Superabsorbent polymers: a review on the characteristics and applications of synthetic, polysaccharide-based, semi-synthetic and 'smart' derivatives

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Abstract

The current review provides an overview of different types of superabsorbent polymers (SAPs) together with appropriate strategies elaborated to enable their synthesis. The main focus will be on polysaccharide-based, semi-synthetic and 'smart' SAPs along with their derivatives. SAPs have already shown their use in a plethora of applications including diapers, the biomedical field, agriculture, etc. The different polymer classification possibilities are discussed, as well as the classification of the constituting building blocks. The main part of SAPs still has a synthetic origin. However, as they are often not biocompatible, biodegradable or renewable, natural SAPs based on polysaccharides have gained increasing interest. Due to the low solubility of synthetic polymers, purification problems or the need for organic solvents, a trend has emerged towards combining polysaccharides with synthetic monomers to create semi-synthetic, hybrid SAPs for specialized applications with fine-tuned properties including wound dressings, fertilizers or self-healing concrete. These specialized, semi-synthetic SAPs offer strong potential for a series of applications in the future. However, future research in this respect is still needed to optimize homogeneity and to increase gel fractions. A final part of this review includes 'smart' SAPs such as SAPs with a T-, electro- and pH-sensitivity. These 'smart' SAPs are especially becoming useful for certain biomedical applications such as drug release for which an in vivo location can be targeted. The use of 'smart', semi-synthetic SAPs with fine-tuned characteristics combining the best characteristics of both synthetic and natural SAPs, offer the greatest potential for the future.

Keywords

Superabsorbent polymer
Smart polymer
Polysaccharide
Semi-synthetic

Highlights

- Polysaccharide-based SAPs sustainable alternative for conventional, synthetic SAPs
- Semi-synthetic SAPs with fine-tuned properties for specialized applications
- Smart SAPs particularly interesting for specific applications such as drug delivery

Content

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

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

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

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

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

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

3. Overview of polymer classification possibilities

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

3.1. Classification with respect to morphology

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

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

3.2. Classification with respect to general building blocks

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

3.3. Classification based on the cross-linking mechanism

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

3.4. Classification based on the type of electrical charges present

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

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

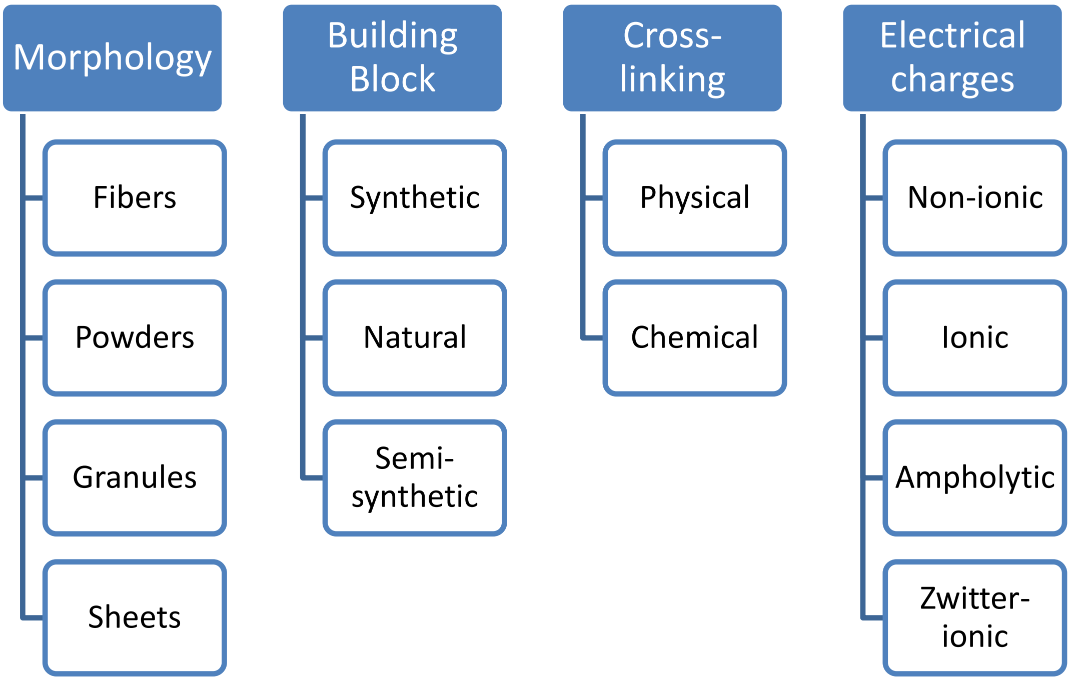

Figure 1: Subdivision of possible SAP classifications.

