K. Mohammad J. Zohuriaan-Mehr Superabsorbent Polymer Materials: A Review, *Iranian*  
661 *Polymer Journal* 17((6)) (2008) 451-477.
- 662 [11] M. Ramazani-Harandi, M. Zohuriaan-Mehr, A. Yousefi, A. Ershad-Langroudi, K. Kabiri,  
663 Rheological determination of the swollen gel strength of superabsorbent polymer hydrogels, *Polymer*  
664 *testing* 25(4) (2006) 470-474.
- 665 [12] K. Kabiri, H. Omidian, M. Zohuriaan-Mehr, S. Doroudiani, Superabsorbent hydrogel composites  
666 and nanocomposites: a review, *Polymer Composites* 32(2) (2011) 277-289.
- 667 [13] J. Maitra, V.K. Shukla, Cross-linking in hydrogels-a review, *Am. J. Polym. Sci* 4(2) (2014) 25-31.
- 668 [14] H. Lee, H. Wong, N. Buenfeld, Effect of alkalinity and calcium concentration of pore solution on  
669 the swelling and ionic exchange of superabsorbent polymers in cement paste, *Cement and Concrete*  
670 *Composites* 88 (2018) 150-164.
- 671 [15] F. Rosa, M. Casquilho, Effect of synthesis parameters and of temperature of swelling on water  
672 absorption by a superabsorbent polymer, *Fuel Processing Technology* 103 (2012) 174-177.

- 673 [16] S.-H. Kang, S.-G. Hong, J. Moon, Absorption kinetics of superabsorbent polymers (SAP) in various  
674 cement-based solutions, *Cement and Concrete Research* 97 (2017) 73-83.
- 675 [17] A. Azizi, K. Kabiri, M.J. Zohuriaan-Mehr, H. Bouhendi, Z. Karami, Transamidation: A feasible  
676 approach of surface modification to improve absorbency under load of agricultural superabsorbent  
677 materials, *Journal of Materials Research* 33(16) (2018) 2327-2335.
- 678 [18] A. Razmjou, G.P. Simon, H. Wang, Effect of particle size on the performance of forward osmosis  
679 desalination by stimuli-responsive polymer hydrogels as a draw agent, *Chemical Engineering Journal*  
680 215 (2013) 913-920.
- 681 [19] M. Zhang, Z. Cheng, T. Zhao, M. Liu, M. Hu, J. Li, Synthesis, Characterization, and Swelling  
682 Behaviors of Salt-Sensitive Maize Bran–Poly(acrylic acid) Superabsorbent Hydrogel, *Journal of*  
683 *Agricultural and Food Chemistry* 62(35) (2014) 8867-8874.
- 684 [20] A. Yabuki, S. Tanabe, I.W. Fathona, Self-healing polymer coating with the microfibers of  
685 superabsorbent polymers provides corrosion inhibition in carbon steel, *Surface and Coatings*  
686 *Technology* 341 (2018) 71-77.
- 687 [21] M.S. Islam, M.S. Rahaman, J.H. Yeum, Electrospun novel super-absorbent based on  
688 polysaccharide–polyvinyl alcohol–montmorillonite clay nanocomposites, *Carbohydrate polymers* 115  
689 (2015) 69-77.
- 690 [22] A. Mignon, G.-J. Graulus, D. Snoeck, J. Martins, N. De Belie, P. Dubruel, S. Van Vlierberghe, pH-  
691 sensitive superabsorbent polymers: a potential candidate material for self-healing concrete, *J Mater Sci*  
692 50(2) (2014) 970-979.
- 693 [23] J. Pelto, M. Leivo, E. Gruyaert, B. Debbaut, D. Snoeck, N. De Belie, Application of encapsulated  
694 superabsorbent polymers in cementitious materials for stimulated autogenous healing, *Smart Materials*  
695 *and Structures* 26(10) (2017) 105043.
- 696 [24] T.K. Mudiyansele, D.C. Neckers, Highly absorbing superabsorbent polymer, *Journal of Polymer*  
697 *Science Part A: Polymer Chemistry* 46(4) (2008) 1357-1364.
- 698 [25] D. Qiao, H. Liu, L. Yu, X. Bao, G.P. Simon, E. Petinakis, L. Chen, Preparation and characterization  
699 of slow-release fertilizer encapsulated by starch-based superabsorbent polymer, *Carbohydrate polymers*  
700 147 (2016) 146-154.
- 701 [26] A. Mignon, D. Snoeck, D. Schaubroeck, N. Luickx, P. Dubruel, S. Van Vlierberghe, N. De Belie,  
702 pH-responsive superabsorbent polymers: a pathway to self-healing of mortar, *Reactive and Functional*  
703 *Polymers* 93 (2015) 68-76.
- 704 [27] S. Nesrinne, A. Djamel, Synthesis, characterization and rheological behavior of pH sensitive poly  
705 (acrylamide-co-acrylic acid) hydrogels, *Arabian Journal of Chemistry* 10(4) (2017) 539-547.
- 706 [28] P. Van den Heede, A. Mignon, G. Habert, N. De Belie, Cradle-to-gate life cycle assessment of self-  
707 healing engineered cementitious composite with in-house developed (semi-) synthetic superabsorbent  
708 polymers, *Cement and Concrete Composites* 94 (2018) 166-180.

709 [29] G. Chaithra, S. Sridhara, Growth and yield of rainfed maize as influenced by application of super  
710 absorbent polymer and Pongamia leaf mulching, *IJCS* 6(5) (2018) 426-430.

711 [30] B. Zhang, Y. Cui, G. Yin, X. Li, L. Liao, X. Cai, Synthesis and swelling properties of protein-poly  
712 (acrylic acid-co-acrylamide) superabsorbent composite, *Polymer Composites* 32(5) (2011) 683-691.

713 [31] T. Liu, Y. Wang, B. Li, H. Deng, Z. Huang, L. Qian, X. Wang, Urea free synthesis of chitin-based  
714 acrylate superabsorbent polymers under homogeneous conditions: effects of the degree of deacetylation  
715 and the molecular weight, *Carbohydrate polymers* 174 (2017) 464-473.

716 [32] S. Fang, G. Wang, P. Li, R. Xing, S. Liu, Y. Qin, H. Yu, X. Chen, K. Li, Synthesis of chitosan  
717 derivative graft acrylic acid superabsorbent polymers and its application as water retaining agent,  
718 *International journal of biological macromolecules* 115 (2018) 754-761.

719 [33] D. Qiao, L. Yu, X. Bao, B. Zhang, F. Jiang, Understanding the microstructure and absorption rate  
720 of starch-based superabsorbent polymers prepared under high starch concentration, *Carbohydrate*  
721 *polymers* 175 (2017) 141-148.

722 [34] G.J. Graulus, A. Mignon, S. Van Vlierberghe, H. Declercq, K. Fehér, M. Cornelissen, J.C. Martins,  
723 P. Dubruel, Cross-linkable alginate-graft-gelatin copolymers for tissue engineering applications,  
724 *European Polymer Journal* 72 (2015) 494-506.

725 [35] P. Pande, Polymer hydrogels and their applications, *International Journal of Materials Science* 12(1)  
726 (2017) 2017.

727 [36] A. Mignon, J. Vermeulen, G.-J. Graulus, J. Martins, P. Dubruel, N. De Belie, S. Van Vlierberghe,  
728 Characterization of methacrylated alginate and acrylic monomers as versatile SAPs, *Carbohydrate*  
729 *Polymers* 168 (2017) 44-51.

730 [37] A. Mignon, D. Devisscher, J. Vermeulen, M. Vagenende, J. Martins, P. Dubruel, N. De Belie, S.  
731 Van Vlierberghe, Characterization of methacrylated polysaccharides in combination with amine-based  
732 monomers for application in mortar, *Carbohydrate Polymers* 168 (2017) 173-181.

733 [38] Y. Wang, J. Wang, Z. Yuan, H. Han, T. Li, L. Li, X. Guo, Chitosan cross-linked poly(acrylic acid)  
734 hydrogels: Drug release control and mechanism, *Colloids and Surfaces B: Biointerfaces* 152 (2017) 252-  
735 259.

736 [39] E. Caló, V.V. Khutoryanskiy, Biomedical applications of hydrogels: A review of patents and  
737 commercial products, *European Polymer Journal* 65 (2015) 252-267.

