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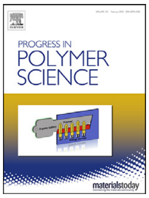

Superabsorbent Polymers: From long-established, microplastics generating systems, to sustainable, biodegradable and future proof alternatives

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ABSTRACT

Superabsorbent polymers (SAPs) play important roles in our daily life, as they are applied in products for hygiene, agriculture, construction, etc. The most successful commercially used types of SAPs are acrylate-based, which include poly(acrylic acid)s, poly(acrylamide)s, poly(acrylonitrile)s and their salts. The acrylate-based SAPs have superior water-absorbent properties, but they have high molecular weight and in addition an entirely carbon atom-based and cross-linked backbone. These factors endow them with poor (bio)degradability, which has a devastating impact on the environment where such SAP-containing materials may end up at the end of their lifetime. Furthermore, the raw materials for production of acrylate-based SAPs are mostly petroleum-based. From the viewpoint of sustainability, a bio-based resource would be the ideal candidate to replace the fossil-based ones. To overcome the shortcomings of the existing SAPs, bio-based and degradable SAPs are required. This review will then cover the following topics: (1) the technology development history and state-of-the-art of current SAPs; (2) the product designing principles of SAPs; (3) an in-depth introduction and discussion of the structural characteristics and properties of different kinds of SAPs derived from both fossil or renewable resources and (4) novel polycondensate-based, potentially biodegradable SAPs with promising industrial applicability.

1. Introduction

Synthetic plastics are an essential part of our everyday life and the global economy. Over 330 million tons of plastics are produced annually, accompanied by consumption of massive petrochemical resources and generation of a huge amount of plastic waste due to their ubiquity and durability [1]. Currently, only about 9% of plastic waste can be recycled; 10% is incinerated and over 80% is accumulated in landfills or released into the natural environment [2]. Environmental contamination with plastics of all sizes is becoming one of the most widespread and long-lasting anthropogenic changes to the biosphere of our planet. Particularly, microplastics, with diameters <5 mm, have posed immeasurable hazards to the ecosystem, by adsorbing persistent organic pollutants and transferring along the food chain [3–5].

Superabsorbent polymers (SAPs) are a kind of synthetic specialty polymers featured by remarkably high water uptake capacity. A typical SAP is highly hydrophilic networks that can imbibe and retain huge amounts of water or aqueous solutions even under pressure [6–8]. Water absorption capacity is a standard parameter describing the water retention ability of SAPs, which is defined as the weight of absorbed liquid (g) divided by the dried weight of SAP (g). SAPs can take up as much water as a thousand times of their own weight while general hydrogels can only take up no more than 10 times their own weight. They have become increasingly important nowadays and are widely used in many fields including hygiene and bio-related areas [9–17], agriculture [18–37], construction [38–55] and so forth [56–63]. Disposable health care products (DHCPs), such as baby diapers, female sanitary and adult incontinence products are the biggest application area of SAPs, taking more than 95% market share (Fig. 1) [56,64]. Because of the continuously increasing world population and average age of people, the market of SAPs is projected to grow from 9.0 billion USD in 2019 to 12.9 billion USD by 2024 at a Compound Annual Growth Rate (CAGR) of 7.4% with global production capacity of over 3000,000 tons/year in 2015 [65].

Currently, SAPs used in commercial DHCPs are predominately non-biodegradable cross-linked polyacrylic acid-based microbeads with particle sizes ranging from 150 to 850 μm [66,67]. Compared

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Nomenclature

AA	acrylic acid
AM	acrylamide
AMPS	2-acrylamido-2-methyl-1-propanesulfonic acid
APS	ammonium persulfate
BC	bacterial cellulose
CA	citric acid
CAN	ceric ammonium nitrate
CG	carrageenan
CMC	carboxymethylcellulose
CMCNa	carboxymethylcellulose sodium salt
CMCS	carboxymethyl chitosan
CMPWS	chemically modified pulverized wheat straw
CS	chitosan
DMDAAC	dimethyl diallyl ammonium chloride
DVS	divinyl sulfone
ECM	extracellular matrix
ECH	epichlorohydrin
EDCH	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride
EDTA	ethylenediaminetetraacetic acid
EDTAD	ethylenediaminetetraacetic dianhydride
EGDMA	ethylene glycol dimethacrylate
GA	glutaraldehyde
HEA	2-hydroxyethyl acrylate
HEC	hydroxyethylcellulose
IA	itaconic acid
IMA	isobutylene maleic anhydride
IPN	interpenetrating network
KPS	potassium persulfate
MAA	methacrylic acid
MBA	*N*, *N*’-methylenebisacrylamide
MC	methylcellulose
MCSC	maleylated cotton stalk cellulose
MMT	montmorillonite
Na-MMT	sodium montmorillonite
PC	plant cellulose
PLA	polylactic acid
PHA	polyhydroxyalkanoates
PIA	poly(itaconic acid)
PBS	polybutylene succinate
PBST	polybutylene succinate-co-terephthalate
PBAT	polybutylene adipate-co-terephthalate
PVA	poly(vinyl alcohol)
SA	sodium alginate
SAP	superabsorbent polymers
SH	sodium humate
SHS	sodium hydrogen sulfite
TEMED	*N*, *N*, *N*’, *N*’-tetramethylethylenediamine
USDA	United States Department of Agriculture
Vc	ascorbic acid
WMCAA	waste material cultured Auricularia Auricula

to other plastics, DHCPs, together with SAPs in the inner layers, are usually heavily contaminated after use with a high liquid content, which are particularly difficult to be recycled or are unsuitable for energy regeneration via incineration. It is reported that full degradation of one piece of used diaper will take 500 years [68]. They thus become the major pollutants in landfills and undoubtedly a key source of primary microplastics. In view of the clear global trend of banning the use of disposable plastic products in the (near) future, especially persistent microplastics-generating species (see ECHA Annex XV Restriction Report on microplastics [69]), we believe that development of biodegradable alternatives can be the ultimate ecofriendly solution for tackling above issues.

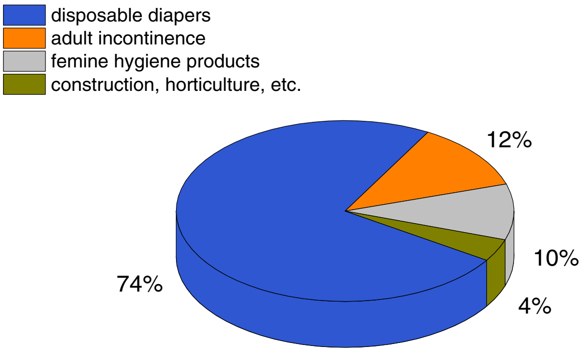


Fig. 1. Global applications (based on the total weights) of SAPs in 2014. Report from Future Market Insight (FMI) [64]: Heavy Investments to Increase Production Sales to Positively Impact Growth of Market for SAP.

There have been a few review articles published on this topic. A few researchers focus on discussing the production method and kinetic model of SAPs [72–75], while the others introduced the major applications of these fascinating materials, such as agricultural [76–79], personal care [80], or non-hygienic [81] applications. As the subject of sustainability became more important in recent years, the SAPs prepared from specific types of natural raw materials including agricultural waste [82], shellfish waste [83], polysaccharide like chitosan [84], cellulose [80,85], proteins [86] and poly(amino acid) [87] have also been summarized. Other reviews [88–90] focusing on all the classifications, production methods and applications of SAPs. In light of new legislation on microplastics that will be enacted within the next few years, we believe that paying attention to this increasingly severe environmental problem is of great value. The potential biodegradability of all classes of SAPs are discussed in this review.

Considering the raw materials used in DHCPs, we may expect that the existing non-biodegradable PE-, PP- or PET-based nonwoven/film parts, which are typically used as the surface or diversion layers of these products can potentially be replaced in relatively short term by biodegradable polymers (e.g. PLA, PHAs, PBS, PBST, PBAT, etc.) given their fast industrial development in recent years [70,71]. Nevertheless, as the core functional components, SAPs have been rarely investigated towards sustainable alternatives with good productivity and material properties. Until now, no biodegradable SAPs exhibiting sufficient water absorption have been commercialized. The attempts to achieve this goal have been focusing on natural-polymer based SAPs and the recently emerged polycondensate-type of synthetic SAPs. The former strategy is more concentrated on structural modification to gain higher water absorbing capacity, while the latter strategy is also highly promising yet the innovative and holistic developing protocols are desired to meet the overall challenging requirements for SAPs.

In this review, we will cover: (1) the technology development history and state-of-the art of current SAPs; (2) the product designing principles of SAPs; and (3) an in-depth introduction and discussion of the structural characteristics and properties of different kinds of SAPs derived from both fossil and renewable resources. In addition, novel polycondensate-based SAPs with promising industrial applicability will be reviewed to shed light on possible developments of sustainable, biodegradable and future-proof alternatives.

2. Technology development history of SAPs

Due to the steady increase of the average human lifespan in the last decades, the global geriatric population has witnessed

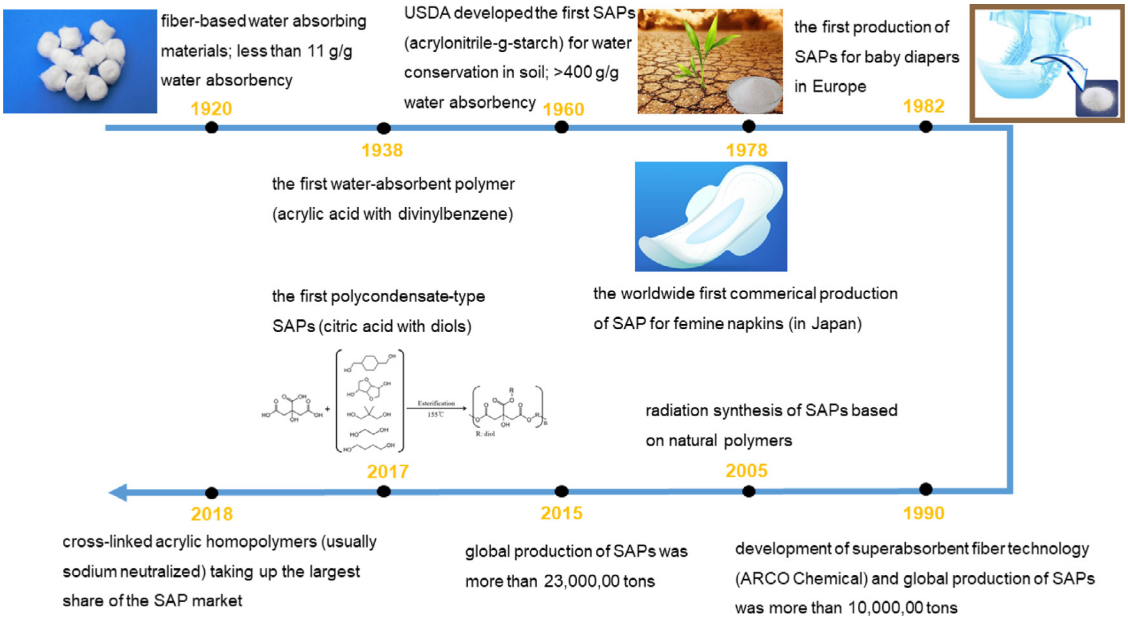


Fig. 2. Timeline of major technology development in SAPs.

a steady increase and will continuously grow in the future. The prevalence rates for adult incontinence disorders has also been increased accordingly. Such a trend is expected to play a vital role in shaping the global superabsorbent market over the forecasted period.

The development of SAPs has experienced a history of more than 80 years (Fig. 2). In the 1940's, the first water-absorbent polymer was synthesized by divinylbenzene and acrylic acid (AA) in solution which afforded a network product. The resulting product shows a certain degree of swelling property (no more than 50%) [91]. Commercialization of SAPs was first introduced by Union Carbide in the 1960's for horticultural application to accelerate early growth of sugar seedlings [92]. In the 1970's, they were developed to allow growing plants in deserts. However, commercial promotion of such products were not so successful because of their high cost and unsatisfactory lifetime [93]. Commercially convenient production of SAPs for feminine napkin use began in Japan in 1978 [94]. In the early 1980's, SAPs were widely developed in Japan for the baby diaper market which led to newer, more relevantly swelling polymers; some species have relatively long lifetimes were further applied for agricultural applications. In 1980, European countries further developed the super water-absorbent materials for use in baby diapers. They innovatively mixed the polyacrylate-based synthetic SAPs with cellulose-based fluff filler, resulting in a high water absorption capacity and a much reduced amount of SAPs (approximately 1–2 g/product). Later on, a thinner product containing 4–5 g SAPs and less fluff fillers was marketed in Japan [95]. Besides granular super absorbent polymers, ARCO Chemical developed a super absorbent fiber technology in the early 1990s [96].

The first actual superabsorbent was a starch-grafted cross-linked polyacrylate polymer developed by the United States Department of Agriculture (USDA) with a trademark of "Super Slurper". The water absorption capability of this product was significantly enhanced to be greater than 400 times its own weight [97,98]. Cross-linked polyacrylates eventually replaced the previously-developed superabsorbents, and became the major SAPs until today [99]. Till 2018, sodium polyacrylate which was first developed in 1994 accounted for the largest share of the SAP market [65]. The USDA gave the technical know-how to several US companies for further development of the basic technology. Under this guideline, a wide range of grafting functional groups onto natural polymers were attempted including acrylic acid, acrylamide and polyvinyl alcohol (PVA) [99]. Japanese initiated independent research by using starch, carboxy methyl cellulose (CMC), acrylic acid, polyvinyl alcohol (PVA) and isobutylene maleic anhydride (IMA) [100].

Over the years, SAP technology has progressed significantly while the initially developed starch-grafted SAPs has been rarely used due to their limited water absorption (about 100 g distilled water/g SAP) [31,101]. The currently used SAPs typically are cross-linked acrylic acid-based polymers frequently existing as the neutralized sodium salts.

Although acrylic SAPs exhibit superior water absorbent properties, as already mentioned, they are non-biodegradable. As the global concerns of the plastic pollution continuously increases, from 1990's on, a growing interest has been received by the development of SAP materials based on various natural polymers including polysaccharides (e.g. cellulose, starch, chitosan) and proteins [102–105], which are regarded as bio-based, biodegradable and hence ecofriendly materials. A high water absorption capacity of these materials was usually achieved by grafting acrylic acid onto the natural polymer main chains [7,106–109].

In 2017, a Korean research group [110] introduced a promising ground-up method with high potential to produce polycondensate-type SAPs by melt polymerization. The maximum absorbency of their citric acid (CA)-based SAP produced by this method was around 22 g distilled water/g SAP, which was not as high as the absorbency of acrylic SAPs, but nevertheless this product blazed a new trail to synthesize novel synthetic biodegradable SAPs.

Throughout the last 50 years, SAP research has shown a growing tendency evidenced by the amount of published research articles and patents covering 'superabsorbent polymers' (Fig. 3). Development of more ecofriendly SAPs, especially the biodegradable species, which prevent generation of persistent microplastics will play increasingly important roles in industry and academia in the near future.