4. Importance of SAPs

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

4.1. Comparative study on SAP and hydrogel publications

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

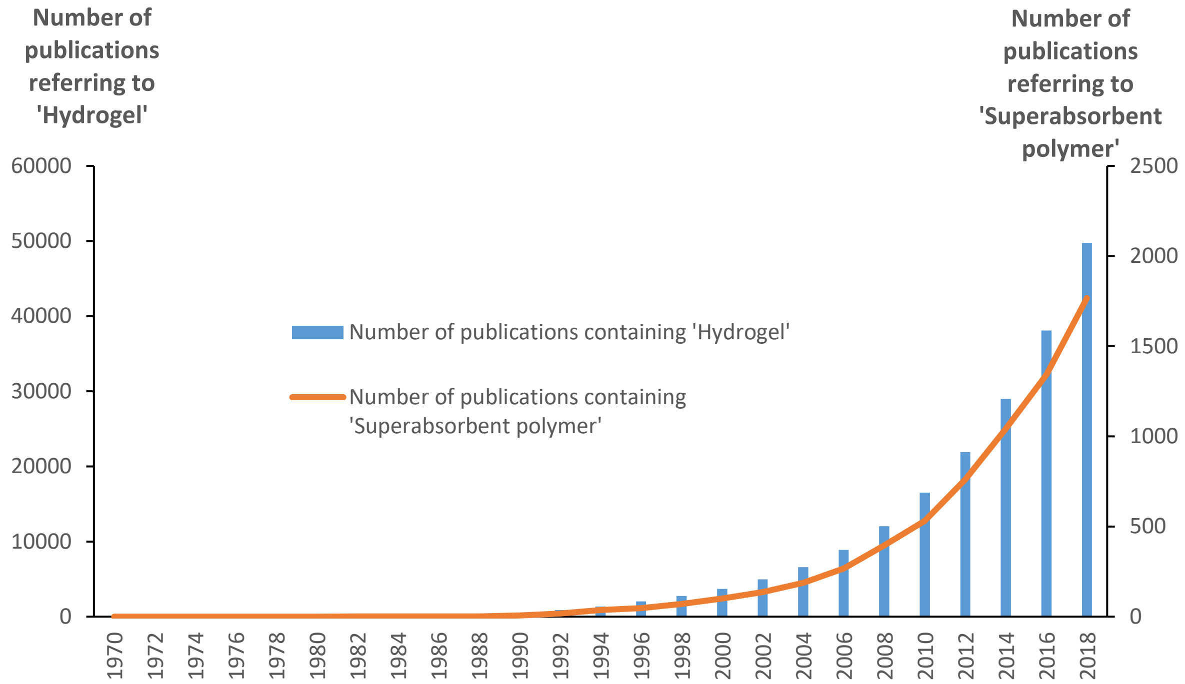

Figure 2: Cumulative number of publications containing the words ‘hydrogel’ or ‘superabsorbent polymer’ in their abstract according to Web of Science as a function of the publication year.

4.2. Overview of SAP applications

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

As such, the field of SAPs is already crowded in a plethora of applications while potential retains in many others. An overview of the different biomedical and non-biomedical applications using SAPs and hydrogels is listed in Table 1. A whole range of different SAPs is used for the applications described in the current section. The following section will subdivide the SAPs according to their general building blocks and go into more detail on the their respective advantages and disadvantages.