738 [40] S. Dey, D. Kenneally, M. Odio, I. Hatzopoulos, Modern diaper performance: construction,  
739 materials, and safety review, *International journal of dermatology* 55 (2016) 18-20.

740 [41] S. Sharma, A. Dua, A. Malik, Biocompatible stimuli responsive superabsorbent polymer for  
741 controlled release of GHK-Cu peptide for wound dressing application, *Journal of Polymer Research*  
742 24(7) (2017) 104.

743 [42] D.W. Kim, K.S. Kim, Y.G. Seo, B.-J. Lee, Y.J. Park, Y.S. Youn, J.O. Kim, C.S. Yong, S.G. Jin,  
744 H.-G. Choi, Novel sodium fusidate-loaded film-forming hydrogel with easy application and excellent  
745 wound healing, *International Journal of Pharmaceutics* 495(1) (2015) 67-74.

746 [43] M. Sadeghi, H. Hosseinzadeh, Synthesis of Starch—Poly(Sodium Acrylate-co-Acrylamide)  
747 Superabsorbent Hydrogel with Salt and pH-Responsiveness Properties as a Drug Delivery System,  
748 *Journal of Bioactive and Compatible Polymers* 23(4) (2008) 381-404.

749 [44] T.K. Giri, A. Thakur, A. Alexander, H. Badwaik, D.K. Tripathi, Modified chitosan hydrogels as  
750 drug delivery and tissue engineering systems: present status and applications, *Acta Pharmaceutica Sinica*  
751 *B* 2(5) (2012) 439-449.

752 [45] H. Thissen, T. Gengenbach, R. du Toit, D.F. Sweeney, P. Kingshott, H.J. Griesser, L. Meagher,  
753 Clinical observations of biofouling on PEO coated silicone hydrogel contact lenses, *Biomaterials* 31(21)  
754 (2010) 5510-5519.

755 [46] V. Franklin, M. Broadbent, A. Panaser, B. Tighe, Effects of daily disposable silicone hydrogel  
756 lenses on the tear film lipid layer, *Contact Lens and Anterior Eye* 38 (2015) e29.

757 [47] M.R. Guilherme, F.A. Aouada, A.R. Fajardo, A.F. Martins, A.T. Paulino, M.F.T. Davi, A.F. Rubira,  
758 E.C. Muniz, Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil  
759 conditioner and nutrient carrier: A review, *European Polymer Journal* 72 (2015) 365-385.

760 [48] P.C. Parvathy, A.N. Jyothi, K.S. John, J. Sreekumar, Cassava Starch Based Superabsorbent  
761 Polymer as Soil Conditioner: Impact on Soil Physico-Chemical and Biological Properties and Plant  
762 Growth, *CLEAN—Soil, Air, Water* 42(11) (2014) 1610-1617.

763 [49] L. Yang, Y. Yang, Z. Chen, C. Guo, S. Li, Influence of super absorbent polymer on soil water  
764 retention, seed germination and plant survivals for rocky slopes eco-engineering, *Ecological*  
765 *Engineering* 62 (2014) 27-32.

766 [50] R. Vundavalli, S. Vundavalli, M. Nakka, D.S. Rao, Biodegradable Nano-Hydrogels in Agricultural  
767 Farming-Alternative Source For Water Resources, *Procedia Materials Science* 10 (2015) 548-554.

768 [51] C. Demitri, F. Scalera, M. Madaghiele, A. Sannino, A. Maffezzoli, Potential of cellulose-based  
769 superabsorbent hydrogels as water reservoir in agriculture, *International Journal of Polymer Science*  
770 2013 (2013).

771 [52] C. Mo, Z. Shu-quan, L. Hua-Min, H. Zhan-bin, L. Shu-qin, Synthesis of poly(acrylic acid)/sodium  
772 humate superabsorbent composite for agricultural use, *Journal of Applied Polymer Science* 102(6)  
773 (2006) 5137-5143.

774 [53] N. Thombare, S. Mishra, M. Siddiqui, U. Jha, D. Singh, G.R. Mahajan, Design and development  
775 of guar gum based novel, superabsorbent and moisture retaining hydrogels for agricultural applications,  
776 *Carbohydrate polymers* 185 (2018) 169-178.

777 [54] A.M. Elbarbary, H.A.A. El-Rehim, N.M. El-Sawy, E.-S.A. Hegazy, E.-S.A. Soliman, Radiation  
778 induced crosslinking of polyacrylamide incorporated low molecular weights natural polymers for  
779 possible use in the agricultural applications, *Carbohydrate polymers* 176 (2017) 19-28.

780 [55] L.C. Davies, J.M. Novais, S. Martins-Dias, Detoxification of olive mill wastewater using  
781 superabsorbent polymers, *Environmental technology* 25(1) (2004) 89-100.

782 [56] S.L. Loo, Superabsorbent cryogels decorated with silver nanoparticles as a novel technology for  
783 emergency point-of-use water treatment. Doctoral thesis, 2016.

784 [57] N.A. Oladoja, E.I. Unuabonah, O.S. Amuda, O.M. Kolawole, Progress and Prospects of  
785 Polysaccharide Composites as Adsorbents for Water and Wastewater Treatment, Polysaccharides as a  
786 Green and Sustainable Resources for Water and Wastewater Treatment, Springer2017, pp. 65-90.

787 [58] M.R. Guilherme, F.A. Aouada, A.R. Fajardo, A.F. Martins, A.T. Paulino, M.F. Davi, A.F. Rubira,  
788 E.C. Muniz, Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil  
789 conditioner and nutrient carrier: A review, *European Polymer Journal* 72 (2015) 365-385.

790 [59] D. Kramer, U. Schneider, G. Jarre, M. Schuster, N. Zaplatilek, M. Sutter, I. Smith, Textile fabric  
791 for preventing the penetration and the spreading of water in cables, Google Patents, 2017.

792 [60] A.G. Bringuier, M. Fitzgerald, W.W. McAlpine, J.L. Parker, Fiber optic cable with extruded tape,  
793 Google Patents, 2017.

794 [61] T. Matsubayashi, M. Tenjimbayashi, M. Komine, K. Manabe, S. Shiratori, Bioinspired hydrogel-  
795 coated mesh with superhydrophilicity and underwater superoleophobicity for efficient and ultrafast  
796 oil/water separation in harsh environments, *Industrial & Engineering Chemistry Research* 56(24) (2017)  
797 7080-7085.

798 [62] X. Zhang, X. Wang, L. Li, R. Wu, S. Zhang, J. Wu, W. Wu, A novel polyacrylamide-based  
799 superabsorbent with temperature switch for steam breakthrough blockage, *Journal of Applied Polymer*  
800 *Science* 132(24) (2015).

801 [63] A.K. Alhuraishawy, B. Bai, A. Imqam, M. Wei, Experimental study of combining low salinity  
802 water flooding and preformed particle gel to enhance oil recovery for fractured carbonate reservoirs,  
803 *Fuel* 214 (2018) 342-350.

804 [64] B. Craeye, M. Geirnaert, G.D. Schutter, Super absorbing polymers as an internal curing agent for  
805 mitigation of early-age cracking of high-performance concrete bridge decks, *Construction and Building*  
806 *Materials* 25(1) (2011) 1-13.

807 [65] J. Wang, D. Snoeck, S. Van Vlierberghe, W. Verstraete, N. De Belie, Application of hydrogel  
808 encapsulated carbonate precipitating bacteria for approaching a realistic self-healing in concrete,  
809 *Construction and Building Materials* 68(0) (2014) 110-119.

810 [66] D. Snoeck, K. Van Tittelboom, N. De Belie, S. Steuperaert, P. Dubrueel, The use of superabsorbent  
811 polymers as a crack sealing and crack healing mechanism in cementitious materials, *Concrete Repair,*  
812 *Rehabilitation and Retrofitting III: 3rd International Conference on Concrete Repair, Rehabilitation and*  
813 *Retrofitting, ICCRRR-3, 3-5 September 2012, Cape Town, South Africa, CRC Press, 2012, p. 58.*

814 [67] A. Mignon, D. Snoeck, D. Schaubroeck, N. Luickx, P. Dubrueel, S. Van Vlierberghe, N. De Belie,  
815 pH-responsive superabsorbent polymers: A pathway to self-healing of mortar, *Reactive and Functional*  
816 *Polymers* 93(0) (2015) 68-76.