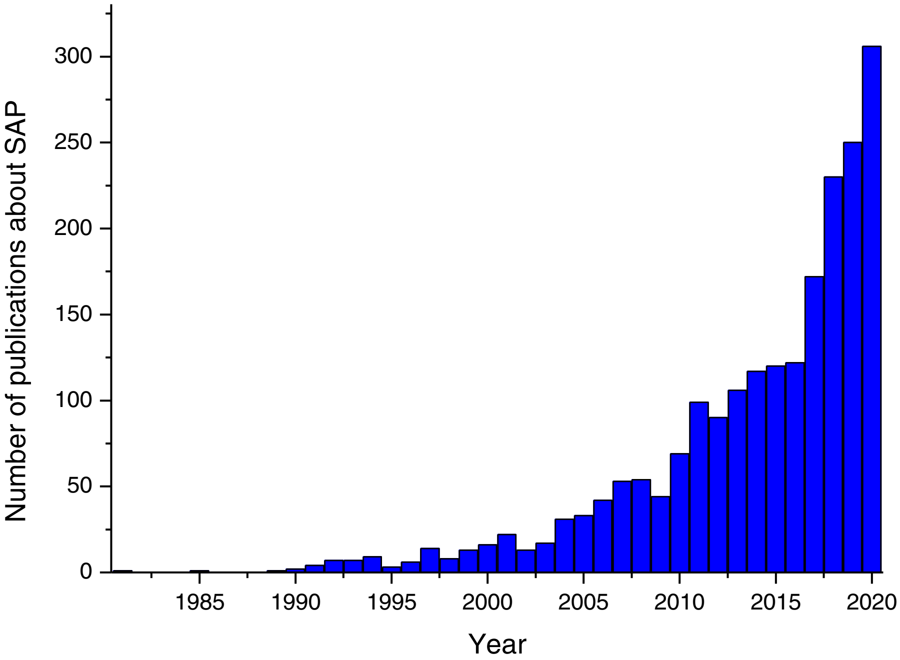


Fig. 3. Evolution of the number of superabsorbent polymers (SAP) publications over the years. The data is from Web of Science.

3. Design principles of SAPs

3.1. Structural characteristics of SAPs

A typical superabsorbent polymer is a highly hydrophilic material with cross-linked network structure and normally appear as micro-beads, which can imbibe and retain a large amount of water or aqueous solutions inside the beads even under pressure [6–8]. They can take up as much water as a thousand times of their own weight, while general hydrogels can only absorb no more than 100% of their weight in water [56,95]. The unique properties of SAPs derived from their extreme hydrophilicity, mainly due to the presence of hydrophilic groups and the properly cross-linked structure, and their absorption mechanism is based on osmotic pressure [105].

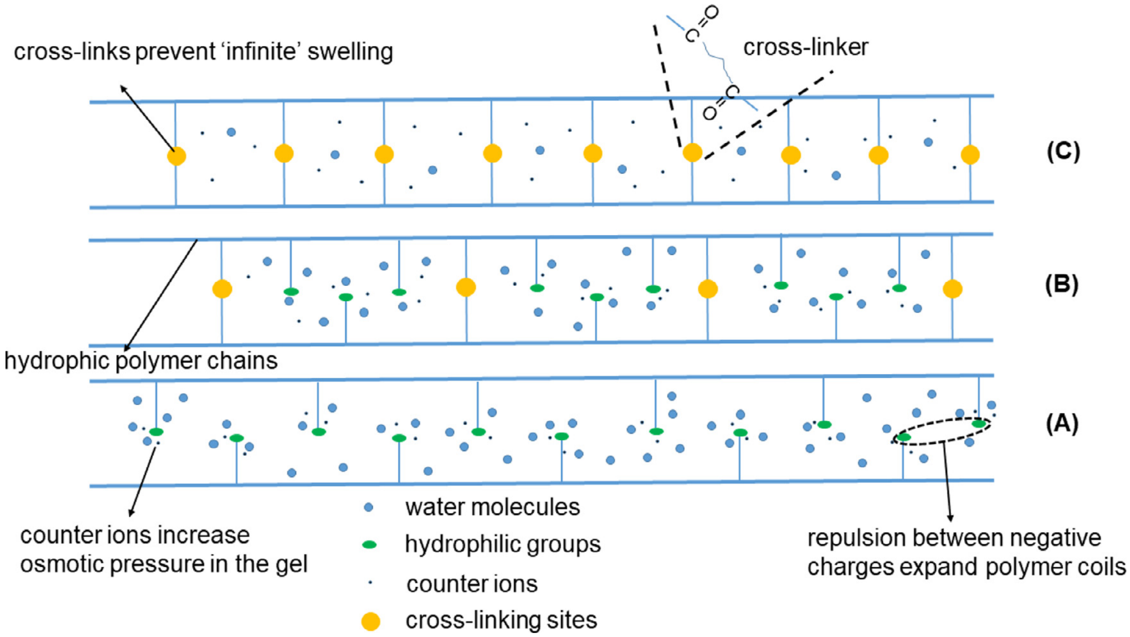
To ensure excellent water absorbent properties, a sufficient amount of strongly hydrophilic groups is necessary in the structure of SAPs. Generally speaking, these functional groups are highly polar, sometimes ionic after neutralization with metal ions (M^+), such as -OH, $-COOH/-COO^-M^+$, $-CONH_2$, $-SO_3H/-SO_3-M^+$, etc. and some of these groups can form hydrogen bonds with water molecules (Scheme 1). SAPs swell enormously when placed in the liquid due to the strong interactions between their hydrophilic groups with water molecules. Nevertheless, the water absorbent capability cannot be infinite, since eventually the polymer can dissolve in the liquid. Therefore, the formation of a 3D network via cross-linking is necessary to prevent the hydrophilic polymers from dissolving into the liquid solvent.

3.2. Cross-linking agents

Cross-linking is a critical process to obtain stable SAPs, since a good balance between a good water absorbing property, a certain resistance to solubilization in water and a good structural stability under load must be assured. With respect to the last aspect, SAP particles are easily deformed and even clogged together under load, if they are not or not sufficiently cross-linked. Thus, the cross-linking density is a key parameter determining structural stability of SAPs. Nevertheless, it must be noted that a too high cross-linking density should also be avoided since it decreases the water absorbent capability.

Two types of cross-linking protocols are often adopted in the production of SAPs, *viz*., bulk cross-linking and surface cross-linking, which are illustrated in Fig. 4. Bulk cross-linking, also called core cross-linking, normally takes place during the polymerization stage of superabsorbent production [111,112]. Taking a di-alkene type cross-linker as an example, when acrylic acid monomer polymerizes, the cross-linker molecules can be incorporated into the backbone of the polymer chains during the radical polymerization (Fig. 4(a)). This protocol normally affords the SAPs with relatively higher cross-linking densities and accordingly a more stable structure and a higher gel strength. However, their water absorption capacity can be negatively influenced because at the free space for accommodating water molecules is significantly reduced due to the rather dense cross-linking network. Once the liquid supplying voids are closed, further water permeation into the beads will be prevented, leading to the occurrence of a so-called ‘gel blocking’ phenomenon. To avoid this effect, surface cross-linking appears to be a good method to maintain sufficient gel strength by the shell layer and sufficient water absorption capacity in the core [113]. Specifically, surface cross-linking normally takes place at the pendant group (e.g. carboxylic group) of a pre-formed backbone polymer. This step is often the final stage of the whole SAP production process. After polymerization, the polymer product will be dried, milled, sized, and then surface-cross-linked. Surface cross-linking can increase the cross-linking density on the surface of polymer particles and give them a core-shell structure (Fig. 4(b)). Surface cross-linking ensure SAP’s structural stability while less cross-linking in the core make it more absorbent.

Based on above understandings, it is extremely important to control the cross-linking process when constructing SAP particles, which is substantially influenced by the properties of a cross-linking agent. Cross-linking agents (or cross-linkers), are normally multi-functional and at least di-functional molecules. In the production of SAPs, a coupling reaction between the functional groups of the pre-formed polymer and cross-linkers can be initiated by heating or UV irradiation. Depending on the reaction mechanisms, different kinds of cross-linking agents can be chosen. For exam-



Scheme 1. Network structure of SAPs after swelling. (A) non-cross-linked (B) lightly cross-linked (C) fully cross-linked.

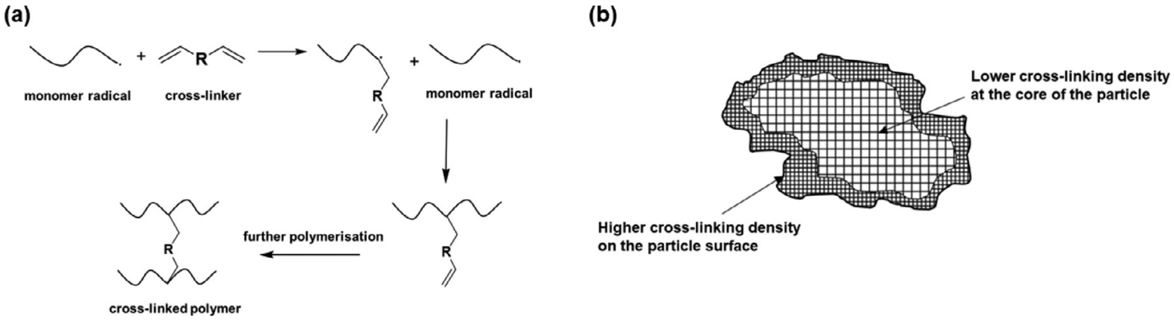


Fig. 4. (a) Exemplified illustration of a bulk cross-linking process of SAPs by using an alkene type cross-linker. (b) A surface cross-linked superabsorbent polymer particle.

ple, for bulk cross-linking, usually the carbon-carbon double bonds of the polymers are cross-linked by *N, N'*-methylenebisacrylamide (MBA, Fig. 5). For surface cross-linking, usually the functional pendant groups (e.g. carboxylic acid or hydroxyl groups) of the backbone polymer are cross-linked by the cross-linkers such as polyhydric alcohols, diglycidyl ethers, polyfunctional acids or quaternary amines. For a UV-initiated cross-linking process, the substrates are cross-linked by the free radicals when exposed to a UV source. The chemical structures of the well-known cross-linkers and the cross-linking reaction mechanisms are illustrated in Fig. 5. Thus far, MBA is the most widely adopted cross-linking agent for the production of SAPs because of its high reactivity [114–117] with vinyl groups and low toxicity after cross-linking [118,119]. For vinyl-monomers-based SAPs, such as poly(acrylic acid) and poly(acrylamide), the reactivity ratio of cross-linkers and the corresponding vinyl monomers plays an important role in determining the network structure of SAPs. Reactivity ratios are a measure of the affinity for each of the reaction components to react with each other, i.e. does an acrylic acid molecule prefer to react with one like itself or something else like a cross-linker molecule for example. If the cross-linker has a high reactivity ratio, then most of the cross-linker molecules will be consumed in the early stages of the polymerization and any polymer chains made during the latter stages will be less likely to cross-link and most probably end up as extractable chains. Cross-linkers with low reactivity ratios have the opposite tendency [111].

In conclusion, according to starting materials (vinyl monomers or natural macromolecules) and specific network structure, different kinds of cross-linkers can be chosen. In addition, cross-linkers should be chosen from a cost perspective when considering industrial SAP products.

3.3. Water absorbing mechanism of SAPs

There are normally four main mechanisms for absorbing materials to absorb liquid [95]: (1) by reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts); (2) by physical entrapment of water by capillary forces in their macroporous structure (e.g., soft polyurethane sponge); (3) by a combination of mechanism (2) and hydration of functional groups (e.g., tissue paper); (4) by a combination of mechanisms (3) and natural dissolution of hydrophilic polymer segments and thermodynamically favored expansion of the macromolecular chains restrained by cross-links, which is also the main mechanism of SAPs materials. Visual and schematic illustrations of a representative example of SAPs (acrylic-based anionic SAPs) in the dry and water-swollen states [120] are given in Scheme 2. Compared to the natural material-based species, the synthetic acrylic-based SAPs exhibit much enhanced capability of water absorption (eg. HySorb in Fig. 6).

To evaluate the water absorption capacity of SAPs, three key parameters are crucial to be characterized, namely: the absorption

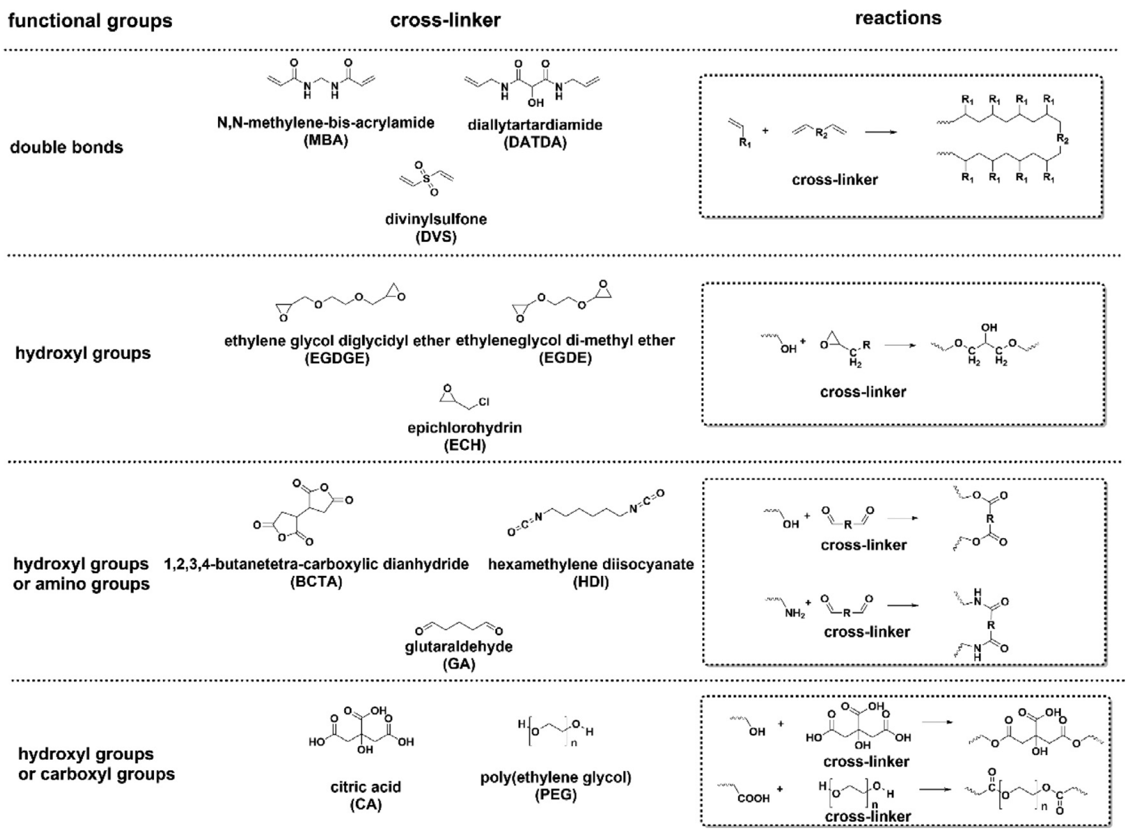
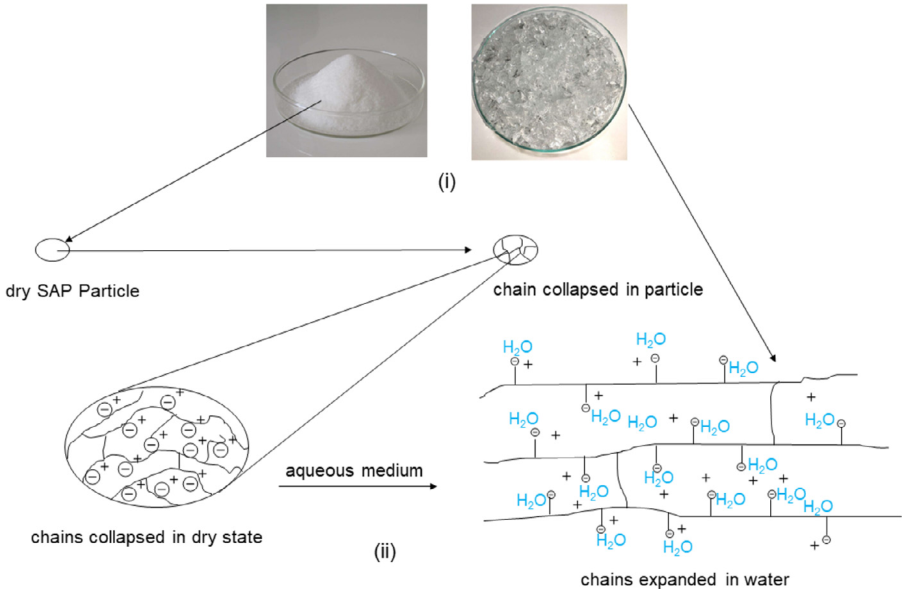


Fig. 5. Classification of common used cross-linkers according to acting-on functional groups and reaction mechanism in the production of SAPs.