5. Synthetic vs. polysaccharide-based natural SAPs

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

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

They have experienced a growing interest because of their designation as being biodegradable, readily available, biocompatible, non-toxic, renewable and sustainable. In addition, due to the increasing cost and finite nature of crude oil, natural polymers form a cost-effective and sustainable alternative [87, 88]. Indeed, their renewability causes them to cause a lower environmental burden than synthetic SAPs [28]. Water-soluble polysaccharides carry functional groups such as alcohols, carboxylic acids and/or amines. These moieties can be used for cross-linking or grafting of other polymers. The upcoming section provides an overview of the origin, the composition and the application field of both synthetic as well as natural SAPs. The most often used natural polymers including alginate, chitosan, agarose, κ-carrageenan, cellulose and starch will be covered in greater detail. An overview of the different advantages, disadvantages and recent examples of synthetic, natural and semi-synthetic SAPs can be 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)**
Synthetic	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
Natural	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 Shelf-life/sensitive storage conditions	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] [97]	Personal care, water purification, water reservoir, tissue engineering
			Lignin	[98]	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

Semi-synthetic	Advantages of both synthetic/natural, fine-tuned properties	Phase separation Loss of biodegradability Homogeneity	Starch-poly(acrylamide)	[33]	Slow release fertilizer
			Acrylic acid/gelatin	[8]	Drug release
			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)/nanofibirllated cellulose	[105]	Slow release fertilizer
			Cellulose/Polyethylenimine	[106]	Personal care, diapers
				[107]	CO_2 capture

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

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

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

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

7. Natural SAPs based on different polysaccharides

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

7.1. Natural SAPs based on alginate and its derivatives

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

Interestingly, when NaAlg is combined with multivalent cations such as calcium (Ca^{2+}, originating from salts such as calcium chloride, $CaCl_2$), a ionically cross-linked network is formed as the carboxylate moieties become coordinated by the cations, thereby becoming insoluble in water. The anionic groups will attract water into the structure, leading to SAP behavior. Helical chains are formed in the presence of calcium ions and arrange into the so-called 'egg-box' model, as illustrated in Figure 3 [130]. Another way to induce gel formation is by forming intermolecular hydrogen bonds by lowering the pH of the alginate solution below the pKa of both uronic acid groups. These gels are however more brittle compared to the ionic calcium alginate gels . This increased brittleness is related to the presence of interconnected random aggregates compared to the calcium alginate.

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

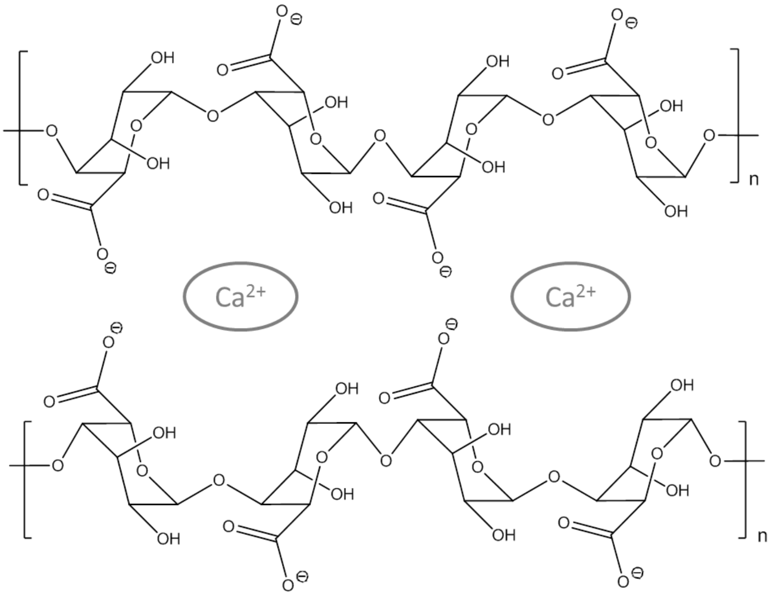

Figure 3: Calcium coordination of the egg box model of calcium alginate (-GMGM-) formed only by the G-blocks.

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

The hydroxyl groups of alginate can be modified by acetylation to increase the swelling potential of calcium gels [139], by phosphorylation which increases their resistance towards degradation [140] and by sulfation to ensure blood-compatibility and anticoagulant activity [141]. Its interaction with a cellular environment can be enhanced by the introduction of cell-signaling molecules [142-144]. To induce hydrophobic or amphiphilic characteristics, hydrophobic moieties have already been attached onto the hydrophilic alginate backbone to prevent erosion in drug release applications [145-147].