817 [68] A. Mignon, D. Snoeck, K. D'Halluin, L. Balcaen, F. Vanhaecke, P. Dubruel, S. Van Vlierberghe,  
818 N. De Belie, Alginate biopolymers: Counteracting the impact of superabsorbent polymers on mortar  
819 strength, *Construction and Building Materials* 110 (2016) 169-174.

820 [69] V. Mechtcherine, L. Dudziak, J. Schulze, H. Staehr, Internal curing by super absorbent polymers  
821 (SAP)—Effects on material properties of self-compacting fibre-reinforced high performance concrete,  
822 *Int RILEM Conf on Volume Changes of Hardening Concrete: Testing and Mitigation*, Lyngby,  
823 Denmark, 2006, pp. 87-96.

824 [70] J. Wang, A. Mignon, D. Snoeck, V. Wiktor, S. Van Vlierberghe, N. Boon, N. De Belie, Application  
825 of modified-alginate encapsulated carbonate producing bacteria in concrete: a promising strategy for  
826 crack self-healing, *Frontiers in microbiology* 6(October 2015) (2015).

827 [71] D. Snoeck, Self-healing and microstructure of cementitious materials with microfibres and  
828 superabsorbent polymers, Ghent University, 2015.

829 [72] S. Hua, A. Wang, Synthesis, characterization and swelling behaviors of sodium alginate-g-poly  
830 (acrylic acid)/sodium humate superabsorbent, *Carbohydrate Polymers* 75(1) (2009) 79-84.

831 [73] Y. Chen, Y. Zhang, F. Wang, W. Meng, X. Yang, P. Li, J. Jiang, H. Tan, Y. Zheng, Preparation of  
832 porous carboxymethyl chitosan grafted poly (acrylic acid) superabsorbent by solvent precipitation and  
833 its application as a hemostatic wound dressing, *Materials Science and Engineering: C* 63 (2016) 18-29.

834 [74] A. Cuadri, A. Romero, C. Bengoechea, A. Guerrero, Natural superabsorbent plastic materials based  
835 on a functionalized soy protein, *Polymer Testing* 58 (2017) 126-134.

836 [75] W. Song, J. Xin, J. Zhang, One-pot synthesis of soy protein (SP)-poly (acrylic acid)(PAA)  
837 superabsorbent hydrogels via facile preparation of SP macromonomer, *Industrial crops and products*  
838 100 (2017) 117-125.

839 [76] M. Rinaudo, Main properties and current applications of some polysaccharides as biomaterials,  
840 *Polymer International* 57(3) (2008) 397-430.

841 [77] E. Percival, The polysaccharides of green, red and brown seaweeds: their basic structure,  
842 biosynthesis and function, *British Phycological Journal* 14(2) (1979) 103-117.

843 [78] M. Rinaudo, Biomaterials based on a natural polysaccharide: alginate, TIP. *Revista especializada*  
844 *en ciencias químico-biológicas* 17 (2014) 92-96.

845 [79] Y.J. Kim, K.J. Yoon, S.W. Ko, Preparation and properties of alginate superabsorbent filament fibers  
846 crosslinked with glutaraldehyde, *Journal of Applied Polymer Science* 78(10) (2000) 1797-1804.

847 [80] J.K. Dutkiewicz, Superabsorbent materials from shellfish waste—a review, *Journal of Biomedical*  
848 *Materials Research* 63(3) (2002) 373-381.

849 [81] J. Wang, A. Mignon, G. Trensou, S. Van Vlierberghe, N. Boon, N. De Belie, A chitosan based pH-  
850 responsive hydrogel for encapsulation of bacteria for self-sealing concrete, *Cement and Concrete*  
851 *Composites* 93 (2018) 309-322.



852 [82] A. Pourjavadi, B. Farhadpour, F. Seidi, Synthesis and investigation of swelling behavior of new  
853 agar based superabsorbent hydrogel as a candidate for agrochemical delivery, *Journal of polymer*  
854 *research* 16(6) (2009) 655-665.

855 [83] S.M. Mihaila, A.K. Gaharwar, R.L. Reis, A.P. Marques, M.E. Gomes, A. Khademhosseini,  
856 Photocrosslinkable Kappa-Carrageenan Hydrogels for Tissue Engineering Applications, *Advanced*  
857 *healthcare materials* 2(6) (2013) 895-907.

858 [84] X. Ding, L. Li, P.s. Liu, J. Zhang, N.I. Zhou, S. Lu, S.h. Wei, J. Shen, The preparation and properties  
859 of dextrin-graft-acrylic acid/montmorillonite superabsorbent nanocomposite, *Polymer Composites*  
860 30(7) (2009) 976-981.

861 [85] F. Nnadi, C. Brave, Environmentally friendly superabsorbent polymers for water conservation in  
862 agricultural lands, *Journal of Soil Science and Environmental Management* 2(7) (2011) 206-211.

863 [86] D.F. Coutinho, S.V. Sant, H. Shin, J.T. Oliveira, M.E. Gomes, N.M. Neves, A. Khademhosseini,  
864 R.L. Reis, Modified Gellan Gum hydrogels with tunable physical and mechanical properties,  
865 *Biomaterials* 31(29) (2010) 7494-7502.

866 [87] S. Thakur, B. Sharma, A. Verma, J. Chaudhary, S. Tamulevicius, V.K. Thakur, Recent progress in  
867 sodium alginate based sustainable hydrogels for environmental applications, *Journal of cleaner*  
868 *production* 198 (2018) 143-159.

869 [88] H. Tu, Y. Yu, J. Chen, X. Shi, J. Zhou, H. Deng, Y. Du, Highly cost-effective and high-strength  
870 hydrogels as dye adsorbents from natural polymers: chitosan and cellulose, *Polymer Chemistry* 8(19)  
871 (2017) 2913-2921.

872 [89] S. Shahi, H.R. Motasadizadeh, M.J. Zohuriaan-Mehr, Surface modification of superabsorbing  
873 hydrogels through a feasible esterification reaction: Toward tunable superabsorbent for hygienic  
874 applications, *International Journal of Polymeric Materials and Polymeric Biomaterials* 66(11) (2017)  
875 544-557.

876 [90] A. Mignon, G.-J. Graulus, D. Snoeck, J. Martins, N. De Belie, P. Dubruel, S. Van Vlierberghe, pH-  
877 sensitive superabsorbent polymers: a potential candidate material for self-healing concrete, *Journal of*  
878 *materials science* 50(2) (2015) 970-979.

879 [91] B.W. Hanak, C.Y. Hsieh, W. Donaldson, S.R. Browd, K.K. Lau, W. Shain, Reduced cell attachment  
880 to poly (2-hydroxyethyl methacrylate)-coated ventricular catheters in vitro, *Journal of Biomedical*  
881 *Materials Research Part B: Applied Biomaterials* 106(3) (2018) 1268-1279.

882 [92] H. Chen, X. Xing, H. Tan, Y. Jia, T. Zhou, Y. Chen, Z. Ling, X. Hu, Covalently antibacterial  
883 alginate-chitosan hydrogel dressing integrated gelatin microspheres containing tetracycline  
884 hydrochloride for wound healing, *Materials Science and Engineering: C* 70 (2017) 287-295.

885 [93] S.L. Percival, S.M. McCarty, Silver and alginates: role in wound healing and biofilm control,  
886 *Advances in wound care* 4(7) (2015) 407-414.

887 [94] A. Bashari, A. Rouhani Shirvan, M. Shakeri, Cellulose-based hydrogels for personal care products,  
888 *Polymers for Advanced Technologies* 29(12) (2018).

889 [95] H. Voisin, L. Bergström, P. Liu, A.P. Mathew, Nanocellulose-based materials for water  
890 purification, *Nanomaterials* 7(3) (2017) 57.

891 [96] S.I. Mussatto, M. van Loosdrecht, Cellulose: a key polymer for a greener, healthier, and bio-based  
892 future, *Biofuel Research Journal* 3(4) (2016) 482-482.

893 [97] S. Thakur, P.P. Govender, M.A. Mamo, S. Tamulevicius, Y.K. Mishra, V.K. Thakur, Progress in  
894 lignin hydrogels and nanocomposites for water purification: Future perspectives, *Vacuum* 146 (2017)  
895 342-355.