Scheme 2. Illustration of absorbing mechanism. [95], Copyright 2008. Adapted with permission from Springer Nature Publishing AG.

capacity under free pressure, the absorption capacity under pressure, and the absorption speed:

(1) *The absorption capacity under free pressure*, abbreviated as 'absorption capacity' in this review, is the most common parameter used in studies of SAPs. When the term 'absorption capacity' without specific condition is mentioned, it implies the capability of uptake of distilled water or saline (0.9 wt% NaCl solution) under free pressure [112]. Various kinds of methods can be utilized to measure absorption capacity, such as tea bag method, centrifuge method, demand wettability method [121]. Among them, the tea bag method is the most conventional and used one. For the tea bag method, typical testing procedure is as such: a SAP sample (W_1 = 0.3–1.0 g) is weighed in a tea bag with fine mesh, the total weight is measured (W_2), and the sample is immersed in an excess of distilled water/saline for 1 h. The recovered tea bag is hung until free excess water/saline is no longer observed, and then, the tea bag/SAP/(water/saline) sample is weighed (W_3). The blank experiment is conducted in the same procedure with an empty tea

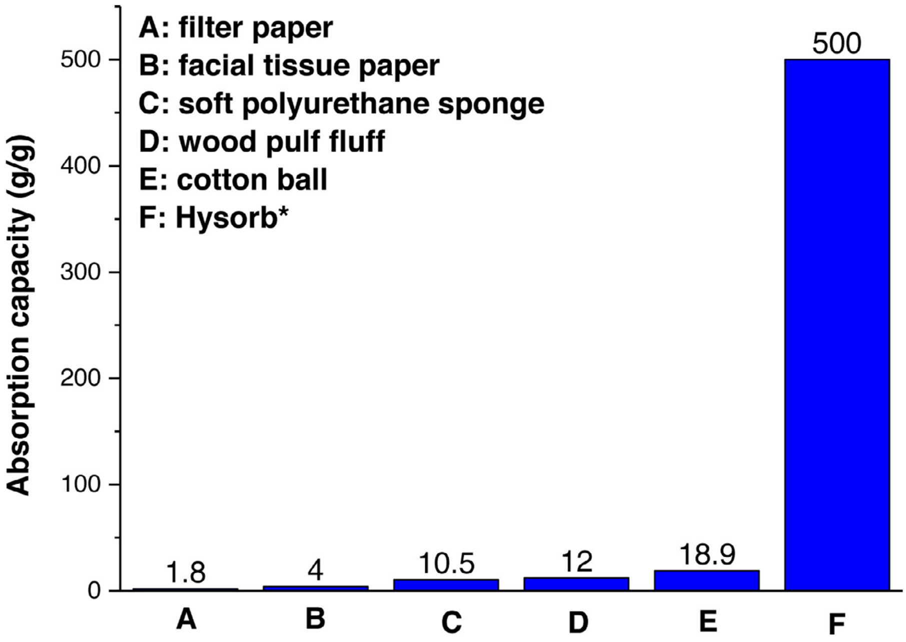


Fig. 6. Absorption capacity of different absorbent materials [91,95]. (a). All absorption capacity is measured in distilled water; (b) hysorb is a commercial SAP produced by the BASF SE company.

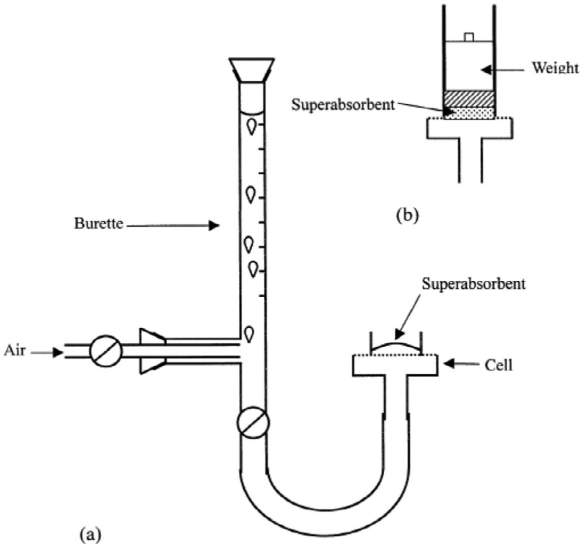


Fig. 7. Demand wettability test apparatus and piston assembly. [121], Copyright 2000. Adapted with permission from Elsevier Science Ltd.

bag (W_4) and the tea bag/(water/saline) sample is weighed (W_5). Absorption capacity is calculated as follows:

$$\text{Absorption capacity}(g/g) = [(W_3 - W_2) - (W_5 - W_4)]/W_1 \qquad (1)$$

(2) *The absorption capacity under pressure* is defined as the ability of SAP materials to take up liquid under free pressure. This property is important to evaluate the performance of SAPs used under pressure such as in baby diapers or adult care products. The method to measure absorption under pressure is similar to that under free pressure, and details of the method are given below: A SAP sample (W_1 = 0.1–0.2 g) is placed in a cylinder with a nylon mesh bottom under a pressure of 46.7 g/cm^2. The total weight is measured (W_2), the sample is put on the stage of demand wettability method (also a common method to measure absorption under free pressure, Fig. 7) for 1 h, and finally the total weight is measured (W_3). The absorption capacity under pressure is calculated as follows:

$$\text{Absorption capacity under pressure}(g/g) = (W_3 - W_2)/W_1 \qquad (2)$$

(3) *The absorption speed*, also called swelling rate, is also a key technical features of SAPs, which is a parameter of absorption capacity under free pressure versus time of a SAP sample. There are many methods including tea-bag method, sieve method and filtration method to measure it, among which tea-bag method is the most common one. This method is given above for the measurement of absorption capacity under free pressure. At consecutive time intervals, SAPs' absorption capacities under free pressure is obtained and then they are fitted into a Voigt model [122] as described by Eq. (3):

$$S_t = S_e(1 - e^{-t/r}) \qquad (3)$$

where t is the absorption time, r is the rate parameter, which is the time required to 63% of the equilibrium absorption, S_t is the absorption (swelling) capacity at time point t, S_e is the equilibrium absorption (swelling) capacity.

3.4. Influential factors of absorption capacity

Many factors can influence absorption capacity of SAPs, including the types of hydrophilic groups and molecular weight of the substrates, types of cross-linking, the cross-linking density, the neutralization degree when applicable [123], and physical property such as surface area.

Absorption capacity under free pressure is mainly determined by chemical properties of SAPs, such as types of hydrophilic groups, neutralization degree, molecular weight of the substrates, and the cross-linking density. The hydrophilicity of the most commonly existing hydrophilic functional groups is in the order: $-SO_3H > -COOH > -CONH_2 > -OH$. Strategies to enhance absorption capacity based on gel swelling theory to increase osmotic pressure are actively pursued. In order to increase osmotic pressure, introduction of strong acid groups such as sulfonic acid on polymer chain has been investigated [124]. Another approach for improvement of osmotic pressure is cross-linking polysaccharide with ionic

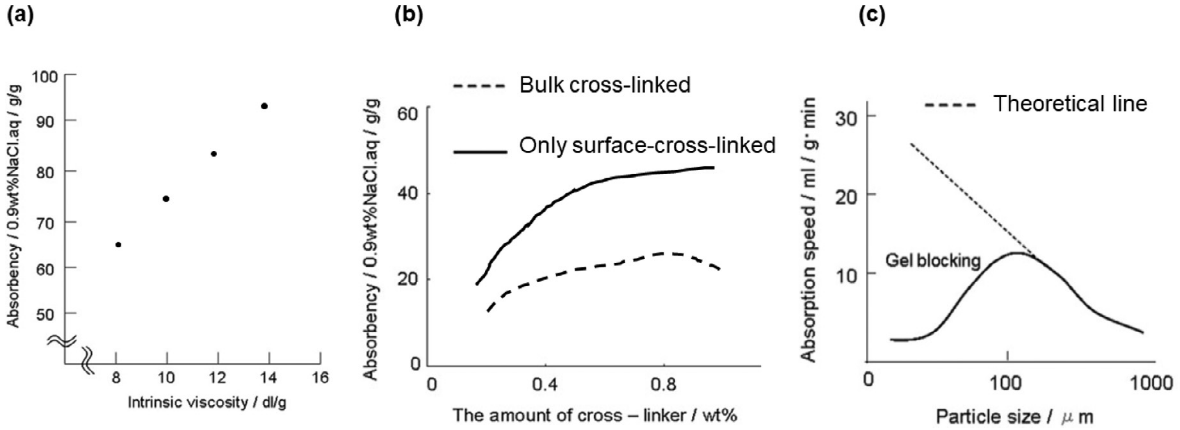


Fig. 8. (a) Effect of molecular weight of poly(acrylic acids) on absorbency. Poly(acrylic acids) are cross-linked by ethylene glycol diglycidyl ether. Absorbency is measured by the centrifuge method. Intrinsic viscosity is used to evaluate the molecular weight of polymer. (b) Effect of surface cross-linking of sodium polyacrylate SAP on absorbency under pressure. (c) Effect of particle size of cross-linked sodium polyacrylate SAPs on absorption speed. The data is from Masuda et al's work (In Encyclopedia of Polymeric Nanomaterials, Kobayashi, S.; Müllen, K., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 2351–2366.).

groups. The difference is attributed to the difference in flexibility of the underlying polymer chain; poly(acrylic acids) is flexible while the polysaccharide backbone is stiff. The stiffness increases the distance between ionic groups and lowers the surface charge density, thus effectively lowering the ionic strength. Carboxymethyl cellulose and carboxymethyl starch cross-linked by radiation are known to exhibit higher water absorption than sodium polyacrylate type SAP [125]. The third approach for improvement of osmotic pressure is neutralization of hydrophilic groups. Taking carboxyl groups (-COOH) as an example, when it is neutralized by sodium ions (Na^+), after SAPs contact with water, the ions tend to dissociate after liquids are imbibed into the SAPs, creating a gradient in ion concentration between the SAP and the external water. This generates a difference in osmotic pressure that will be the driving force for the diffusion of water into the SAP (Scheme 1). Partially neutralized SAPs usually have better absorption capacity under free pressure than those not neutralized for this reason.

Given that SAP is based on cross-linked network structures, increasing the molecular weight of the polymers cross-linked for creating the 3D network continues to hold promise for creating a SAP with high absorbing ability [126]. Fig. 8(a) shows the water absorption capacity under free pressure of SAPs which are cross-linked poly(acrylic acids) with different molecular weights as indicated by changes in intrinsic viscosity under the constant cross-linker concentration. Absorption increases as the molecular weight of poly(acrylic acids) increases.

As stated earlier, to avoid the dissolution of the polymers during swelling (Scheme 1, State A), the polymer chains need to be cross-linked to ensure a 3D network structure. However, there is usually an optimal value of the cross-linking density; when it is too high, the available space inside SAP beads for retaining water or other liquids is limited (Scheme 1, State B), thus decreasing the absorption capacity.

Absorption capacity under pressure is mainly affected by types of cross-linking. When a high pressure is applied, the effect of water diffusion rate on the overall water absorption capacity of SAPs outweighs the effect of molecular weight of the polymer and osmotic pressure because once that gel forms at the surface, water diffusion towards the interior of the particle is strongly interfered (also called as 'gel blocking', as described above) and thus water uptake is much slowed down. To avoid this phenomenon, surface cross-linking appears to be a more promising approach. If compression of the surface occurs under pressure, the diameters of surface voids are reduced and the density of the surface gel is subsequently increased. If the gel density is high, diffusion of water through the gel to the interior of the particle is reduced, and thus, regardless of the structure of the interior of the particle, total water absorption is decreased. In order to take advantage of improved internal water diffusion and absorption under pressure by increasing internal cross-linkers, reduction of the diameters of surface pores must be prevented. Cross-linking specific to the surface has been shown to be effective in maintaining surface void structures even under pressure and without loss of the potential for polymer chains to expand inside of the SAP as water absorption under pressure increases [127], as shown in Fig. 8(b).

The absorption speed is more influenced by physical factors than by chemical composition. The main factors for improving absorption speed are (i) increasing surface area and (ii) suppressing gel blocking. To increase the effective surface area of SAP particles, SAP particles are reduced in size [128]. The absorption speed increases as the SAP particle diameter decreases; however, at diameters less than about 100 mm, the absorption speed begins to decrease because of gel blocking (Fig. 8(c)). Increasing the surface area of the SAP particle by forming porous or botryoidal structures [129] is an effective approach for increasing absorption speed and obviates the need to reduce particle size. As described above, gel blocking is a state where initially adsorbed water on the surface of a SAP particle forms a hydrogel which inhibits water diffusion to the interior of the SAP particle. Gel blocking can be suppressed through addition of inorganic particles (e.g., silica, talc, kaolin) to the SAP and by surface cross-linking (vide supra). The inorganic particles promote the formation of voids within any gel that forms and consequently promote water diffusion to the interior of the particle [130]. If the density of cross-linking on the particle surface is higher than in the interior of the particle, the swelling ratio on the surface of SAP will be suppressed relative to the particle interior. Under such conditions, the particles retain their shape and voids that permit diffusion of water to the interior [131].

In addition to these factors above, some others can play a role in absorbing water, like the presence of inorganic additives, or the existence of a super porous morphology.

4. Classification of SAPs

SAPs can be classified based upon different aspects. In this section the most important types of classifications are listed.

4.1. Classification according to charging

The water absorbing function of non-ionic SAPs mainly rely on the presence of a large number of hydrophilic groups along the polymer chain and hence on their interactions with water, via van der Waals dipolar interactions and/or hydrogen bonding. Therefore, SAPs can be categorized into two groups on the basis of the presence or absence of electrical charges located in the cross-linked chains, namely non-ionic and ionic (either anionic or cationic).

For ionic SAPs, when they appear as metal salts, neutralization will introduce metal ions into the polymer network and subsequent development of negatively charged hydrophilic groups such as carboxyl group. These groups set up an electrostatic repulsion between negative charges which tends to expand the polymer network which provide more space for absorbed liquid [132,133]. Usually the ionic SAPs have higher absorbency than their non-ionic counterparts. The majority of commercial SAPs are of the anionic type and the most common one is poly(acrylic acid), while polyacrylamide is known as the most common non-ionic species.

4.2. Classification according to the type of monomeric unit

SAPs are also classified based on the type of monomeric unit used in their chemical structure, thus the most SAPs can be classified into one of the following categories [63]:

(a) cross-linked polyacrylates and polyacrylamides,
(b) cross-linked copolymers of acrylates and acrylamides
(c) polyacrylates-grafted natural polymers (including cellulose, starch, chitosan, etc.)

The cross-linked polyacrylates SAPs have the best absorption capacity while the polyacrylamide homopolymer and copolymer SAPs have better salt resistance performance for their non-ionic nature. Compared with acrylate-based SAPs, natural polymers-based SAPs have better biodegradability which are environment-friendly products. However, the water absorbing performance of these greener products remain less sufficient compared with the polyacrylate-based synthetic SAPs.

4.3. Classification according to origin of raw materials and potential biodegradability

Due to the enormous variability of the possible monomers and macromolecular structures, numerous kinds of SAPs can be made. From the viewpoint of original raw material sources, all SAPs can be subdivided into two main groups: fossil-based or bio-based ones. Further by considering their biodegradability, SAPs are subdivided into four major classes as shown in Fig. 9.