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

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

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

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

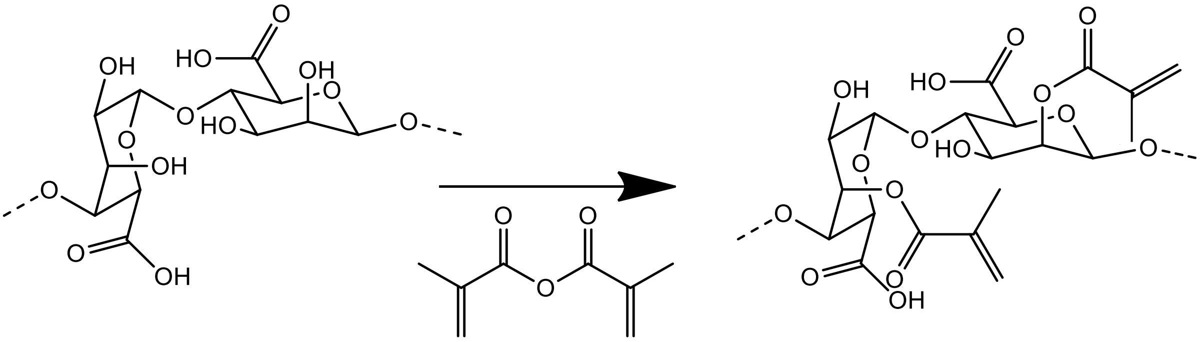

Figure 4: Methacrylation of alginate using methacrylic anhydride. Activated double bonds are incorporated in the alginate backbone to serve as a functional handle for subsequent free radical polymerization.

7.2. Natural SAPs based on chitosan and its derivatives

Chitosan (Figure 5) is a linear polysaccharide composed of glucosamine building blocks. Glucosamine is a so-called amino sugar as it has the same structure as glucose with the hydroxyl moiety at the C_2-position being replaced by an amine. Chitosan is made from chitin, which can be extracted from the exoskeleton of invertebrates such as crabs and shrimps. It can also be found in the cell walls of fungi, by partial deacetylation in an alkaline environment of N-acetylamino groups or by enzymatic hydrolysis in the presence of a chitin deacetylase. Since complete deacetylation is difficult to achieve, commercial resources always report the degree of deacetylation (DDA). Chitin with a DDA higher than 50% is considered as chitosan. A major disadvantage is that chitin is impossible to dissolve in most solvents [161]. Chitosan, on the other hand, has a pK_a value for the conjugated acid of 6.0 which results in protonation in acidic environments and increases the solubility in acidic aqueous media [80, 162, 163]. This renders chitosan interesting to develop pH-responsive SAPs, which is further discussed in the section tackling ‘smart’ SAPs (see section 1.8.3.).

Chitosan has many applications in the biomedical sector including among other as tissue engineering scaffold, wound dressing, for hair treatment and drug delivery. It has also already been used for the depollution of waste water and in the agricultural sector as a seed treatment, as biopesticide against fungal infections and in winemaking as a preservative given its biocompatibility [99, 162, 164-166]. Global chitosan production exceeds 118,000 tonnes annually [167].

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

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

7.3. Natural SAPs based on agarose and its derivatives

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

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

7.4. Natural SAPs based on carrageenan and its derivatives

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

There exist a series of chemical modifications to modulate the physico-chemical properties of carrageenan. For splitting the ι-carrageenan chain, the Smith periodate degradation can be used [181]. K-carrageenan containing hydroxyalkyl groups has already been developed to create a gel with a decreased syneresis and therefore, a broader industrial scope [182]. The association of κ-carrageenan with $CaCl_2$ changes the swelling capacity of the gel [183]. Another often used derivatization type characteristic for these polysaccharides is alkalization. Different types of carrageenan can undergo cyclization when using a concentrated 1M sodium hydroxide solution at a temperature of 80°C. The latter improves the gelling properties as reflected by their strength [184-186]. By using alkaline hydrolysis or microwave irradiation, carrageenan gels have already been 'cross-linked' with poly(acrylamide) [187-189], acrylic acid [190] and methyl methacrylate [191]. In addition, a copolymerization with acrylic acid and 2-acrylamido-2-methylpropane-sulfonic acid has already been performed as well [192]. The latter hydrogels are especially very promising for the industrial immobilization of enzymes [193]. More specifically, by precipitating calcium phosphate into a κ-carrageenan matrix, porous nanocomposites could be prepared which are useful for bone tissue engineering [194]. Other derivatizations performed earlier include acetylation, oversulfatation and phosphorylation of κ-carrageenan [195, 196]. These modifications can enhance the antioxidant activity of carrageenan [197]. Synthetic κ-seleno-carrageenan may inhibit the proliferation of breast cancer cells [198]. Alternatively, an *O*-maleoyl derivative of κ-carrageenan could be manifested by the reaction of tetrabutylammonium salt of the anionic carrageenan fragments with maleic anhydride, 4-dimethylaminopyridine and tributylamine under homogeneous conditions in *N*,*N*-dimethylformamide [199]. As indicated by the many highlighted examples, the derivatization of carrageenan is very versatile[200].