896 [98] S. Thakur, P.P. Govender, M.A. Mamo, S. Tamulevicius, V.K. Thakur, Recent progress in gelatin  
897 hydrogel nanocomposites for water purification and beyond, *Vacuum* 146 (2017) 396-408.

898 [99] M.G. Paulraj, S. Ignacimuthu, M.R. Gandhi, A. Shajahan, P. Ganesan, S.M. Packiam, N.A. Al-  
899 Dhabi, Comparative studies of tripolyphosphate and glutaraldehyde cross-linked chitosan-botanical  
900 pesticide nanoparticles and their agricultural applications, *International journal of biological*  
901 *macromolecules* 104 (2017) 1813-1819.

902 [100] E. Abdel Bary, A.N. Harmal, A. Saeed, M.A. Gouda, Design, Synthesis, Characterization,  
903 Swelling and in Vitro Drug Release Behavior of Composite Hydrogel Beads Based on Methotrexate and  
904 Chitosan Incorporating Antipyrine Moiety, *Polymer-Plastics Technology and Engineering* (2018) 1-9.

905 [101] A. Pourjavadi, S. Barzegar, Synthesis and Evaluation of pH and Thermosensitive Pectin-Based  
906 Superabsorbent Hydrogel for Oral Drug Delivery Systems, *Starch - Stärke* 61(3-4) (2009) 161-172.

907 [102] S.C. Sutradhar, M.M.R. Khan, M.M. Rahman, N.C. Dafadar, The Synthesis of Superabsorbent  
908 Polymers from a Carboxymethylcellulose/acrylic Acid Blend Using Gamma Radiation and its  
909 Application in Agriculture, *Journal of Physical Science* 26(2) (2015) 23-39.

910 [103] P. Treenate, P. Monvisade, In vitro drug release profiles of pH-sensitive hydroxyethylacryl  
911 chitosan/sodium alginate hydrogels using paracetamol as a soluble model drug, *International journal of*  
912 *biological macromolecules* 99 (2017) 71-78.

913 [104] Q. Zhou, H. Kang, M. Bielec, X. Wu, Q. Cheng, W. Wei, H. Dai, Influence of different divalent  
914 ions cross-linking Sodium Alginate-Polyacrylamide hydrogels on antibacterial properties and wound  
915 healing, *Carbohydrate Polymers* 197 (2018) 292-304.

916 [105] K. Alharbi, A. Ghoneim, A. Ebid, H. El-Hamshary, M.H. El-Newehy, Controlled release of  
917 phosphorous fertilizer bound to carboxymethyl starch-g-polyacrylamide and maintaining a hydration  
918 level for the plant, *International journal of biological macromolecules* 116 (2018) 224-231.

919 [106] Y. Wen, X. Zhu, D.E. Gauthier, X. An, D. Cheng, Y. Ni, L. Yin, Development of poly (acrylic  
920 acid)/nanofibrillated cellulose superabsorbent composites by ultraviolet light induced polymerization,  
921 *Cellulose* 22(4) (2015) 2499-2506.

922 [107] H. Sehaqui, M.E. Gálvez, V. Becatinni, Y. cheng Ng, A. Steinfeld, T. Zimmermann, P. Tingaut,  
923 Fast and Reversible Direct CO<sub>2</sub> Capture from Air onto All-Polymer Nanofibrillated Cellulose  
924 Polyethylenimine Foams, *Environmental science & technology* 49(5) (2015) 3167-3174.

925 [108] W.A. El-Tohamy, H.M. El-Abagy, E.M. Ahmed, F.S. Aggor, S.I. Hawash, Application of super  
926 absorbent hydrogel poly (acrylate/acrylic acid) for Water conservation in Sandy soil, Transaction of the  
927 Egyptian society of chemical engineering 40(2) (2014) 1-8.

928 [109] T.-M. Don, M.-L. Huang, A.-C. Chiu, K.-H. Kuo, W.-Y. Chiu, L.-H. Chiu, Preparation of thermo-  
929 responsive acrylic hydrogels useful for the application in transdermal drug delivery systems, Materials  
930 Chemistry and Physics 107(2-3) (2008) 266-273.

931 [110] A. Pourjavadi, M. Kurdtabar, R.G. Mahdavinia, H. Hosseinzadeh, Synthesis and super-swelling  
932 behavior of a novel protein-based superabsorbent hydrogel, Polymer Bulletin 57(6) (2006) 813-824.

933 [111] D.G. Ahearn, D.T. Grace, M.J. Jennings, R.N. Borazjani, K.J. Boles, L.J. Rose, R.B. Simmons,  
934 E.N. Ahanotu, Effects of hydrogel/silver coatings on in vitro adhesion to catheters of bacteria associated  
935 with urinary tract infections, Current microbiology 41(2) (2000) 120-125.

936 [112] G.D. Mogoşanu, A.M. Grumezescu, Natural and synthetic polymers for wounds and burns  
937 dressing, International Journal of Pharmaceutics 463(2) (2014) 127-136.

938 [113] E.A. Kamoun, E.-R.S. Kenawy, X. Chen, A review on polymeric hydrogel membranes for wound  
939 dressing applications: PVA-based hydrogel dressings, Journal of advanced research 8(3) (2017) 217-  
940 233.

941 [114] T.R. Hoare, D.S. Kohane, Hydrogels in drug delivery: progress and challenges, Polymer 49(8)  
942 (2008) 1993-2007.

943 [115] T. Kubo, N. Nishimura, H. Furuta, K. Kubota, T. Naito, K. Otsuka, Tunable separations based on  
944 a molecular size effect for biomolecules by poly (ethylene glycol) gel-based capillary electrophoresis,  
945 Journal of Chromatography A 1523 (2017) 107-113.

946 [116] A. Huettermann, L.J. Orikiriza, H. Agaba, Application of superabsorbent polymers for improving  
947 the ecological chemistry of degraded or polluted lands, CLEAN–Soil, Air, Water 37(7) (2009) 517-526.

948 [117] Y.-H. La, B.D. McCloskey, R. Sooriyakumaran, A. Vora, B. Freeman, M. Nassar, J. Hedrick, A.  
949 Nelson, R. Allen, Bifunctional hydrogel coatings for water purification membranes: Improved fouling  
950 resistance and antimicrobial activity, Journal of Membrane Science 372(1-2) (2011) 285-291.

951 [118] G. Umachitra, Disposable baby diaper--a threat to the health and environment, Journal of  
952 environmental science & engineering 54(3) (2012) 447-452.

953 [119] N.A. Choudhury, S. Sampath, A.K. Shukla, Hydrogel-polymer electrolytes for electrochemical  
954 capacitors: an overview, Energy & Environmental Science 2(1) (2009) 55-67.

955 [120] C. Schröfl, V. Mechtcherine, M. Gorges, Relation between the molecular structure and the  
956 efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage,  
957 Cement and Concrete Research 42(6) (2012) 865-873.

958 [121] S.K.H. Gulrez, G.O. Phillips, S. Al-Assaf, Hydrogels: methods of preparation, characterisation  
959 and applications, INTECH Open Access Publisher 2011.

960 [122] S. Kaihara, S. Matsumura, J.P. Fisher, Synthesis and characterization of cyclic acetal based  
961 degradable hydrogels, European Journal of Pharmaceutics and Biopharmaceutics 68(1) (2008) 67-73.

962 [123] S.L. Cardoso, C.S.D. Costa, E. Nishikawa, M.G.C. da Silva, M.G.A. Vieira, Biosorption of toxic  
963 metals using the alginate extraction residue from the brown algae *Sargassum filipendula* as a natural  
964 ion-exchanger, *Journal of cleaner production* 165 (2017) 491-499.

965 [124] K.Y. Lee, D.J. Mooney, Alginate: properties and biomedical applications, *Progress in polymer*  
966 *science* 37(1) (2012) 106-126.

967 [125] J. Comaposada, P. Gou, B. Marcos, J. Arnau, Physical properties of sodium alginate solutions and  
968 edible wet calcium alginate coatings, *LWT-Food Science and Technology* 64(1) (2015) 212-219.

969 [126] A. Usman, S. Khalid, A. Usman, Z. Hussain, Y. Wang, Algal polysaccharides, novel application,  
970 and outlook, *Algae based polymers, blends, and composites*, Elsevier2017, pp. 115-153.