Processes inducing any physical or chemical changes in the polymer due to physical, chemical or biological reactions resulting in bond scission and subsequent chemical transformations are defined as polymer degradation [69]. Biodegradation was accordingly defined as a decomposition process of substances by the action of microorganisms, which leads to the recycle of carbon, the mineralization (CO_2, H_2O and salts) of organic compounds and the generation of new biomass [134]. Now the complexity of biodegradation is better understood [135,136]. The biodegradation of polymeric materials includes several steps and the process can stop at each stage. A typical biodegradation process includes the following steps: **a**. polymers are fragmented into tiny fractions by a variety of physical and biological forces (known as 'biodeterioration'); **b**. microorganisms secrete catalytic agents able to cleave polymers and reduce their molecular weight (known as 'depolymerization'). This step generates different small MW products, such as oligomers, dimers and monomers; **c**. some of these small molecules are recognized by receptors of microbial cells and then are up-taken into the cells through their plasmic membrane. The other molecules stay in the extracellular surroundings and can be the object of different modifications; **d**. in the cytoplasm, the transported molecules integrate themselves into the microbial metabolism to produce energy, new biomass, storage vesicles and numerous primary and secondary metabolites (known as 'bioassimilation'); **e**. concomitantly, some simple and complex metabolites may be excreted into the extracellular surroundings. Simple molecules as CO_2, N_2, CH_4, H_2O and different salts from intracellular metabolites that are completely oxidized are released in the environment (known as 'mineralization').

The biodegradability of polymer is closely associated with their chemical and physical properties. Surface conditions (surface area, hydrophilic, and hydrophobic properties), the first order structures (chemical structure, molecular weight and molecular weight distribution) and the high order structures (glass transition temperature, melting temperature, modulus of elasticity, crystallinity and crystalline structure) of polymers can all play a role. Aliphatic polyesters and polycarbonates are two typical polymers that show high potential for use as biodegradable plastics owing to the susceptibilities of ester or carbonate bonds to lipolytic enzymes and microbial degradation [137]. As a functional polymer, SAPs' chemical structures play a most important roles in their biodegradability. Taking polyacrylate-based SAP as an example, its polymer backbone consisting of fully carbon-carbon bonds make it non-biodegradable. The biodegradation rate decreases as molecular weight of non-cross-linked polyacrylates increases. This phenomenon is also frequently found in other polymers such as aliphatic polyesters. Cross-linking density also plays a role in SAPs' biodegradability; the stability of SAPs' network structure increases as their cross-linking density increases, and thus they are less vulnerable to the attack of microorganisms or enzyme. It can be imagined physical properties (surface condition) can also play a role in SAPs' biodegradability, however, not any illustration about this factor can be found in any specific paper, so this part will not be discussed in this review.

4.3.1. Non-biodegradable, fossil-based SAPs

Polyacrylates-based SAPs are thus far the most successful commercialized SAPs due to their highest hydrophilic group content in the shortest/smallest repeating units and hence the highest absorption capacity. Acrylates-based monomers used to produce these SAPs are mainly petroleum-based, such as acrylic acid (AA), the AA salts, acrylamide (AM) and acrylonitrile (AN). By looking at the 3D network structure (Fig. 10), it is apparent that the main chain of polymer as well as the chemical cross-links existing in SAPs are entirely built up by the highly stable, non-biodegradable carbon-carbon bonds constructed by a radical chain growth polymerization. Even though acrylic acid (AA) can be partially produced by bio-based route [138–140] (Scheme 3) which solves the raw material issue to some extent, these acrylate-based SAPs prove to have unsatisfied biodegradability [141] proved by a detailed study on biodegradability of polyacrylate backbone by measurement of the $^{13}CO_2$ efflux from ^{13}C-labelled SAP in soil incubations [142]. In this study, after 24 weeks incubation in four agricultural soils at three temperatures (20, 25, and 30 °C), less than 0.85% biodegradation happened [142]. Deposition of such SAPs in our environment will generate persistent microplastics eventually ending up in our food chain.

4.3.2. Biodegradable, fossil-based SAPs

Besides polyacryates, other fossil-based polymers, like polyvinyl alcohol (PVA) [36,143] and polyethylene oxide (PEO) [144], have also been studied for superabsorbent use, while both polymers are biodegradable. However, these two polymers are (graft) copolymerized with other polymers such as polyacrylates or cellulose, not the

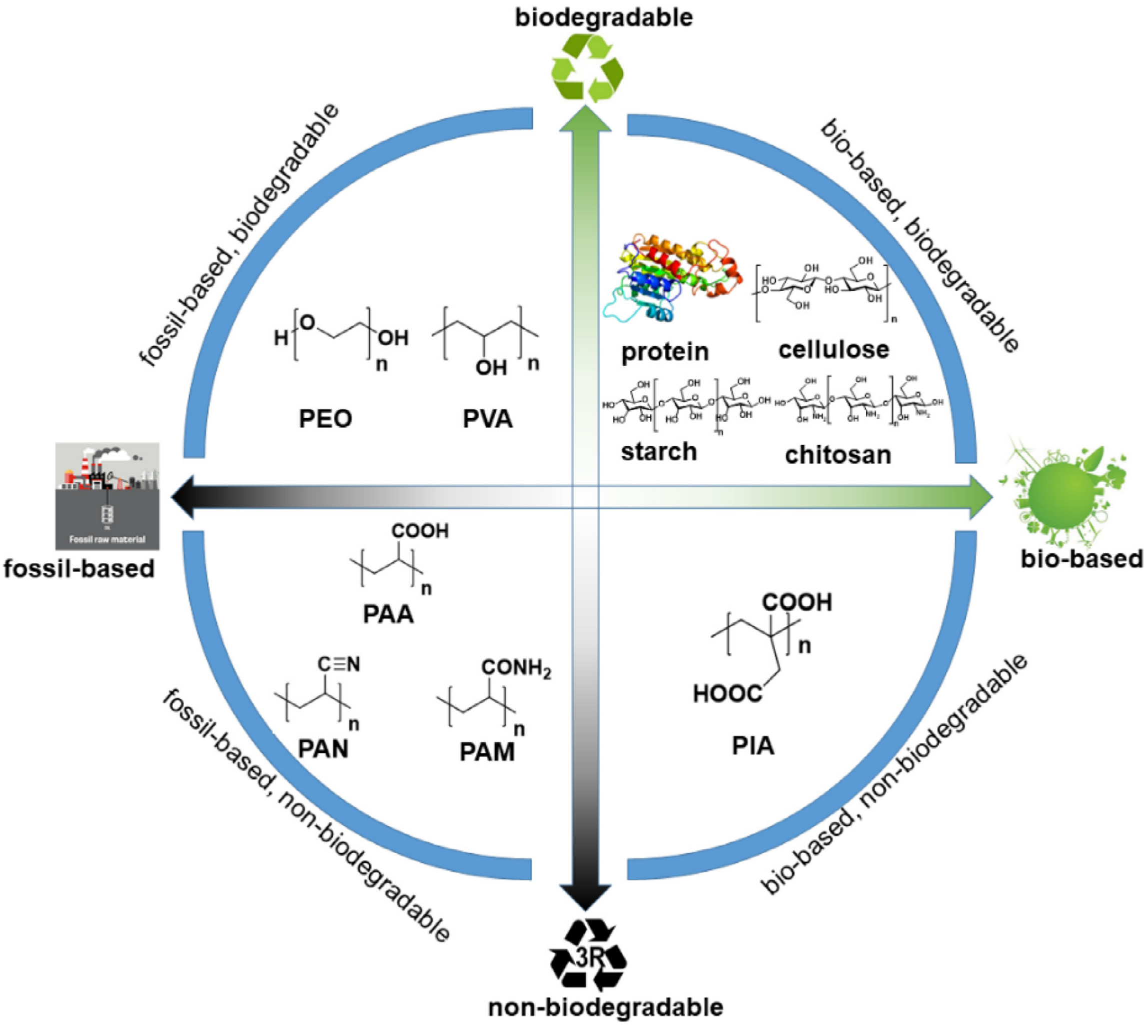


Fig. 9. Classification of SAPs according to their origin and biodegradability and the representative examples of the four classes.

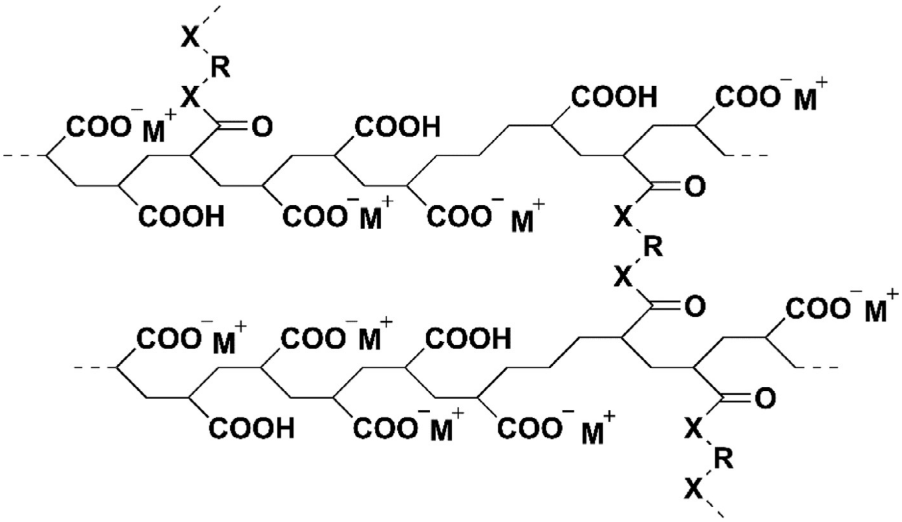
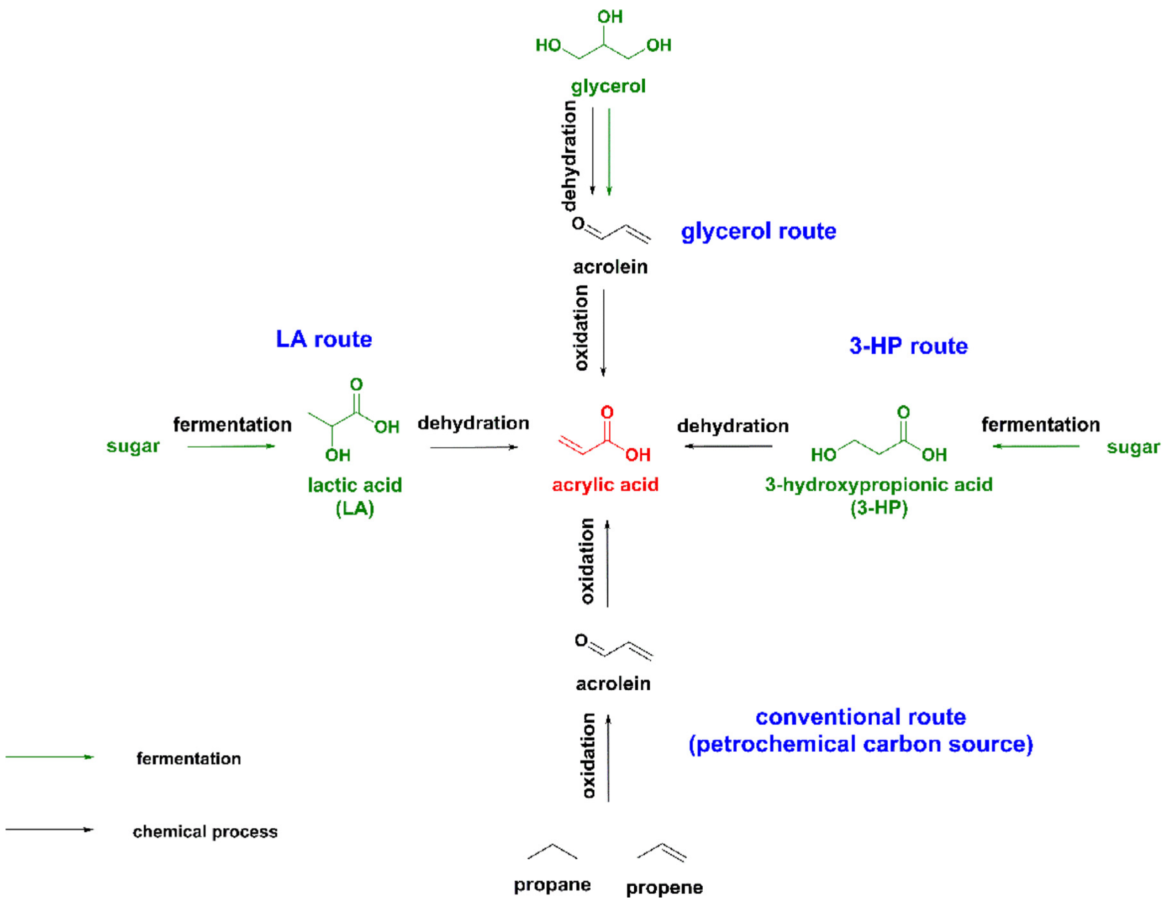


Fig. 10. Network structure of acrylate-based SAPs. X-R-X stands for cross-linker; M stands for metal ions, usually sodium or potassium cations. [95], Copyright 2008. Reproduced with permission from Springer Nature Publishing AG.



Scheme 3. Different production route of acrylic acid. [138], Copyright 2015. Adapted with permission from Elsevier Science Ltd.

main substrate of the SAPs. In addition, there are just a few reports about these SAPs, this part will not be discussed in detail in this review.

4.3.3. Non-biodegradable, bio-based SAPs

Due to the need for more sustainable polymeric materials, the worldwide interest in bio-based polymers has increased enormously in recent years [32,101,145,146]. Bio-based synthetic SAPs produced from bio-based monomers, although are sustainable from the perspective of the origin of raw materials, they are not necessarily biodegradable. An example is the itaconic acid (IA)-based SAPs, which are usually obtained with limited cross-linking density due to the high steric hindrance faced by vinyl functional groups and hence relatively lower reactivity [147–150]. This polymer is not biodegradable; the reason is that like poly(acrylic acid), poly(itaconic acid) obtained by a radical polymerization process also generating non-degradable carbon-carbon bonds in the main chains of the SAPs based thereon.

4.3.4. Biodegradable, bio-based SAPs

Recently, synthetic SAPs have been gradually replaced by natural ones because of their advantages such as high gel strength, biocompatibility, and good resistance against gel blocking [151]. Also, the perception of parents that bio-based diapers are safer for their babies is playing a role in this substitution process. The biodegradable SAPs based on natural polymers come from either polysaccharides or polypeptides (proteins) substrates, which are usually prepared through addition of some synthetic parts, often vinyl monomers, e.g. acrylic acid, onto the natural substrates [152]. Theoretically, these bio-based SAPs are biodegradable, at least the natural polymer substrate parts are. Nevertheless, in view of their less hydrophilic groups coming from native natural polymers, these SAPs are less absorbent than petroleum-based analogues made from neutralized acrylic acids.

5. Polyacrylate-based SAPs: the main group

5.1. Properties of polyacrylate-based SAPs

The synthetic polyacrylate-based SAPs derived from acrylic acid (AA) and its derivatives have emerged as an important type of absorbent, dominating the SAP market. The cross-linked insoluble polyacrylate or polyacrylate/polyacrylamide copolymers are used in a range of products because of their superior superabsorbent properties. Polyacrylates SAPs are mainly used in hygiene and food packaging products, while polyacrylate/polyacrylamide copolymers are valuable as soil amendments in arid regions and for reforestation. The wide application of these materials is related to the relatively cheap price of AA raw material and an ease of polymerization towards high molecular weight products. The MW of poly(acrylic acid) primary polymer chain before cross-linking post-treatment can reach 10,000,000 g/mol [153–155]. At the same time, the content of carboxylic acid groups or their neutralized derivatives, the groups that are directly determining the water absorption, is higher for poly(acrylic acid) than for any other polymer material and cross-linking process is also extremely simple. Because of the unique structure including the presence of extremely high concentrations of hydrophilic groups, the high polymer chain flexibility and the availability of a large free volume between polymeric chains, acrylate-based SAPs have superior absorption capacity for their high density of hydrophilic groups and molecular weight (Table 1) [156]. Partially neutralized poly(methacrylic

Table 1
Composition and properties of fossil-based synthetic SAPs.