7.5. Natural SAPs based on cellulose and its derivatives

Cellulose (Figure 5) is considered as the most abundant organic compound which is derived from biomass [96]. In addition to its main origin being wood, other sources include plant fibers (leaf, stalk, fruit or the rigid structure), marine animals, algae… [201]. Total production of primary cellulose sources was estimated at 1200-1500 million tons/year in 2011 [202]. It is a linear homopolysaccharide composed of β-1,4-anhydro-D-glucose units [203]. The hydroxyl groups present can lead to strong hydrogen bonding. It shows a multi-scale microfibrillated structure which is useful for many of its applications. Additionally, it is characterized by hierarchical crystalline and amorphous regions and shows a highly cohesive nature. Some of its main applications can be found in paper, textile and the material industry. Interestingly, cellulose in combination with carboxymethylcellulose has already resulted in promising SAPs with biomedical applications enabling the controlled release of bovine serum albumin [204]. Nano-fibrillated cellulose (NFC) has already been combined with acrylic acid during the UV-initiated polymerization to improve the swelling properties of poly(acrylic acid) to become applied in agriculture or for sanitary purposes [106]. SAPs based on cellulose nanofibrils and chitosan-graft-poly(acrylic acid) could potentially be used for the drug release properties of solutes [205].

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

7.6. Natural SAPs based on starch and its derivatives

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