971 [127] S.N. Pawar, K.J. Edgar, Alginate derivatization: a review of chemistry, properties and  
972 applications, *Biomaterials* 33(11) (2012) 3279-3305.

973 [128] A. Blaeser, D.F. Duarte Campos, U. Puster, W. Richtering, M.M. Stevens, H. Fischer, Controlling  
974 shear stress in 3D bioprinting is a key factor to balance printing resolution and stem cell integrity,  
975 *Advanced healthcare materials* 5(3) (2016) 326-333.

976 [129] L. Picaut, O. Ronsin, C. Caroli, T. Baumberger, Experimental evidence of a helical, supercritical  
977 instability in pipe flow of shear thinning fluids, *Physical Review Fluids* 2(8) (2017) 083303.

978 [130] L. Zhang, T. Liu, N. Chen, Y. Jia, R. Cai, W. Theis, X. Yang, Y. Xia, D. Yang, X. Yao, Scalable  
979 and controllable synthesis of atomic metal electrocatalysts assisted by an egg-box in alginate, *Journal*  
980 *of Materials Chemistry A* 6(38) (2018) 18417-18425.

981 [131] N. Nallamuthu, M. Braden, M.P. Patel, Dimensional changes of alginate dental impression  
982 materials, *Journal of Materials Science: Materials in Medicine* 17(12) (2006) 1205-1210.

983 [132] S.G. Jin, A.M. Yousaf, K.S. Kim, D.W. Kim, D.S. Kim, J.K. Kim, C.S. Yong, Y.S. Youn, J.O.  
984 Kim, H.-G. Choi, Influence of hydrophilic polymers on functional properties and wound healing  
985 efficacy of hydrocolloid based wound dressings, *International Journal of Pharmaceutics* 501(1) (2016)  
986 160-166.

987 [133] Z. Cui, Y. Zhang, J. Zhang, H. Kong, X. Tang, L. Pan, K. Xia, A. Aldalbah, A. Li, R. Tai, Sodium  
988 alginate-functionalized nanodiamonds as sustained chemotherapeutic drug-release vectors, *Carbon* 97  
989 (2016) 78-86.

990 [134] S. Dhivya, V.V. Padma, E. Santhini, Wound dressings—a review, *BioMedicine* 5(4) (2015).

991 [135] J.A. Sirviö, A. Kolehmainen, H. Liimatainen, J. Niinimäki, O.E.O. Hormi, Biocomposite  
992 cellulose-alginate films: promising packaging materials, *Food chemistry* 151 (2014) 343-351.

993 [136] M.A. Fawzy, M. Gomaa, A.F. Hifney, K.M. Abdel-Gawad, Optimization of alginate alkaline  
994 extraction technology from *Sargassum latifolium* and its potential antioxidant and emulsifying  
995 properties, *Carbohydrate polymers* 157 (2017) 1903-1912.

996 [137] M. Augello, S.M. Dell, E.H. Bliefernich, Edible MCC/PGA coating composition. U.S. Patent No.  
997 6,500,462. 31 Dec. 2002., Google Patents, 2002.

998 [138] C. Mellinas, A. Valdés, M. Ramos, N. Burgos, M.d.C. Garrigós, A. Jiménez, Active edible films:  
999 Current state and future trends, *Journal of Applied Polymer Science* 133(2) (2016).

1000 [139] A. Eskhan, F. Banat, Removal of Oil from Water by Calcium Alginate Hydrogel Modified with  
1001 Maleic Anhydride, *Journal of Polymers and the Environment* (2018) 1-16.

1002 [140] R.J. Coleman, G. Lawrie, L.K. Lambert, M. Whittaker, K.S. Jack, L. Grøndahl, Phosphorylation  
1003 of Alginate: Synthesis, Characterization, and Evaluation of in Vitro Mineralization Capacity,  
1004 *Biomacromolecules* 12(4) (2011) 889-897.

1005 [141] E. Salimi, A. Ghaee, A.F. Ismail, M. Karimi, Anti-thrombogenicity and permeability of  
1006 polyethersulfone hollow fiber membrane with sulfonated alginate toward blood purification,  
1007 *International journal of biological macromolecules* 116 (2018) 364-377.

1008 [142] J.A. Rowley, G. Madlambayan, D.J. Mooney, Alginate hydrogels as synthetic extracellular matrix  
1009 materials, *Biomaterials* 20(1) (1999) 45-53.

1010 [143] I. Donati, K.I. Draget, M. Borgogna, S. Paoletti, G. Skjåk-Bræk, Tailor-made alginate bearing  
1011 galactose moieties on mannuronic residues: selective modification achieved by a chemoenzymatic  
1012 strategy, *Biomacromolecules* 6(1) (2005) 88-98.

1013 [144] J. Candiello, T. Richardson, K. Padgaonkar, K. Task, P.N. Kumta, I. Banerjee, Alginate  
1014 encapsulation of chitosan nanoparticles: a viable alternative to soluble chemical signaling in definitive  
1015 endoderm induction of human embryonic stem cells, *Journal of Materials Chemistry B* 4(20) (2016)  
1016 3575-3583.

1017 [145] S. Pelletier, P. Hubert, F. Lapique, E. Payan, E. Dellacherie, Amphiphilic derivatives of sodium  
1018 alginate and hyaluronate: synthesis and physico-chemical properties of aqueous dilute solutions,  
1019 *Carbohydrate Polymers* 43(4) (2000) 343-349.

1020 [146] V.G. Babak, E.A. Skotnikova, I.G. Lukina, S. Pelletier, P. Hubert, E. Dellacherie,  
1021 Hydrophobically associating alginate derivatives: surface tension properties of their mixed aqueous  
1022 solutions with oppositely charged surfactants, *Journal of colloid and interface science* 225(2) (2000)  
1023 505-510.

1024 [147] S. Basumallick, Alginates in Drug Delivery, *Alginates: Applications in the Biomedical and Food*  
1025 *Industries* (2019) 141-151.

1026 [148] G. Leone, P. Torricelli, A. Chiumiento, A. Facchini, R. Barbucci, Amidic alginate hydrogel for  
1027 nucleus pulposus replacement, *Journal of Biomedical Materials Research Part A* 84(2) (2008) 391-401.

1028 [149] N. Işıklan, F. Kurşun, M. İnal, Graft copolymerization of itaconic acid onto sodium alginate using  
1029 ceric ammonium nitrate as initiator, *Journal of Applied Polymer Science* 114(1) (2009) 40-48.

1030 [150] N. Işıklan, F. Kurşun, M. İnal, Graft copolymerization of itaconic acid onto sodium alginate using  
1031 benzoyl peroxide, *Carbohydrate Polymers* 79(3) (2010) 665-672.

1032 [151] A. Rashidzadeh, A. Olad, D. Salari, A. Reyhanitabar, On the preparation and swelling properties  
1033 of hydrogel nanocomposite based on Sodium alginate-g-Poly (acrylic acid-co-acrylamide)/Clinoptilolite  
1034 and its application as slow release fertilizer, *Journal of Polymer Research* 21(2) (2014) 344.

1035 [152] A. Mittal, R. Ahmad, I. Hasan, Poly (methyl methacrylate)-grafted alginate/Fe<sub>3</sub>O<sub>4</sub>  
1036 nanocomposite: synthesis and its application for the removal of heavy metal ions, *Desalination and*  
1037 *Water Treatment* 57(42) (2016) 19820-19833.

1038 [153] J.H. Kim, S.B. Lee, S.J. Kim, Y.M. Lee, Rapid temperature/pH response of porous alginate-g-  
1039 poly (N-isopropylacrylamide) hydrogels, *Polymer* 43(26) (2002) 7549-7558.

1040 [154] M. Liu, X. Song, Y. Wen, J.-L. Zhu, J. Li, Injectable thermoresponsive hydrogel formed by  
1041 alginate-g-poly (N-isopropylacrylamide) that releases doxorubicin-encapsulated micelles as a smart  
1042 drug delivery system, *ACS applied materials & interfaces* 9(41) (2017) 35673-35682.

1043 [155] M. Grasselli, L.E. Diaz, O. Cascone, Beaded matrices from cross-linked alginate for affinity and  
1044 ion exchange chromatography of proteins, *Biotechnology techniques* 7(10) (1993) 707-712.