Polymer[a]	Cross-linker	Initiator	Absorption capacity[b] (g/g)	Reference[b]
Poly(acylamide)	MBA	Irradiation	700	[158,159]
		KPS, $NaHSO_3$	70[d]	[160]
Poly(acrylic acid)	MBA	APS	820–965	[28]
		APS, SHS	450	[161]
		H_2O_2, Vc	54	[162]
	NA	KPS	680 180 (Tap water) 40 (0.9% NaCl solution)	[163]
Poly(acrylic acid-co-acrylamide)	MBA	APS	70–384	[19,33]
		$Na_2S_2O_8$	100	[164]
		KPS	400	[165]
	EGDMA	KPS	620	[166,167]
Poly(acrylic acid-co-maleic acid)	MBA	APS	900	[27]
Poly(vinyl alcohol)	H_3PO_4	NA	480	[36]
poly(acrylic acid -co- 2-acrylamido-2-methyl propane sulfonic acid)	NA	irradiation	4310 269 (Artificial blood) 288 (Artificial urine)	[13]
Poly(acrylic acid -co- acrylamide –co- methacrylic acid -co-2-hydroxyethyl methacrylate)	MBA	APS	400 112 (1% NaCl solution)	[168]

[a] The polymers need to be cross-linked.
[b] If not indicated specifically, absorption capacity is measured in distilled water.
[c] Degradability of these SAPs is not studied in these references.
[d] This means the absorbency of a SAP microspheres.

acid) and poly(acrylic acid)-based SAPs and their respective copolymers with poly(acrylamide) are most important due to their very high water absorption and retention capacity for longer time [157]. As shown in Table 1, compared with chemical initiation, irradiation is a better way to synthesize high-absorption-capacity SAPs. Poly(acrylamide) SAPs produced with KPS and $NaHSO_3$ as initiator have an absorption capacity of 70 g distilled water/g SAP while the corresponding value of those produced by irradiation is 700. This phenomenon was explained by the author that irradiation generates a stress field that gives rise to molecular rearrangement by expansion or contraction [158]. In addition, the amount of initiator plays an important role on water absorbing performance of SAPs. As Ma et al. (*J Appl Polym Sci.* 2004, 93, 2532–2541) claimed, at low amount of initiator, the water absorbency increase with increasing content of initiator for higher conversion of monomer, but decrease with increasing content of initiator at high amount of initiator, because the collision between monomer-free radicals also increase which give higher percentage of soluble part. It is striking that the water absorbing property of poly(acrylic acid-co-2-acrylamido-2-methyl propane sulfonic acid) SAPs produced by irradiation can reach up to 4310 g distilled water/g SAP for their high content of strongest hydrophilic groups (-COO^- and –SO_3^-) [13].

5.2. Environmental impacts of polyacrylate-based SAPs

All published studies on the toxicity of acrylate-based SAPs have shown that these substances have a positive toxicological profile and can be considered environmentally compatible as such [169–174]. The influence of polyacrylates on microbial communities of forest soils has been studied by Carbellas et al. by incubating the polyacrylate copolymer Firesorb in the soil [175,176]. The authors concluded that the polymer had no adverse effects on the microbial community of the forest floor after examining several biochemical properties of the incubating soils, including microbial biomass C, hydrolysis of FDA, β-glucosidase, urease and N mineralization.

The environmental fate of SAPs is also a highly important aspect to evaluation their ecological impacts given their significantly increased use in various products. Although the existing studies have demonstrated that the acrylate-based SAPs are generally biocompatible, micro-organisms are unable to degrade these materials because of the high stability of the carbon-carbon backbone, the extremely high molecular mass and the low water-solubility of these polymers due to the cross-linking [142]. SAPs, especially the polyacrylates ones, might pose long-time environmental problems as persistent landfill and lead to increasing pollution concerns in the future [177]. In view of increasing worldwide awareness about environmental issues and gradually implemented banning on microplastics generating products, the non-biodegradability of polyacrylates-based SAPs' is mostly likely to limit their continuously use in hygiene products and other disposable application fields [63,178,179].

5.3. Modification of polyacrylate-based SAPs

To meet the requirements for different applications, modification of the SAP materials is often necessary to gain better absorption capacity, mechanical properties and/or anti-bacterial properties, or even to reduce the overall production cost. Among all kinds of modification, addition of inorganic particles is the most common and effective way to do so. Recently, there have been many reports [180–187] on introducing inorganic additives into SAPs in order to improve swelling property, hydrogel strengths, and reduce production costs. Some of SAPs modified by these inorganic additives can be used in the personal care products industry. Taking montmorillonite (MMT) as an example, it is a layered aluminum silicate with exchangeable cations and reactive -OH groups on the surface which ensure strong interaction between virgin SAPs and it. Addition of only 5.4 wt% montmorillonite can enhance absorption capacity of poly(acrylic acid-co-acrylamide)/montmorillonite composite from 789 g distilled water/g SAP (MMT-free) to 952 g distilled water/g SAP [185]. In addition, modification by montmorillonite (MMT) can improve this SAPs composite's reswelling capacity from 18% for MMT-free SAPs to 83% for SAP composite while the addition of montmorillonite does not enhance the biodegradability of these SAPs because it does not change the unsatisfied biodegradability of acrylate-based polymers.

Similar to montmorillonite (MMT), kaolin, vermiculite, $Al_2(SO_4)_3$, and other inorganic additives can be chosen for modification of polyacrylate-based SAPs. Properties and aim of modification are shown in Table 2.

Table 2
Summary of modification of conventional synthetic SAPs by additives.

Polymer[a]	Additives[b]	Absorption capacity[c] (g/g)	Aim of modification	Reference
Poly(acrylic acid-co-acrylamide)	NA	636.5 65.3 (Saline solution)	NA	[188]
Poly(acrylic acid)	NA	200	NA	[189]
Poly(acrylic acid-co-acrylamide)	$Al_2(SO_4)_3$ (4.25 wt%)	60 (Saline solution)	Avoid dissolution of polymer chains and improve absorbency	[181]
Poly(acrylic acid-co-acrylamide)	Montmorillonite (3wt%)	1024 56 (Saline solution)	Improve absorbency	[186]
Poly(acrylic acid-co-acrylamide)	Kaolin (15 wt%)	91 (Tap water)	Improve absorbency	[26]
Poly(acrylic acid)	Vermiculite (20 wt%)	1232 89 (Saline solution)	Improve absorbency	[190]

[a] The polymers need to be cross-linked.
[b] Percentage of additives is indicated to that give optimal properties of SAPs.
[c] If not indicated specifically, absorption capacity is measured in distilled water.

6. Cellulose-based SAPs

6.1. Structural characteristics of cellulose-based SAPs and biodegradation of cellulose

As one of the most abundant naturally occurring polymers, cellulose exists as one of the main components of plants. Some bacteria, for example, *Acetobacter Xylinum*, have also been trained by human beings to synthesize cellulose on a large scale [191]. The product produced by such procedure is called bacterial cellulose (BC), which is chemically identical to plant cellulose (PC) but with a much higher purity, distinct macromolecular structures and hence different physical properties [192]. The total global production of cellulose fibers amounted to 7×10^6 tons in 2019. Cellulose is widely used in chemical fibers, paper products, consumables, miscellaneous, pharmaceuticals, etc.

The chemical structure of cellulose is featured by the presence of a large number of hydroxyl groups on the glucose units held together by 1, 4-β-glucosidic linkages. This natural polymer thus is a relatively hydrophilic material and is expected to be a potential candidate for developing novel bio-based and biodegradable superabsorbent polymers [193]. Nevertheless, the high crystallinity of cellulose (usually in the range 40–60% for PC and above 60% for BC) make it difficult to be dissolved in water or most of the solvents. In addition, unlike many petroleum based polymers, cellulose will not melt but decompose at elevated temperatures, which make it also difficult to be melt processed [194]. Chemical modification of cellulose (Fig. 11), usually involving esterification or etherification of the hydroxyl groups [193,195], is frequently performed to produce cellulose derivatives with enhanced solubility and machinability. Among all derivatives of cellulose, carboxymethylcellulose (CMC) and hydroxyethyl cellulose (HEC) are the most used for the production of SAPs.

Cellulose can be degraded by a wide range of bacteria and fungi present in air, water and soil by excreting cellulose-specific enzymes (i.e. cellulases) [196]. General understandings regarding the biodegradation mechanism of cellulose is given below. Therefore, cellulose-based materials are generally perceived as new generation of environmentally-friendly alternatives to the conventional fossil-based non-biodegradable synthetic polymers.

Hoppe-Seyler (1883) and de Bary (1886) first reported the biodegradation mechanism of cellulose in nature. This process can occur with or without the presence of oxygen. When oxygen is present, viz. under an aerobic conditions, cellulose is mainly oxidized to CO_2 and returned into the atmospheric circulation, while under an anaerobic condition, this natural biomass is predominantly converted to methane and CO_2 [197]. A number of fungi can degrade cellulose and the representative fungi are white-rot fungi, brown-rot fungi, soft-rot fungi, and anaerobic fungi [197]. The biodegradation of cellulose by bacteria can also occur aerobically or anaerobically. Therefore, these cellulolytic bacteria are commonly classified as aerobic bacteria (e.g. *Cellulomonas Species, Bacillus Species, Pseudomonas Species, Cytophaga Group, Actinomycetes Group, Actinomycetes*) and anaerobic bacteria (e.g. *C. thermocellum*). Here, we take white-rot fungi as an example to illustrate how cellulose is degraded in this process and the mechanism [198] is shown in Scheme 4.

Recent advances regarding the application of cellulose in SAPs development are concentrated on progressively implementing feasible and more ideally ‘green’ production process [199]. In the latter context, development of nontoxic cross-linking agents or innovative cross-linking processes avoiding the use of toxic cross-linking agents, for instance, gamma radiation-initiated cross-linking [200] are highly promising to ensure a real ‘sustainable’ virtue for such products from the perspective of the entire life cycle.

6.2. Synthetic strategies of SAPs based on cellulose

To successfully develop cellulose-based SAPs, one must to consider appropriate graft copolymerization and cross-linking method. Although the virgin cellulose is highly hydrophilic, the water absorbing capacity of this material remains insufficient (0.04 g distilled water/g cellulose) [201]. To solve this issue, various kinds of acrylic-based vinyl polymers have been introduced onto cellulose or its derivatives by graft copolymerization to achieve excellent water absorbing properties [146,180,184] These water-absorbing functional units can be grafted onto the polysaccharide substrate either by a ‘grafting-from’ or a ‘grafting-to’ approach (Fig. 12) [202–204]. In a ‘grafting-from’ approach, free radicals of natural macromolecule-substrates are firstly formed with the presence of chemical initiators or under physical treatment (eg. irradiation with UV or gamma rays), which initiate the copolymerization of vinyl monomers and hence afford the grafted polymer products. Formation of the final SAP product with the desired 3D network structure are further achieved by chemical/physical protocols in similar manners as previously discussed for the typical polyacrylates-based SAPs. In contrast, in a ‘grafting-to’ approach, the SAP products were formed between the reactive end-group of a pre-formed polymer and the pendant functional groups (carboxyl, hydroxyl, amino groups) of polysaccharides. Similar to the ‘grafting-from’ approach, hydrophilic pendant groups from the preformed polymers endow the SAPs better water absorption capacity. Thus far, the cellulose-based SAPs are mostly synthesized by grafting-from approach which is also the case for chitosan-based or starch-based SAPs. Compared to the other protocol, an easy access of the reactive groups of the vinyl monomers to the chain ends of the growing polymers is critical to obtain the final products with relatively high grafting density and hence high water absorption capacity.

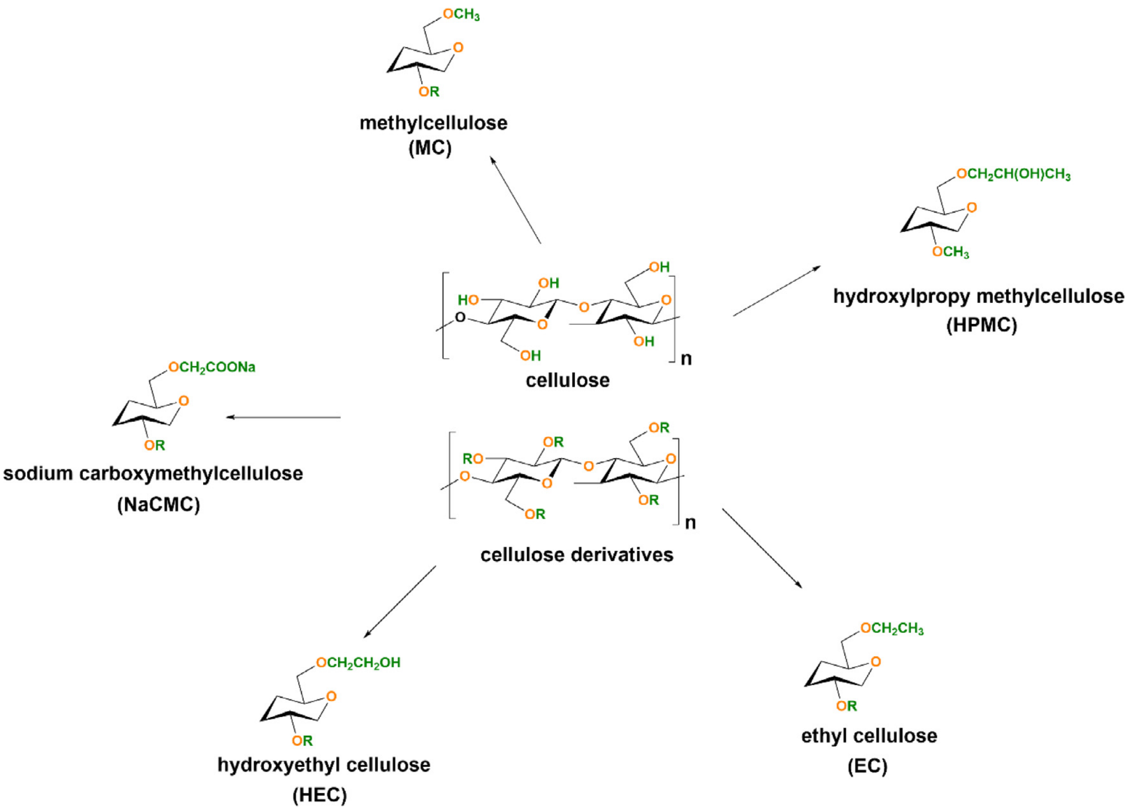


Fig. 11. Repeating units of cellulose and its derivatives; MC (methylcellulose), HPMC(hydroxypropyl methylcellulose), EC(ethyl cellulose), HEC(hydroxyethyl cellulose), NaCMC(sodium carboxymethyl cellulose).

However grafting of these non-biodegradable acrylic polymers will sacrifice their biodegradability [146]. Besides these, some studies focus on SAPs synthesized from cellulose and its derivatives without grafted acrylics to ensure good biodegradability [111,187,199,205–207]. Addition of inorganic particles is another way to enhance water absorption capacity of cellulose-based SAPs.