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

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

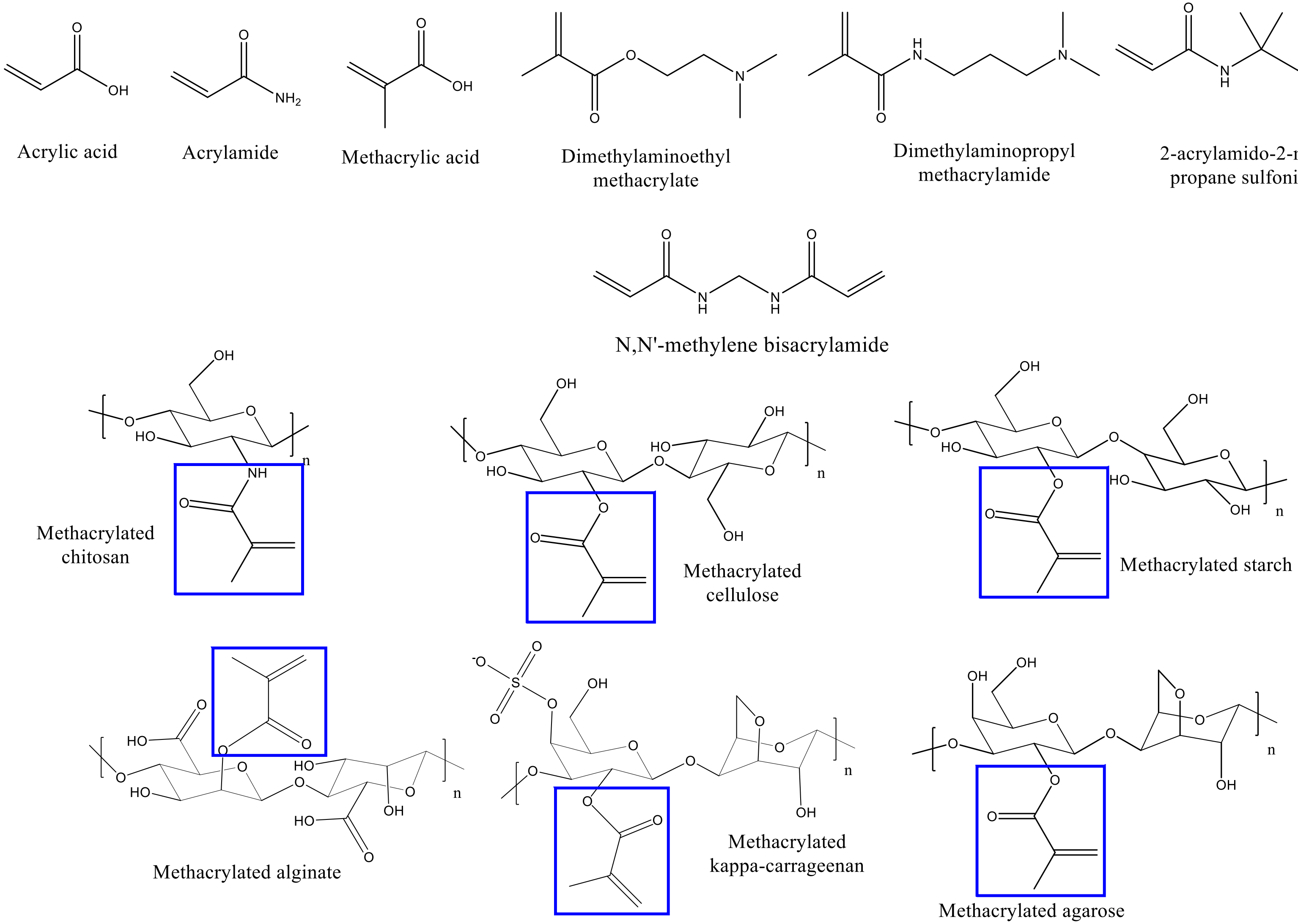

Figure 5: Chemical structure of the most common synthetic monomers (upper panel), the most used synthetic cross-linker (center) and methacrylated polysaccharides of which alcohol moieties can be modified into a methacrylate (lower panel). The latter can act as natural cross-linkers.

8. ‘Smart’ SAPs

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

8.1. Characteristics and applications of thermo-responsive SAPs

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

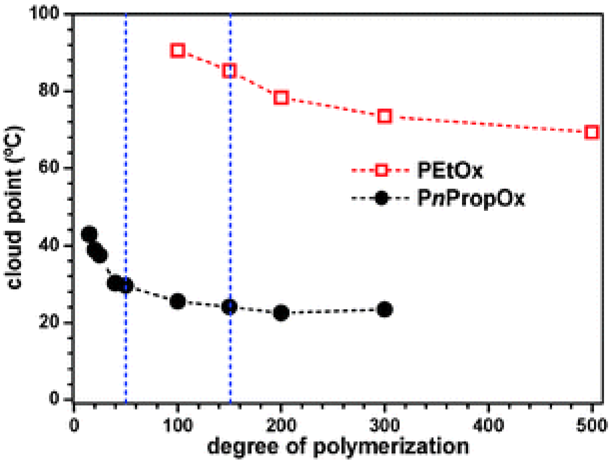

Figure 6: Cloud point as a function of chain length for poly(ethyloxazoline) and poly(n-propyloxazoline) [237].

8.2. Characteristics and applications of pH-sensitive SAPs

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

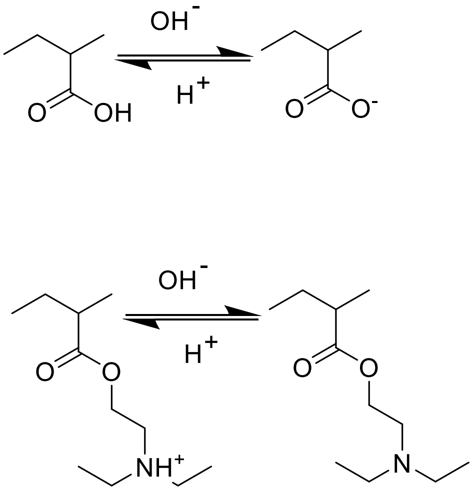

Figure 7: pH-dependent ionization of poly(acrylic acid) (top) and poly(*N*,*N′*-diethylaminoethyl methacrylate) (bottom).

8.3. Characteristics and applications of photo- and electro-sensitive SAPs

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

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

Conclusions and future perspectives

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

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

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Data availability

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

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