1045 [156] S.T. Moe, G. Skjåk-Bræk, O. Smidsrød, Covalently cross-linked sodium alginate beads, *Food*  
1046 *Hydrocolloids* 5(1) (1991) 119-123.

1047 [157] S. Kumar, I. Haq, J. Prakash, A. Raj, Improved enzyme properties upon glutaraldehyde cross-  
1048 linking of alginate entrapped xylanase from *Bacillus licheniformis*, *International journal of biological*  
1049 *macromolecules* 98 (2017) 24-33.

1050 [158] A.D. Rouillard, C.M. Berglund, J.Y. Lee, W.J. Polacheck, Y. Tsui, L.J. Bonassar, B.J. Kirby,  
1051 Methods for photocrosslinking alginate hydrogel scaffolds with high cell viability, *Tissue Engineering*  
1052 *Part C: Methods* 17(2) (2010) 173-179.

1053 [159] A.I. Chou, S.B. Nicoll, Characterization of photocrosslinked alginate hydrogels for nucleus  
1054 pulposus cell encapsulation, *Journal of Biomedical Materials Research Part A* 91A(1) (2009) 187-194.

1055 [160] O. Jeon, J.E. Samorezov, E. Alsberg, Single and dual crosslinked oxidized methacrylated  
1056 alginate/PEG hydrogels for bioadhesive applications, *Acta biomaterialia* 10(1) (2014) 47-55.

1057 [161] Y. Fang, R. Zhang, B. Duan, M. Liu, A. Lu, L. Zhang, Recyclable Universal Solvents for Chitin  
1058 to Chitosan with Various Degrees of Acetylation and Construction of Robust Hydrogels, *ACS*  
1059 *Sustainable Chemistry & Engineering* 5(3) (2017) 2725-2733.

1060 [162] R. Jayakumar, M. Prabakaran, P.T.S. Kumar, S.V. Nair, H. Tamura, Biomaterials based on chitin  
1061 and chitosan in wound dressing applications, *Biotechnology advances* 29(3) (2011) 322-337.

1062 [163] M. Arkoun, F. Daigle, R.A. Holley, M.C. Heuzey, A. Aji, Chitosan-based nanofibers as bioactive  
1063 meat packaging materials, *Packaging Technology and Science* 31(4) (2018) 185-195.

1064 [164] A. Bernkop-Schnürch, S. Dünnhaupt, Chitosan-based drug delivery systems, *European Journal of*  
1065 *Pharmaceutics and Biopharmaceutics* 81(3) (2012) 463-469.

1066 [165] F. Croisier, C. Jérôme, Chitosan-based biomaterials for tissue engineering, *European Polymer*  
1067 *Journal* 49(4) (2013) 780-792.

1068 [166] T. Wu, S. Zivanovic, Determination of the degree of acetylation (DA) of chitin and chitosan by  
1069 an improved first derivative UV method, *Carbohydrate Polymers* 73(2) (2008) 248-253.

1070 [167] D. Gómez-Ríos, R. Barrera-Zapata, R. Ríos-Esteva, Comparison of process technologies for  
1071 chitosan production from shrimp shell waste: A techno-economic approach using Aspen Plus®, Food  
1072 and bioproducts processing 103 (2017) 49-57.

1073 [168] R. Jayakumar, H. Nagahama, T. Furuike, H. Tamura, Synthesis of phosphorylated chitosan by  
1074 novel method and its characterization, International Journal of Biological Macromolecules 42(4) (2008)  
1075 335-339.

1076 [169] M. Rinaudo, P. Le Dung, C. Gey, M. Milas, Substituent distribution on O, N-  
1077 carboxymethylchitosans by <sup>1</sup>H and <sup>13</sup>C NMR, International Journal of Biological Macromolecules  
1078 14(3) (1992) 122-128.

1079 [170] F.-L. Mi, S.-J. Wu, F.-M. Lin, Adsorption of copper (II) ions by a chitosan–oxalate complex  
1080 biosorbent, International Journal of Biological Macromolecules 72 (2015) 136-144.

1081 [171] J.M. Dang, D.D.N. Sun, Y. Shin-Ya, A.N. Sieber, J.P. Kostuik, K.W. Leong, Temperature-  
1082 responsive hydroxybutyl chitosan for the culture of mesenchymal stem cells and intervertebral disk cells,  
1083 Biomaterials 27(3) (2006) 406-418.

1084 [172] B. Zhu, C. Wei, C. Hou, Q. Gu, D. Chen, Preparation and characterization of hydroxybutyl  
1085 chitosan, e-Polymers 10(1) (2010) 883-892.

1086 [173] W.-K. Lee, Y.-Y. Lim, A.T.-C. Leow, P. Namasivayam, J.O. Abdullah, C.-L. Ho, Factors  
1087 affecting yield and gelling properties of agar, Journal of Applied Phycology 29(3) (2017) 1527-1540.

1088 [174] A.A. Al Mousa, S.S. Al-Deyab, Antimicrobial hydrogel wound dressing. US20130052257A1,  
1089 Google Patents, 2011.

1090 [175] N. Rhein-Knudsen, M. Ale, A. Meyer, Seaweed hydrocolloid production: an update on enzyme  
1091 assisted extraction and modification technologies, Marine drugs 13(6) (2015) 3340-3359.

1092 [176] D. Hernandez Armada, Immobilization of oligosaccharides in affinity chromatography and  
1093 applications to screening human milk oligosaccharide receptors, (2015).

1094 [177] D.I. Bezbradica, C. Mateo, J.M. Guisan, Novel support for enzyme immobilization prepared by  
1095 chemical activation with cysteine and glutaraldehyde, Journal of Molecular Catalysis B: Enzymatic 102  
1096 (2014) 218-224.

1097 [178] G.P. Dillon, X. Yu, A. Sridharan, J.P. Ranieri, R.V. Bellamkonda, The influence of physical  
1098 structure and charge on neurite extension in a 3D hydrogel scaffold, Journal of Biomaterials Science,  
1099 Polymer Edition 9(10) (1998) 1049-1069.

1100 [179] G. Rezanejade Bardajee, Z. Hooshyar, Y. Pourhasan, The effect of multidentate biopolymer based  
1101 on polyacrylamide grafted onto Kappa-Carrageenan on the spectrofluorometric properties of water-  
1102 soluble CdS quantum dots, International Journal of Spectroscopy 2011 (2011) 6.

1103 [180] V.L. Campo, D.F. Kawano, D.B. da Silva, I. Carvalho, Carrageenans: Biological properties,  
1104 chemical modifications and structural analysis—A review, Carbohydrate Polymers 77(2) (2009) 167-  
1105 180.