6.3. Preparation and properties of cellulose-based SAPs

Grafting the additional hydrophilic vinyl units on cellulose substrate has proved to be a highly effective way to afford the products with satisfactory water absorption capacity. SAPs produced from acrylic acid and maleated cotton stalk cellulose (Fig. 13) have been reported to exhibit an excellent absorption capacity of 1125 g distilled water/g SAP [146]. In this work, cellulose was separated from cotton stalks by alkali pretreatment method and then was reacted with maleic anhydride to afford a maleated cellulose derivative (MCSC). The final SAPs was fabricated by an ultraviolet (UV) initiated photo-polymerization process conducted in an aqueous solution at room temperature with MCSC and acrylic acid. Under UV irradiation, photoinitiators absorbed light in specific range and convert light to chemical energy in the form of reactive intermedi-

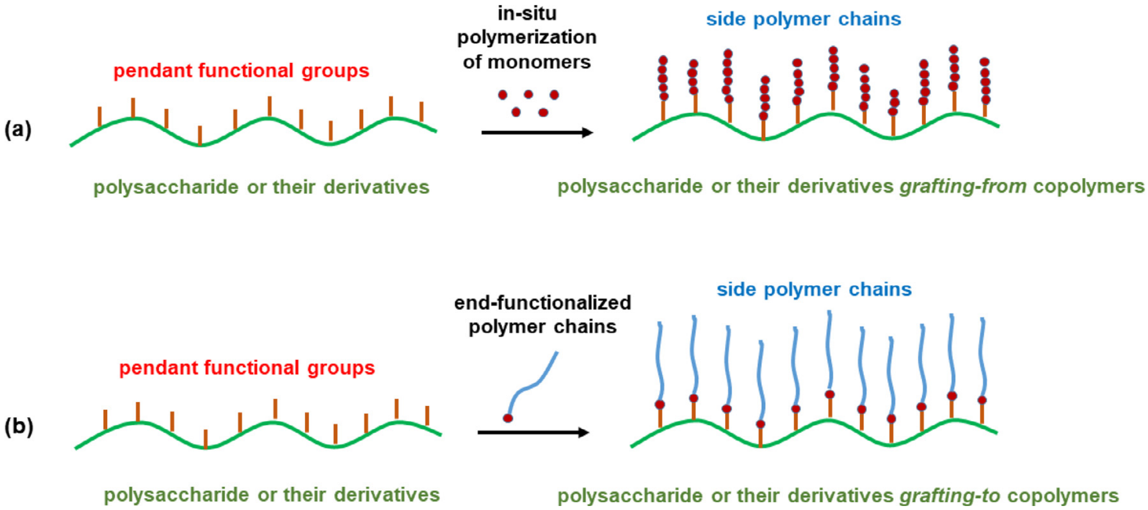
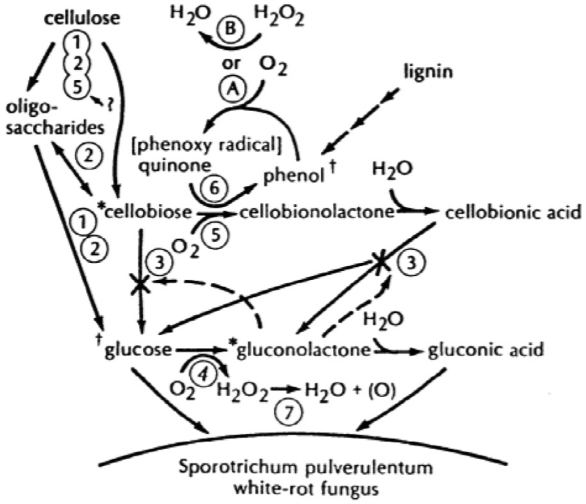


Fig. 12. Schematic representation of the (a) *grafting-from*, and (b) grafting-to approaches for graft copolymerization of polysaccharides (eg. cellulose, chitin, chitosan and starch) [208,209].



Scheme 4. Enzymatic degradation mechanisms of cellulose by the white-rot fungus *S. pulverulentum*. 1. Endo-1,4-β-glucanases; 2. exo-1,4-β-glucanases; 3. 1,4-β-glucosidases; 4. glucose oxidase; 5. cellobiose oxidase; 6. cellobiose: quinone oxidoreductase; 7. Catalase. [198], Copyright 1978. Reproduced with permission from John Wiley & Sons, Inc.

ates, *viz.* free radicals. These free radicals can be added to acrylic acid or the vinyl fraction of MCSC, which led to chain growth or formation of active macroradicals, respectively. These different free radicals reacted with MCSC or acrylic acid led to growth of branched macroradicals, following the 3D network via combination of branched macroradicals. Based on the biodegradability test in soil at 20% moisture by weight, the weight loss of this SAP was observed to be 46.7% after 150 days, which proved its good biodegradability. It is worth noting weight loss of the SAP is higher than mass fraction of MSCS to the MCSC-g-PAA SAP, which indicates the grafting PAA fraction dissociate from the MSCS macromolecules.

Carboxymethylcellulose (CMC) is another commonly used cellulose derivative in which the pendant hydroxyl groups are substituted by the more hydrophilic carboxymethyl groups (Fig. 13). To achieve better water absorbing property, sometimes the carboxymethyl groups are neutralized into sodium or potassium salts. Hydroxyethyl cellulose (HEC) is hydroxyethyl ether of cellulose, which is largely used as water-binder and thickening agent. It has been reported [210] cross-linking efficiency is poor if only CMC is used due to the electrostatic repulsion between charged macromolecules (The CMC is usually neutralized). Addition of HEC can promote intermolecular cross-linking to improve poor cross-linking of CMC for non-polyelectrolyte nature of HEC. Mele and coworkers [200] synthesized a SAP by cross-linking NaCMC and HEC by their pendant hydroxyl groups with DVS in the presence of KOH as catalyst and leave –COO⁻ free as hydrophilic groups. The water absorption capacity of this SAP could reach up to 800 g distilled water/g SAP. The authors claimed this SAP is totally biodegradable, but unfortunately they did not carry out any biodegradability test on it.

Sannino et al. [145,205] reported a novel polyelectrolyte-type SAPs formed by NaCMC and HEC with cross-linkers divinyl sulfone (DVS) or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (WSC). When cross-linker was DVS [205], The water absorption capacity of this SAP is 420 g distilled water/g SAP, which is comparable with those displayed by acrylic SAPs. If WSC [145] was chosen as cross-linker, water absorption capacity is only 90 g distilled water/g SAP due to its poor cross-linking efficiency. The promising results when DVS was chosen as cross-linker were achieved by inducing a microporous structure in the hydrogel through a phase inversion desiccation technique performed in acetone (i.e., a poor-solvent for cellulose) evidenced by the presence of foldings and voids on the surface in electron microscopy (SEM) images. The created micro-capillarity effect significantly increased the water absorption capacity by enhancing the swelling kinetics. Demitri et al. [205] also reported the preparation of superabsorbent hydrogels based on NaCMC and HEC cross-linked with citric acid (CA). This was the first time CA was used to cross-link NaCMC and HEC. Compared to the SAPs cross-linked by DVS (Fig. 14) or WSC, this system shows additional benefits of avoiding the use of toxic intermediates and also introducing extra hydrophilic carboxylic groups and hence in overall exhibit higher water absorption capacity (900 g distilled water/g SAP). The authors also claimed that the degradation of the SAPs occurred over a period of approximately 6 months but without supplying the relevant supporting information of this property.

Cellulose and its derivatives can also be cross-linked by irradiation or chemical cross-linker with other polysaccharides, like starch and chitin. Fekete et al. [200] mentioned that carboxymethyl cellulose/starch SAPs prepared by gamma-irradiation without use of cross-linker, work better than pure cellulose-based SAPs in the context of a higher water uptake (about 400 g distilled water/g SAP) at a higher electrolyte concentration. Tang and coworkers [211] reported that chitin and CMC could be cross-linked by ECH and it showed an excellent water absorption capacity (1300 g distilled water/g SAP) with much reduced cost.

Different types of inorganic particles have been also been considered to improve or to obtain certain properties of cellulose-based SAPs, such as water absorption capacity, thermal and/or antibacterial properties [180,184,187]. A detailed comparison of the various properties of cellulose-based SAPs is summarized in Table 3.

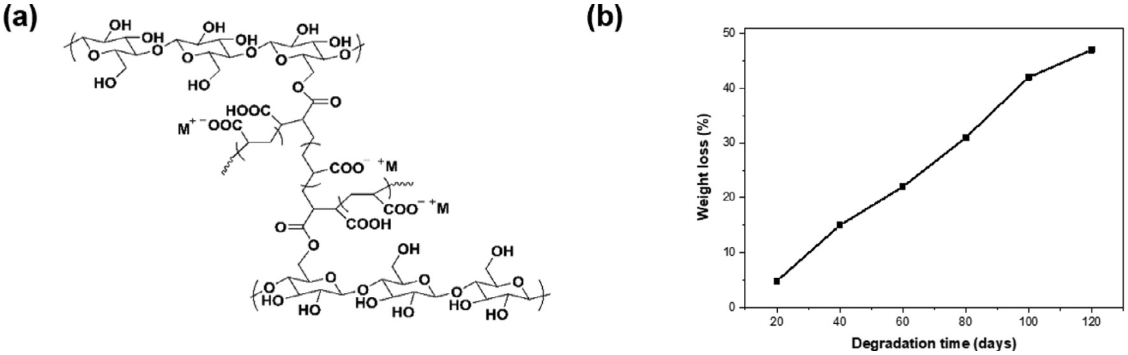


Fig. 13. (a)Chemical structure and (b) weight loss of maleated cellulose-g-poly(acrylic acid) SAPs in soil at 20% moisture by weight. [146], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

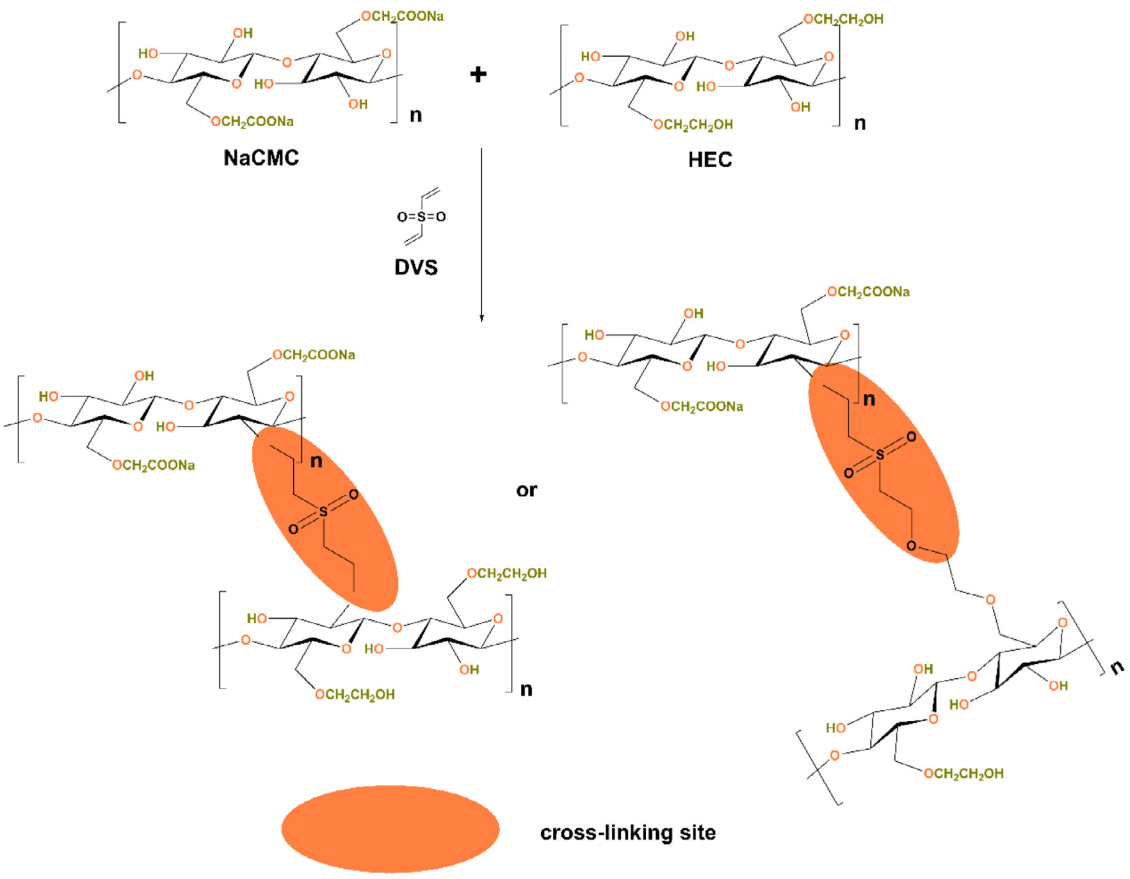


Fig. 14. Schematic representation of cross-linking of NaCMC and HEC with DVS as cross-linker.

Table 3
Summary of composition and properties of cellulose-based SAPs.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
AA/AM/AMPS grafted onto CMCNa /MMT composite	MBA	KPS	670	NA[b]	[180]
MAA grafted onto cellulose/bentonite composite	MBA	KPS	NA	NA	[184]
CMC/Ag nanoparticles composite	NA	NA	12.86	NA	[187]
CMCNa cross-linked with HEC	WSC	NA	90	degradable (in soil)	[145]
AA grafted onto MCSC	NA	Light	1125 126 (saline solution)	46.7% degradation (weight loss) after 150 days in soil	[146]
CMCNa cross-linked with HEC	DVS	NA	420; 80 (artificial urine)	NA	[205]
CMC	DVS	KOH (catalyst)	800	degradable (in soil)	[199]
CMCNa cross-linked with HEC	CA	NA	900	NA	[207]
CMC cross-linked with Chitin	ECH	NA	1300	degradable (in soil)	[211]
CMC cross-linked with Starch	NA	Gamma irradiation	350	NA	[200]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all case.
[b] NA means not available or not applicable.

7. Chitin/Chitosan-based SAPs

7.1. Structural characteristics and biodegradation properties of chitin, chitosan and their derivatives

As the second most abundant natural macromolecules after cellulose (available at a scale of 1 × 10^{13} kg annually) [212], chitin is a linear polysaccharide composed of $\beta_{1\text{–}4}$ linked N-acetylglucosamine (2-(acetylamino-2-deoxy-D-glucose). It widely exist as a primary component of cell walls in fungi, the exoskeletons of arthropods, such as crustaceans and insects, the radulae of molluscs, cephalopod beaks, and the scales of fish and skin of lissamphibians [213]. The molecular structure of chitin is rather similar to cellulose, with one hydroxyl group on cellulose replaced with an acetyl amine group (Fig. 9). The abundant N-acetyl groups at C-2 position have a tendency to form intra- and intermolecular hydrogen bonds resulting in a low solubility of chitin in common solvents, particularly in water at neutral pH [214]. Because of its insolubility in almost all solvents, the utilization of chitin for SAP has been heavily restricted as well.

Chitosan (CS) is an intensively investigated derivative of chitin typically obtained by partially de-acetylating the N-acetyl group of chitin [206]. Similar to chitin and cellulose, CS is a linear polysaccharide composed of randomly distributed $\beta_{1\text{–}4}$ linked D-glucosamine units and N-acetyl-D-glucosamine units (Fig. 15) [215,216]. The existence of amino pendant groups on CS macromolecules are convenient for introducing additional hydrophilic vinyl monomers, such as acrylic acid (AA), by graft copolymeriza-

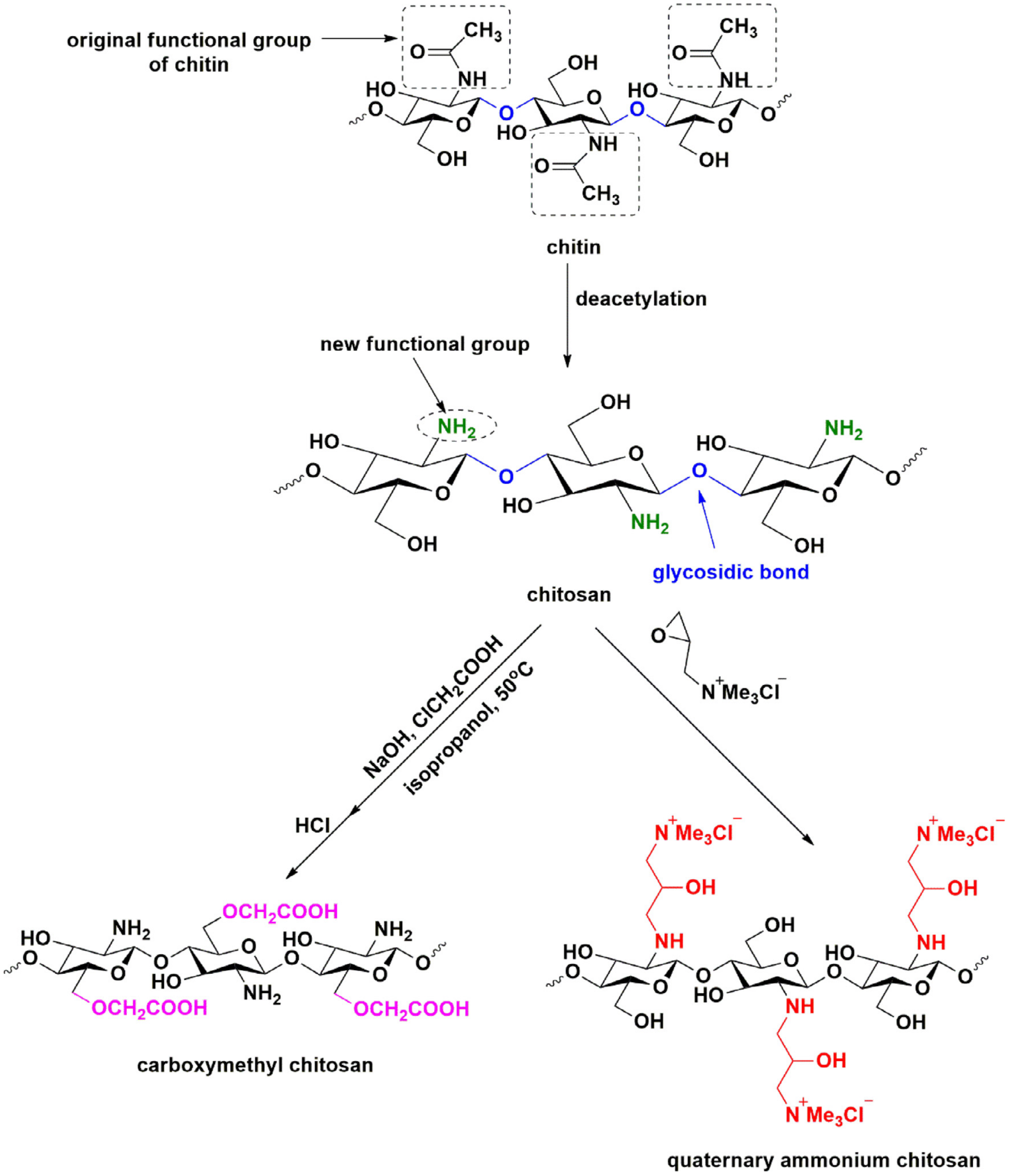


Fig. 15. Structure of chitosan and its derivatives (carboxymethyl chitosan and quaternary ammonium chitosan).

tion under facile reaction conditions [208,209,217] (Fig. 15). Compared with chitin, CS is more promising for the development of SAPs because of its much-improved solubility [218]. Although it remains difficult to dissolve in water or a common organic solvent due to the strong hydrogen bonding effect, CS can be dissolved in dilute aqueous acetic acid solution ascribed to the tendency of protonation of the amino groups at low pH. Additionally, CS is also soluble in aqueous LiOH/urea solution by a freezing–thawing method [219]. Besides CS, other CS-based derivatives, such as carboxymethyl chitosan [61,220–222] and quaternary ammonium chitosan [223], have also been fabricated to gain even better solubility.

In vivo, chitosan may be degraded by several unspecific enzymes, first of all by lysozyme which is present in all mammalian tissues [224,225]. Degradation products of CS are normally the nontoxic oligosaccharides which are either excreted or incorporated to glycosaminoglycans and glycoproteins afterwards in the metabolization pathway of the organisms [226]. The possible degradation mechanism of CS usually begins with random splitting of β-1,4-glycosidic bonds (depolymerization) followed by the hydrolysis of N-acetyl linkage (deacetylation). Consequently, decreases in their molecular weight and an increase in deacetylation degree are normally observed. Also depending on the biodegradation conditions and the related types of microorganisms/enzymes, cleavage of different functional groups (amino, carbonyl, amido and hydroxyl) of CS may occur [227]. Nevertheless, to obtain the SAP material based on these natural polymers, chemical/physical introduction of the more hydrophilic acrylates are also frequently considered, which will affect the overall biodegradability of the SAPs.

7.2. Preparation and properties of chitosan-based SAPs

Compared with other functional groups (hydroxyl or carboxyl groups), amino groups of CS appear to be less hydrophilic and hence, CS exhibits a lower water absorption capacity than that of cellulose, starch and their derivatives [228]. Water absorption capacity of the pure CS is 0.9 g distilled water/g CS [229]. To enhance the water absorption capacity of CS-based SAPs, physical and chemical modifications are necessary.

As discussed earlier, introduction of micro-pores or micro-channels onto the SAP beads is a typical and highly effective physical medication protocol to promote faster water penetration and enhance water absorption capacity. For example, Wang and coworkers [230] prepared a pure CS film with interconnected pores with pore sizes in the range of 50–120 μm by a ternary solvent system (DMSO, dioxane and 1% acetic acid solution). This product shows a remarkably high water absorption capacity of 896 g distilled water/g SAP. In addition, physical initiation methods like Co-60 γ radiation [231–234], electron beam irradiation [235] and direct photo-induction with UV light [236,237] are also employed.

More frequently, CS is chemically-modified to introduce more hydrophilic groups. Most CS-based SAPs are obtained by further introducing acrylates, acrylamide or other hydrophilic vinyl pendant units and then constructing a cross-linking network [168]. Similar as in a typical polyacrylate-based radical polymerizations, chemical initiatiors, e.g. thermal initiators (e.g. APS), redox induced systems [216,238–240], and photoinitiator are mostly adopted in these grafting reactions [103,217,241–243]. Many studies have illustrated the radical copolymerization process of grafting acrylates or other hydrophilic vinyl monomers onto the chitosan backbone affording the products with water absorption capacity ranging from 120 to 600 g distilled water/g SAP [204,217,232,234,243]. The typical procedure is described in 6.2**.**

To form a cross-linked network structure, a polycondensation reaction between the reactive pendent groups of chitosan, eg. amino ($-NH_2$) or hydroxyl (–OH) groups, with the carboxylic acids groups of the cross-linkers, or a Michael addition between the amino group of chitosan and acrylic acid can be considered. Dhamodharan et al. reported a novel SAP synthesized by cross-linking chitosan with an EDTA (ethylenediamine tetraacetic acid)–urea adduct [244]. The condensation between chitosan and EDTA-urea adduct takes place at 100 °C after dissolving chitosan in required quantity of acetic acid and adding calculating amount of urea and EDTA. Solid state NMR measurements confirmed that the product is not just a physically blended mixture but cross-linked with a degree of 0.16. In comparison to a commercial diaper-used SAP material named Huggies®, the product prepared by the authors exhibits a higher water uptake capacity (570 vs. 238 g distilled water/g SAP). Ge et al. demonstrated a cross-linking procedure to prepare polyacrylate-grafted CS SAPs by Michael addition reaction [245,246]. This reaction can proceed at a low temperature (50 °C) in water and the reported water absorbing capacity of the produced SAPs [247,246] was 644 g distilled water/g SAP). The authors also investigated the biodegradability of these SAPs and 30–70% weight loss was observed after incubation in soil for 21 days [244,249].

Epichlorohydrin and glutaraldehyde are the two most used chemical cross-linkers for the production of chitosan-based SAPs. Tang et al. [211] reported a kind of chitosan-based SAPs from chitosan and carboxymethylcellulose (CMC) by using epichlorohydrin as the cross-linker. The hydroxyl groups of chitosan were cross-linked with hydroxyl groups of CMC through nucleophilic attack of the alcoholate anion to form monoethers of chlopropanediols and a new epoxide by chloride displacement. This reaction can occur in a solution of aqueous NaOH/urea solution at 60 °C. This chitosan-based SAP shows excellent absorption capacity (1300 g distilled water/g SAP) and is degradable in soil. Other researchers attempted to form a cross-linked network by using glutaraldehyde [250–253].

The chemical cross-linkers are usually toxic chemicals and their residuals must be completely removed before use for biomedical or personal care applications. Alternatively, introducing physical cross-linking in SAPs, such as ionic cross-linking between chitosan and other components, is an efficient way to prepare 3D network polymers without using toxic chemical cross-linkers. Cao and coworkers [254,255] synthesized a SAP material based on chitosan and hydrolyzed polyacrylamide (HPAM) by applying a two-stage cross-linking process. The electrostatic interactions between Al^{3+} from $AlCl_3$ solution, $-NH_3^+$ of chitosan and $-COO^-$ from HPAM makes the SAPs prepared as such high water absorbing by displaying an extremely high water absorbencies of 3675 g distilled water/g SAP, which is considerably higher than those prepared by chemical cross-linking protocols [237,256]. The authors believed that this remarkable result is possibly due to the porous structure of the complex formed due to the dissociation of Al ions from the complex in an acidic environment inducing the partial destruction of the cross-linked structure. However, the absorption capacity decreased with the metal cations increasing due to the complexing ability from the coordination of the multivalent cations with $-COO^-$. For example, this SAP show excellent water absorption capacity in K^+ containing solution, but almost no water absorption capacity in Al^{3+} solution.

The physical cross-linked SAPs can also be designed to display additional interesting responses upon environmental stimulation. Wang et al. [257] reported an interesting hydrogel composite beads as drug delivery matrices based on sodium alginate, attapulgite and polyacrylate-grafted and Ca^{2+} cross-linked chitosan. The water absorbing performance of such products is pH-dependent: when the pH <5.0, the water swelling ratio of these SAPs is very low (<7 g 3% w/v $CaCl_2$ solution/g SAP), while it increases sharply to 42.5 g 3% w/v $CaCl_2$ solution/g SAP under a weakly basic environment (pH=8.0), and further increases to 45 g 3% w/v $CaCl_2$ solution/g SAP under a strongly basic condition of pH 12.0. The reason for such a pH sensitivity of the system is as follow: under an acidic condition, COO^- groups can convert to, and the hydrogen bonding is formed among the free carboxylic acid (–COOH), hydroxyls (–OH) and the amide (-NHCO) groups, leading to a reduced swelling ratio. In contrary, when under a basic condition, most of the –COOH groups are deprotonated their corresponding ion forms ($-COO^-$) and hence the hydrogen bonding is destroyed and leading to a high affinity of the water. A similar protocol was reported by Mandavinia et al., wherea novel type of SAP was prepared by chitosan and κ-carrageenan. The electrostatic interactions exist between the positively charged amino groups on chitosan and the negatively charged sulfate groups on κ-carrageenan. The whole process is in general rather “green” given no toxic chemical cross-linkers were involved [258].

7.3. Preparation and properties of carboxymethyl chitosan-based SAPs

Carboxymethyl chitosan (CMCS) is a water-soluble derivative of chitosan and has also been employed for SAPs applications. CMCS is typical synthesized by carboxymethylation of the hydroxyl and amine moieties of chitosan. Graft copolymerization of hydrophilic vinyl monomers onto CMCS is the most effective way to produce CMCS-based SAPs like chitosan. It was found that the degree of carboxymethylation has an essential influence of the water absorbing properties of the product. By systematically varying the carboxymethylation conditions (reactant ratios, reaction times), Bidgoli et al. [259] found that the highest degrees of substitution, obtained by using monochloroacetic acid (MCAA), NaOH and chitosan in a weight ratio of 1.75:1.75:1 in 4 h, resulted in a SAP with the highest absorption capacity (104 g distilled water/g SAP).

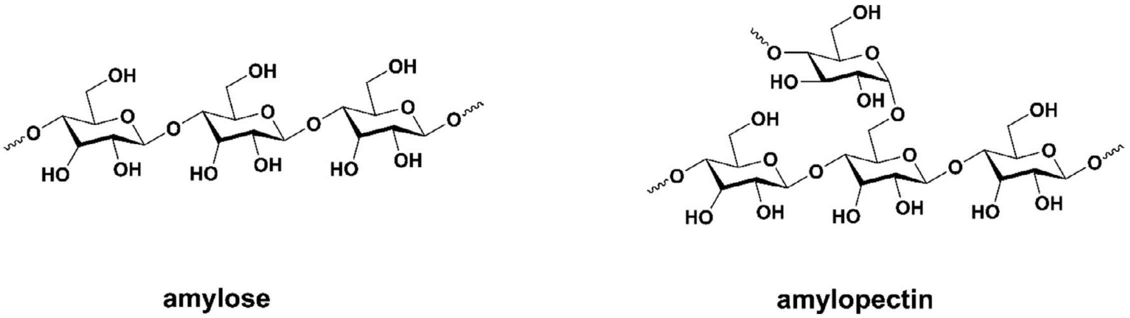


Fig. 16. Chemical structure of amylose and amylopectin.

Although carboxymethyl chitosan apparently displays much enhanced water absorbing properties than the pure chitosan, further grafting acrylates on this substrate is also considered by researchers to gain high water absorbency. Chen et al. [61] prepared a novel SAP by free radical graft copolymerization of acrylic acid onto carboxymethyl chitosan's backbone and simultaneous cross-linking. This SAP showed a water absorption capacity of 800 g distilled water/g SAP. Afterwards, Chen et al. [221] reported that SAP prepared by graft copolymerization of sodium acrylate and a hydrophilic nonionic monomer, 1-vinyl-2-pyrrolidone, onto the chain of carboxymethyl chitosan, showed a good water absorption capacity, viz. 1268 g distilled water/g SAP.

7.4. Preparation and properties of quaternary ammonium chitosan-based SAPs

Quaternary ammonium chitosan is another water-soluble derivative of chitosan, which is well-known for its excellent antibacterial properties [260,261]. He et al. [223] reported a kind of SAPs consisting of quaternary ammonium chitosan-g-poly(acrylic acid-co-acrylamide), which is expected to have good antibacterial properties and at the same time showing excellent absorption capacity (540 g distilled water/g SAP and 87 g 0.9 wt% NaCl solution/g SAP). A detailed comparison of the properties of all these chitosan-based SAPs of all the types discussed in this section can be found in Table 4.

8. Starch-based SAPs

8.1. Structural characteristics of starch-based SAPs

Starch is the most abundant polysaccharide in plants, and exists as granules in the chloroplasts of green leaves and the amyloplasts of seeds, pulses, and tubers [265]. Starches are chemically speaking polysaccharides; they consist of a number of monosaccharides or glucose molecules joined together (Fig. 16). Starch is categorized by two main structural components, namely amylose and amylopectin [266]. Amylose is a mostly linear α-D-(1–4)-glucan, while amylopectin is an α-D-(1–4)-glucan which has α-D-(1–6) linkages at the branch point and contains only glucose as monomer [267,268]. Both fractions are readily hydrolyzed at the acetal link by enzymes, being a first step in the biodegradation process. The two types of glycosidic bonds are susceptible to different enzymes: $\alpha-1$–4-link in both components of starch is mostly attacked by amylase and the $\alpha-1$–6-link in amylopectin can be degraded by glucosidases. The endo-amylases generally hydrolyze only the main chain acetal bonds in either amylose or amylopectin and are not active on the branch points of the latter, but many exo-amylases can cleave the macromolecules either on the main chains or on the branch bonds. The exo-amylases can generate either glucose or the dimer (maltose) or the trimer (maltotriose) by attacking the non-reducing end of the starch molecules [269]. It has been reported that starch can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water [270].

Similar to cellulose, starch is also a type of natural macromolecules having abundant hydroxyl groups, thus theoretically are advantageous of offering highly hydrophilic materials for potentially uses as SAPs. Some of the advantages of using starch as an absorbent are: abundant renewable resource, low cost, ability to be easily modified, high swelling capacity in water and good processability. However, it has some disadvantages such as low surface area, and requires chemical modification to enhance its sorption capacities [244]. In this context, chemical modification, especially grafting copolymerization of vinyl monomers of other polysaccharides like cellulose and chitosan as discussed above, are also applicable for preparation starch-based SAPs.

8.2. Properties of starch-based SAPs

Reactions for preparing the polysaccharide-based SAPs can be conducted by two main approaches: (1) grafting vinyl monomers on polysaccharides and then cross-linked into the final network structure; and (2) direct cross-linking of polysaccharides. Grafting the vinyl units on starch can be initiated by Ce^{4+}as free-radical initiators (Fig. 17), the mechanism of which was initially proposed by Dragan and Apopei [272]. The complex formed by Ce^{4+} with the hydroxyl groups of starch decomposes to generate free radicals, then grafting copolymerization of vinyl monomers took place at the active sites of starch.