- 1106 [181] X. Luo, Y. Duan, W. Yang, H. Zhang, C. Li, J. Zhang, Structural elucidation and  
1107 immunostimulatory activity of polysaccharide isolated by subcritical water extraction from *Cordyceps*  
1108 *militaris*, *Carbohydrate polymers* 157 (2017) 794-802.
- 1109 [182] R. Covis, J.-P. Guégan, J. Jeftić, M. Czjzek, M. Benoit, T. Benvegnu, Structural and rheological  
1110 properties of kappa ( $\kappa$ )-carrageenans covalently modified with cationic moieties, *Journal of Polymer*  
1111 *Research* 23(4) (2016) 78.
- 1112 [183] Ö. Tari, Ö. Pekcan, Swelling of iota-carrageenan gels prepared with various CaCl<sub>2</sub> content: A  
1113 fluorescence study, *e-Polymers* 8(1) (2008) 1-10.
- 1114 [184] D.A. Navarro, C.A. Stortz, Microwave-assisted alkaline modification of red seaweed galactans,  
1115 *Carbohydrate Polymers* 62(2) (2005) 187-191.
- 1116 [185] Y.Y. Tye, A.K. HPS, C.Y. Kok, C.K. Saurabh, Preparation and characterization of modified and  
1117 unmodified carrageenan based films, *IOP Conference Series: Materials Science and Engineering*, IOP  
1118 Publishing, 2018, p. 012020.
- 1119 [186] V. Webber, S.M.d. Carvalho, P.J. Ogliari, L. Hayashi, P.L.M. Barreto, Optimization of the  
1120 extraction of carrageenan from *Kappaphycus alvarezii* using response surface methodology, *Food*  
1121 *Science and Technology* 32(4) (2012) 812-818.
- 1122 [187] H. Hosseinzadeh, A. Pourjavadi, G.R. Mahdavinia, M.J. Zohuriaan-Mehr, Modified carrageenan.  
1123 1. H-CarragPAM, a novel biopolymer-based superabsorbent hydrogel, *Journal of Bioactive and*  
1124 *Compatible Polymers* 20(5) (2005) 475-490.
- 1125 [188] R.V. Kulkarni, R. Boppana, G.K. Mohan, S. Mutalik, N.V. Kalyane, pH-responsive  
1126 interpenetrating network hydrogel beads of poly (acrylamide)-g-carrageenan and sodium alginate for  
1127 intestinal targeted drug delivery: Synthesis, in vitro and in vivo evaluation, *Journal of colloid and*  
1128 *interface science* 367(1) (2012) 509-517.
- 1129 [189] F. Arias, A. Mansilla, B. Matsuhira, J. Pavez, R. Torres, M. Yáñez-Sánchez, Carrageenans from  
1130 nuclear phases of subantarctic *Mazzaella laminarioides* (Gigartinales, Rhodophyta) and graft  
1131 copolymerization of alkali-modified carrageenan with acrylamide, *Journal of applied phycology* 28(2)  
1132 (2016) 1275-1286.
- 1133 [190] A. Pourjavadi, A.M. Harzandi, H. Hosseinzadeh, Modified carrageenan 3. Synthesis of a novel  
1134 polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-  
1135 carrageenan in air, *European Polymer Journal* 40(7) (2004) 1363-1370.
- 1136 [191] K. Prasad, R. Meena, A.K. Siddhanta, Microwave-induced rapid one-pot synthesis of  $\kappa$ -  
1137 carrageenan-g-PMMA copolymer by potassium persulphate initiating system, *Journal of Applied*  
1138 *Polymer Science* 101(1) (2006) 161-166.
- 1139 [192] A. Pourjavadi, S. Barzegar, F. Zeidabadi, Synthesis and properties of biodegradable hydrogels of  
1140  $\kappa$ -carrageenan grafted acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid as candidates for  
1141 drug delivery systems, *Reactive and Functional Polymers* 67(7) (2007) 644-654.



1142 [193] H. Tümtürk, N. Karaca, G. Demirel, F. Şahin, Preparation and application of poly (N, N-  
1143 dimethylacrylamide-co-acrylamide) and poly (N-isopropylacrylamide-co-acrylamide)/κ-Carrageenan  
1144 hydrogels for immobilization of lipase, *International Journal of Biological Macromolecules* 40(3)  
1145 (2007) 281-285.

1146 [194] C. Kelder, A. Bakker, J. Klein-Nulend, D. Wismeijer, The 3D Printing of Calcium Phosphate with  
1147 κ-Carrageenan under Conditions Permitting the Incorporation of Biological Components—A Method,  
1148 *Journal of functional biomaterials* 9(4) (2018) 57.

1149 [195] H. Yuan, W. Zhang, X. Li, X. Lü, N. Li, X. Gao, J. Song, Preparation and in vitro antioxidant  
1150 activity of κ-carrageenan oligosaccharides and their oversulfated, acetylated, and phosphorylated  
1151 derivatives, *Carbohydrate Research* 340(4) (2005) 685-692.

1152 [196] V.A. Cosenza, D.A. Navarro, C.A. Pujol, E.B. Damonte, C.A. Stortz, Partial and total C-6  
1153 oxidation of gelling carrageenans. Modulation of the antiviral activity with the anionic character,  
1154 *Carbohydrate polymers* 128 (2015) 199-206.

1155 [197] H. Yuan, J. Song, W. Zhang, X. Li, N. Li, X. Gao, Antioxidant activity and cytoprotective effect  
1156 of κ-carrageenan oligosaccharides and their different derivatives, *Bioorganic & medicinal chemistry*  
1157 *letters* 16(5) (2006) 1329-1334.

1158 [198] R. L Puntel, D. S Avila, D. H Roos, S. Pinton, Mitochondrial Effects of Organoselenium and  
1159 Organotellurium Compounds, *Current Organic Chemistry* 20(2) (2016) 198-210.

1160 [199] Y.-P. Jiang, X.-K. Guo, O-maleoyl derivative of low-molecular-weight κ-carrageenan: Synthesis  
1161 and characterization, *Carbohydrate Polymers* 61(4) (2005) 441-445.

1162 [200] K.M. Zia, S. Tabasum, M. Nasif, N. Sultan, N. Aslam, A. Noreen, M. Zuber, A review on  
1163 synthesis, properties and applications of natural polymer based carrageenan blends and composites,  
1164 *International journal of biological macromolecules* 96 (2017) 282-301.

1165 [201] N. Lavoine, I. Desloges, A. Dufresne, J. Bras, Microfibrillated cellulose—Its barrier properties and  
1166 applications in cellulosic materials: A review, *Carbohydrate polymers* 90(2) (2012) 735-764.

1167 [202] E.R. Keijsers, G. Yılmaz, J.E. van Dam, The cellulose resource matrix, *Carbohydrate polymers*  
1168 93(1) (2013) 9-21.

1169 [203] G. Siqueira, J. Bras, A. Dufresne, Cellulosic bionanocomposites: a review of preparation,  
1170 properties and applications, *Polymers* 2(4) (2010) 728-765.

1171 [204] C. Chang, B. Duan, J. Cai, L. Zhang, Superabsorbent hydrogels based on cellulose for smart  
1172 swelling and controllable delivery, *European Polymer Journal* 46(1) (2010) 92-100.

1173 [205] C. Spagnol, F.H. Rodrigues, A.G. Pereira, A.R. Fajardo, A.F. Rubira, E.C. Muniz, Superabsorbent  
1174 hydrogel composite made of cellulose nanofibrils and chitosan-graft-poly (acrylic acid), *Carbohydrate*  
1175 *Polymers* 87(3) (2012) 2038-2045.

1176 [206] E. Fortunati, M. Peltzer, I. Armentano, L. Torre, A. Jiménez, J.M. Kenny, Effects of modified  
1177 cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites,  
1178 *Carbohydrate Polymers* 90(2) (2012) 948-956.

1179 [207] Suhas, V.K. Gupta, P.J.M. Carrott, R. Singh, M. Chaudhary, S. Kushwaha, Cellulose: A review  
1180 as natural, modified and activated carbon adsorbent, *Bioresource Technology* 216 (2016) 1066-1076.

1181 [208] Z. He, H. Song, Y. Cui, W. Zhu, K. Du, S. Yao, Porous spherical cellulose carrier modified with  
1182 polyethyleneimine and its adsorption for Cr (III) and Fe (III) from aqueous solutions, *Chinese Journal*  
1183 *of Chemical Engineering* 22(9) (2014) 984-990.

1184 [209] O.K. Júnior, L.V.A. Gurgel, R.P. de Freitas, L.F. Gil, Adsorption of Cu (II), Cd (II), and Pb (II)  
1185 from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse  
1186 chemically modified with EDTA dianhydride (EDTAD), *Carbohydrate Polymers* 77(3) (2009) 643-650.

1187 [210] K. Missoum, M.N. Belgacem, J. Bras, Nanofibrillated cellulose surface modification: a review,  
1188 *Materials* 6(5) (2013) 1745-1766.

1189 [211] L. Wang, J. Li, Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified  
1190 cellulose from flax shive: Kinetics, equilibrium, and thermodynamics, *Industrial Crops and Products* 42  
1191 (2013) 153-158.

1192 [212] A. Sawut, M. Yimit, W. Sun, I. Nurulla, Photopolymerisation and characterization of  
1193 maleylated cellulose-g-poly(acrylic acid) superabsorbent polymer, *Carbohydrate Polymers* 101 (2014)  
1194 231-239.

1195 [213] M.M. Abeer, M. Amin, M.C. Iqbal, C. Martin, A review of bacterial cellulose-based drug delivery  
1196 systems: their biochemistry, current approaches and future prospects, *Journal of Pharmacy and*  
1197 *Pharmacology* 66(8) (2014) 1047-1061.

1198 [214] F. Lecomte, J. Siepmann, M. Walther, R.J. MacRae, R. Bodmeier, pH-sensitive polymer blends  
1199 used as coating materials to control drug release from spherical beads: importance of the type of core,  
1200 *Biomacromolecules* 6(4) (2005) 2074-2083.

1201 [215] D. Le Corre, J. Bras, A. Dufresne, Starch nanoparticles: a review, *Biomacromolecules* 11(5)  
1202 (2010) 1139-1153.

1203 [216] E. Agama-Acevedo, P.C. Flores-Silva, L.A. Bello-Perez, Cereal Starch Production for Food  
1204 Applications, *Starches for Food Application*, Elsevier 2019, pp. 71-102.

1205 [217] W. Zou, L. Yu, X. Liu, L. Chen, X. Zhang, D. Qiao, R. Zhang, Effects of amylose/amylopectin  
1206 ratio on starch-based superabsorbent polymers, *Carbohydrate polymers* 87(2) (2012) 1583-1588.

1207 [218] B. Ghanbarzadeh, H. Almasi, A.A. Entezami, Physical properties of edible modified  
1208 starch/carboxymethyl cellulose films, *Innovative Food Science & Emerging Technologies* 11(4) (2010)  
1209 697-702.

1210 [219] S.-A. Riyajan, Y. Sasithornsonti, P. Phinyocheep, Green natural rubber-g-modified starch for  
1211 controlling urea release, *Carbohydrate Polymers* 89(1) (2012) 251-258.

1212 [220] S.A. Riyajan, P. Keawittarit, A novel natural rubber-graft-cassava starch foam for oil/gasohol  
1213 absorption, *Polymer International* 65(5) (2016) 491-502.

1214 [221] G. Güçlü, E. Al, S. Emik, T.B. İyim, S. Özgümüş, M. Özyürek, Removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions  
1215 from aqueous solutions by starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite  
1216 hydrogels, *Polymer Bulletin* 65(4) (2010) 333-346.

1217 [222] P.C. Parvathy, A.N. Jyothi, Synthesis, characterization and swelling behaviour of superabsorbent  
1218 polymers from cassava starch-graft-poly (acrylamide), *Starch-Stärke* 64(3) (2012) 207-218.

1219 [223] J.J. Kim, K. Park, Smart hydrogels for bioseparation, *Bioseparation* 7(4-5) (07-1998) 177-184.

1220 [224] A.A. Moghanjoughi, D. Khoshnevis, A. Zarrabi, A concise review on smart polymers for  
1221 controlled drug release, *Drug delivery and translational research* 6(3) (2016) 333-340.

1222 [225] P. Gupta, K. Vermani, S. Garg, Hydrogels: from controlled release to pH-responsive drug  
1223 delivery, *Drug Discovery Today* 7(10) (2002) 569-579.

1224 [226] J.P. Best, M.P. Neubauer, S. Javed, H.H. Dam, A. Fery, F. Caruso, Mechanics of pH-Responsive  
1225 Hydrogel Capsules, *Langmuir* 29(31) (2013) 9814-9823.

1226 [227] K.P. Yong Qiu, Environment-sensitive hydrogels for drug delivery, *Advanced Drug Delivery*  
1227 *Reviews* 53(2001) (2001) 321-339.

1228 [228] M. Miyazaki, T. Maeda, K. Hirashima, N. Kurokawa, K. Nagahama, A. Hotta, PEG-based  
1229 nanocomposite hydrogel: Thermoresponsive sol-gel transition controlled by PLGA-PEG-PLGA  
1230 molecular weight and solute concentration, *Polymer* 115 (2017) 246-254.

1231 [229] H. Priya James, R. John, A. Alex, K.R. Anoop, Smart polymers for the controlled delivery of  
1232 drugs – a concise overview, *Acta Pharmaceutica Sinica B* 4(2) (2014) 120-127.

1233 [230] Y. Takashima, S. Hatanaka, M. Otsubo, M. Nakahata, T. Kakuta, A. Hashidzume, H. Yamaguchi,  
1234 A. Harada, Expansion-contraction of photoresponsive artificial muscle regulated by host-guest  
1235 interactions, *Nat Commun* 3(1270) (2012).

1236 [231] T. Manouras, M. Vamvakaki, Field responsive materials: photo-, electro-, magnetic-and  
1237 ultrasound-sensitive polymers, *Polymer Chemistry* 8(1) (2017) 74-96.

1238 [232] M.A. Darabi, A. Khosrozadeh, R. Mbeleck, Y. Liu, Q. Chang, J. Jiang, J. Cai, Q. Wang, G. Luo,  
1239 M. Xing, Skin-Inspired Multifunctional Autonomic-Intrinsic Conductive Self-Healing Hydrogels with  
1240 Pressure Sensitivity, Stretchability, and 3D Printability, *Advanced Materials* 29(31) (2017) 1700533.

1241 [233] D. Kanios, Device for transdermal administration of drugs including acrylic based polymers,  
1242 Google Patents, 2017.

1243 [234] M. Mahkam, Novel pH-sensitive hydrogels for colon-specific drug delivery, *Drug Deliv* 17(3)  
1244 (2010) 158-63.

1245 [235] Z.A.I. Mazrad, E.B. Kang, G. Lee, I. In, S.Y. Park, Temperature-sensitive carbon dots derived  
1246 from poly (N-isopropylacrylamide) for fluorescence on-off properties, *RSC Advances* 7(18) (2017)  
1247 11149-11157.

1248 [236] M. Barbieri, F. Cellini, I. Cacciotti, S.D. Peterson, M. Porfiri, In situ temperature sensing with  
1249 fluorescent chitosan-coated PNIPAAm/alginate beads, *Journal of Materials Science* 52(20) (2017)  
1250 12506-12512.

1251 [237] M.L. Hanneke, J.H.C. Mark, B.M. ávan Lankvelt, W.M. Martin, Tuning the LCST of poly (2-  
1252 oxazoline) s by varying composition and molecular weight: alternatives to poly (N-  
1253 isopropylacrylamide)?, *Chemical Communications* (44) (2008) 5758-5760.

1254 [238] S.P. Miguel, M.P. Ribeiro, H. Brancal, P. Coutinho, I.J. Correia, Thermoresponsive chitosan–  
1255 agarose hydrogel for skin regeneration, *Carbohydrate Polymers* 111 (2014) 366-373.

1256 [239] K.E. Crompton, J.D. Goud, R.V. Bellamkonda, T.R. Gengenbach, D.I. Finkelstein, M.K. Horne,  
1257 J.S. Forsythe, Polylysine-functionalised thermoresponsive chitosan hydrogel for neural tissue  
1258 engineering, *Biomaterials* 28(3) (2007) 441-449.

1259 [240] A. Carreira, F. Gonçalves, P. Mendonça, M. Gil, J. Coelho, Temperature and pH responsive  
1260 polymers based on chitosan: applications and new graft copolymerization strategies based on living  
1261 radical polymerization, *Carbohydrate Polymers* 80(3) (2010) 618-630.

1262 [241] H. Katono, A. Maruyama, K. Sanui, N. Ogata, T. Okano, Y. Sakurai, Thermo-responsive swelling  
1263 and drug release switching of interpenetrating polymer networks composed of poly (acrylamide-co-  
1264 butyl methacrylate) and poly (acrylic acid), *Journal of Controlled Release* 16(1) (1991) 215-227.

1265 [242] J. Liu, Y. Huang, A. Kumar, A. Tan, S. Jin, A. Mozhi, X.-J. Liang, pH-Sensitive nano-systems  
1266 for drug delivery in cancer therapy, *Biotechnology Advances* 32(4) (2014) 693-710.

1267 [243] P. Chatterjee, *Environmentally Responsive Hydrogels: Development and Integration with Hard*  
1268 *Materials*, Arizona State University 2015.

1269 [244] I. Savina, I.Y.U. Galaev, Smart polymers for bioseparation and other biotechnological  
1270 applications, *Smart Polymers and their Applications* (2014) 408.

1271 [245] S. Yang, G. Liu, Y. Cheng, Y. Zheng, Electroresponsive behavior of sodium alginate-g-poly  
1272 (acrylic acid) hydrogel under DC electric field, *Journal of Macromolecular Science®, Part A: Pure and*  
1273 *Applied Chemistry* 46(11) (2009) 1078-1082.

1274