Athawale et al. [273] reported a procedure of grafting acrylic acid onto maize starch initiated by a ceric ion in aqueous medium without cross-linking. The so-prepared SAP candidate was obtained with a good absorption capacity (250 g distilled water/g SAP). In another report, Qiao et al. [31] synthesized a starch-based SAPs grafted with poly(acrylamide) by using the same initiator and cross-linked by MBA for application as slow-release fertilizer material. This product shows an absorption capacity of 126.4 g distilled water/g SAP. The non-cross-linked prepolymer was reported to have a absorption capacity as high as 452.2 g distilled water/g SAP [107].

Alternatively, persulphate can also be used as an initiator, which abstracts hydrogen radicals from the -OH groups of the polysaccharide to form the initiating radicals on the polysaccharide chains. Due to the use of a thermal initiator, this reaction is more influenced by temperature in comparison to that initiated by Ce^{4+}. Zhong et al. [37] reported SAPs based on starch and poly(acrylic acid), cross-linked by MBA using the initiator KPS, for agricultural applications. Similarly Dragan et al. [272] synthesized a kind of pH-sensitive SAP composite by grafting polyacrylamide onto starch, cross-linked by MBA and initiated by APS, exhibiting inferior absorption capacity than their acrylic-acid counterpart (100 g distilled water/g SAP vs. 498 g distilled water/g SAP). Fang et al.

Table 4
Summary of composition and properties of chitosan-based SAPs.

Component		Cross-linker	Initiator or initiating techniques	Absorption capacity [a] (g/g)	Degradability	Reference
Pure chitosan-based SAPs	Chitosan film	NA[b]	NA	896	NA	[230]
	AA grafted onto chitosan	NA	UV irradiation	600	NA	[217]
		NA	Direct current electric field	NA	NA	[243]
		NA	^{60}Co gamma radiation	300	NA	[232]
		NA	NA	Water soluble	67.3% degradation after 21 days in soil	[248]
		MBA	KPS	644	NA	[249]
		MBA	Ceric ion	704	NA	[256]
	AA grafted onto chitosan/ attapulgite composite	MBA	APS	159.6; 42.3(Saline solution)	NA	[108]
	AM grafted onto chitosan	MBA	UV irradiation	106	NA	[237]
	Vinyl acetate grafted onto chitosan	NA	KPS; sodium bisulfite	3	NA	[247]
	AA/AM grafted onto chitosan	MBA	KPS or CAN	235–300	NA	[240,241]
		NA	^{60}Co gamma radiation	120	NA	[234]
	AA grafted onto chitosan/ sodium alginate/attapulgite composite	MBA	APS	45 (Saline solution)	NA	[257]
	HEA grafted onto chitosan	NA	APS or ^{60}Co gamma radiation	NA	NA	[236,242]
	chitosan	EDTA, urea	NA	600	NA	[244]
	Acryl reagents grafted onto chitosan	NA	NA	NA	33.6% degradation after 21 days in soil	[246]
	Glycidyl methacrylate/ chitosan hybrid	NA	NA	NA	NA	[262]
	chitosan/starch IPN	GA	NA	15	NA	[251]
	PVA/chitosan complex	GA	NA	0.7–3	NA	[252]
	k-carrageenan/chitosan /Fe_3O_4 composite	NA	NA	6.5	NA	[258]
chitosan derivatives-based SAPs	CMCS	GA	NA	104–171	NA	[250,259]
			n-Pentane (blowing agent)	107	NA	[253]
	AA grafted onto CMCS	MBA	Peroxysulfate ion	900–960	NA	[61, 220]
	MAA grafted onto CMCS	NA	APS	NA	NA	[222]
	CMCS cross-linked with carboxymethylchitin	NA	Electron beam irradiation	270	NA	[235]
	AA grafted onto chitin	MBA	APS	2833	NA	[263]
	AA/AM grafted onto quaternary ammonium chitosan	MBA	KPS	770 90 (saline solution)	NA	[223]
	Poly(AA/AM)/*O*–CMCS IPN	GA	APS; TEMED	80	NA	[264]
	sodium acrylate/1-vinyl-2-pyrrolidone grafted onto *N*,*O*–CMCS	MBA	Azobis (isobutylaminde hydrochloride)	1268 165 (saline solution) 112 (artificial blood) 121 (artificial urine)	NA	[221]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all case.
[b] NA means not available or not applicable.

[274] synthesized a type of superabsorbent by graft copolymerization of acrylamide and acrylic acid onto starch using poly (ethylene glycol) (PEG) as a cross-linker and a gamma-ray radiation technique. The maximum absorption capacity of the sample in distilled water was 2400 g/g SAP. Fang et al.'s work presented a new cross-linker type which is biodegradable. Apart from KPS and APS, two common persulphate initiators, the graft polymerization of acrylic monomers onto starch could be initiated by starch alkoxide ions and Fenton's initiation system (Fe^{2+}/H_2O_2) [101,152].

In the case of direct cross-linking of polysaccharides (group (2) approach), polyfunctional compounds (e.g., glycerol, glyoxal and epichlorohydrine) or polyvinylic compounds (e.g., divinyl sulphone, DVS) are used [95]. For starch, di- or polycarboxylic acids are mostly used as cross-linkers which include succinic acid, adipic acid, glutaric acid, suberic acid, pimelic acid, butanetetracarboxylic acid, citric acid, etc. [275–277]. Olayide et al. synthesized the carboxymethylated cassava starch and cross-linked it with several nontoxic di- or polyfunctional carboxylic acid-based cross-linkers to produce SAPs [276]. It was found that the polyfunctional carboxylic acids are less effective to inducing cross-linking compared with the difunctional carboxylic acids. The absorbency of these SAPs was around 80 g deionized water/g SAP and around 20 g 0.9% NaCl solution/g SAP.

The addition of inorganic additives proved an effective way to enhance the water absorption of starch-based SAPs composites. When attapulgite [6] or Na-montmorillonite [183] was added

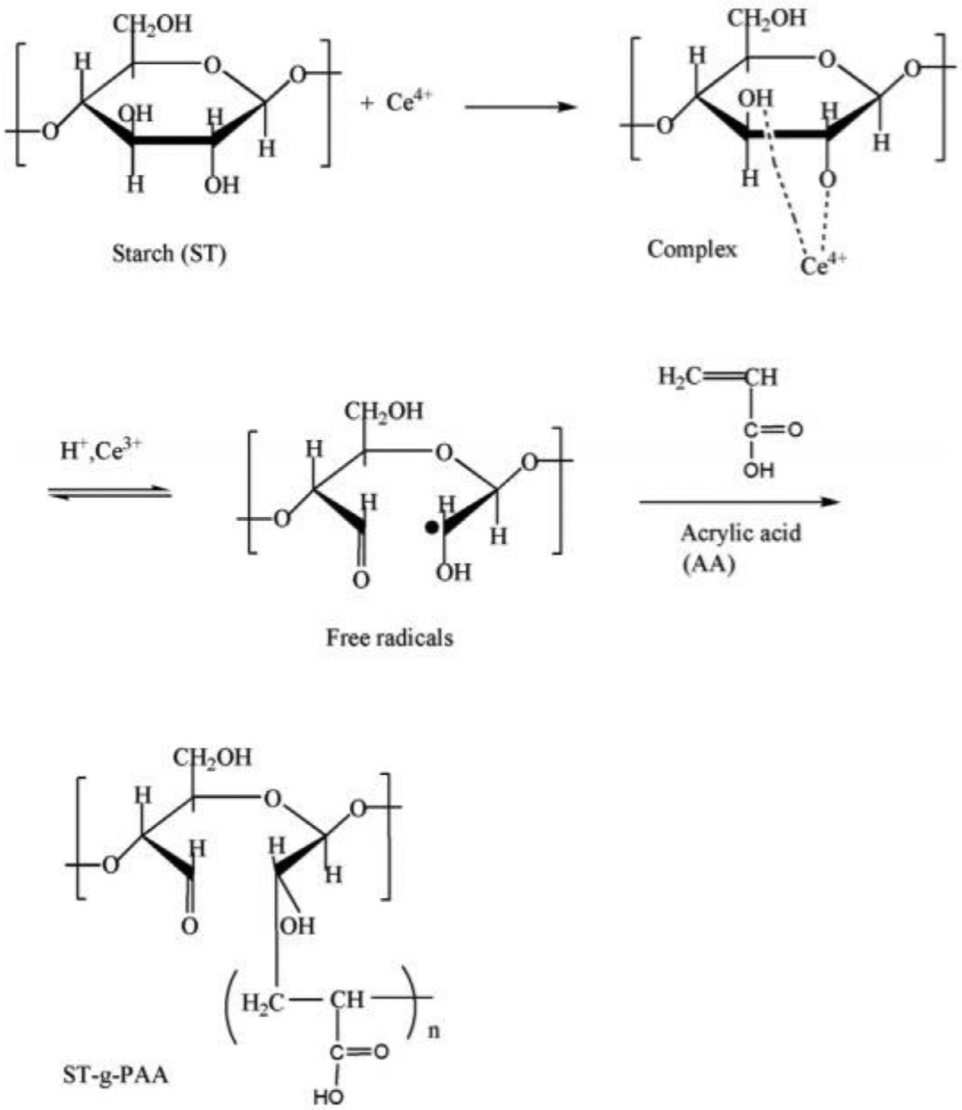


Fig. 17. Mechanism for grafting acrylic acid on starch by using Ce^{4+} as free-radical initiator. [272], Copyright 2011. Reproduced with permission from Elsevier.

to the poly(acrylic acid) grafted starch-based SAPs, the absorption capacity could reach up to 1077 g normal water/g SAP and up to 1000 g distilled water/g SAP, respectively. A detailed comparison of the properties of starch-based SAPs can be found in Table 5.

9. Protein-based SAPs

9.1. Structural characteristics of protein-based SAPs

Proteins are essential nutrients for the human body and animals. The most defining characteristic of proteins is their fascinating double-helix structure constructed by the 20 amino acids via peptide bonds [278]. Molecular weights and amino acid composition vary considerably among different proteins [278], meaning that they are more chemically heterogeneous than the synthetic polymers and polysaccharides. The amino functional groups in protein molecules is a kind of hydrophilic groups like carboxylic groups or hydroxyl groups. These characters are particularly valuable to steer and finely tune the properties for instance hydrophilicity, hence contributing to their potential use in superabsorbent materials [278,279]. In addition, protein-based materials generally have high bioactivity, biocompatibility and biodegradability, and are extensively explored as smart biomaterial candidates for drug delivery, tissue engineering, regenerative medicine and personal care products etc. [280].

The proteins commonly used for production of SAPs are mainly collagens, gelatin and canola proteins. Collagens are fibrous proteins responsible for important mechanical functions throughout the body. The majority of collagens are present in articular and bone tissues, where they provide most of the biochemical properties essential for proper functioning [280]. Gelatin is a heterogeneous mixture of polypeptides derived from collagen, while canola protein is a kind of protein derived from plant canolafamou, which is the second largest produced oilseed in the world after soybean.

Many kinds of vegetable and animal proteins have been utilized to prepare biodegradable polymers for in vivo applications. For instance, collagen is degraded within the body by enzymes e.g. collagenases and metalloproteinases at the peptide linkages yielding the corresponding amino acids residues [280]. Research has also shown that the degradation rate of collagen in biomedicine can be significantly changed if they are enzymatically pre-treated [281].

Table 5
Summary of composition and properties of starch-based SAPs.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
AA grafted onto cassava starch	MBA	Fenton's initiation system (Fe^{2+}/H_2O_2)	110	NA[b]	[101]
AM grafted onto starch	MBA	CAN	126.4	NA	[31]
AA/AM grafted onto starch	Starch alkoxide ions	NA	570	NA	[152]
	PEG	Gamma-ray irradiation	2400	NA	[274]
AA/AM grafted onto gelatinized maize starch	MBA	CAN	510	NA	[157]
AA grafted onto corn starch	MBA	KPS	498; 65 (Saline solution)	NA	[37]
AA grafted onto granular maize starch	ceric ion	NA	250	NA	[273]
AM grafted onto cassava starch	NA	CAN	425.2	NA	[107]
AM grafted onto potatoes starch	MBA	APS	100	NA	[272]
AA grafted onto starch/attapulgite composite	MBA	APS	1077; 61 (saline solution)	NA	[6]
AA grafted onto starch/Na-montmorillonite composite	MBA	CAN	1000	NA	[183]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all case.
[b] NA means not available or not applicable.

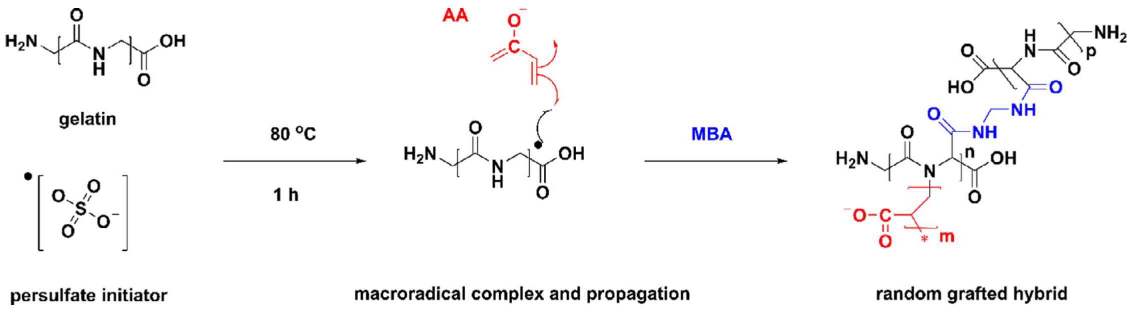


Fig. 18. Graft-polymerization of acrylic acid monomer (AA) onto a protein backbone (e.g., gelatin) and the substrate is further cross-linked with MBA. [291], Copyright 2019. Reproduced with permission from American Chemical Society.

9.2. Properties of protein-based SAPs

It is reported virgin protein does not have satisfactory absorption capacity. To list collagen as an example, absorption capacity of collagen is less than 2 g distilled water/g SAP [282]. To improve the absorption capacity of protein-based SAPs, a few strategies have been evaluated to modify the absorption properties of protein-based materials [95,283–286]. The most effective method remains the radical grafting method to introduce hydrophilic acrylic units onto protein (Fig. 18). As shown in Fig. 18, acrylic acid has been grafted onto proteins to increase their absorption capacity. The proteins include cotton seed protein [287], silk sericin protein [288] and gelatin [289]. The grafting resulted in a maximum water absorption capacity of 2100 g distilled water/g SAP [290].

Marandi et al. [292] produced a series of hydrogel nanocomposites by grafting AA and AM on gelatin in the presence of Na-montmorillonite nanoparticles. The hydrogel nanocomposites exhibits good thermal strength and swells in salt solutions(NaCl, $CaCl_2$, and $AlCl_3$) and deswells in different saline solutions(NaCl, $CuCl_2$, and $CaCl_2$) that make them useful in various application fields such as hygienic, medical and agricultural products. Alternatively, the same research group used collagen as the substrate for same protocol [185], and it turned out that the collagen-based SAPs was obtained with even higher absorption capacity (950 g distilled water/g SAP) than the gelatin-based ones (316 g distilled water/g SAP). Pourjavadi et al. [293] reported an efficient synthesis of the hydrolyzed collagen grafted with poly(sodium acrylate-co-2-hydroxyethyl acrylate) hydrogel by co-grafting two monomers onto the collagen substrate and a further cross-linking process. The product exhibited high absorption capacity under load (39 g 0.15 M NaCl solution/g SAP vs. 18 g 0.15 M NaCl solution/g SAP for the cross-linked poly(acrylic acid) reference), which is considered as sufficient for baby diapers and female hygiene absorbent applications. However, the absorption capacity in distilled water was not so satisfactory because of the absence of inorganic clays. A detailed comparison of the composition and properties of protein-based SAPs can be found in Table 6.

In addition, chemical functionalization is also an effective method to improve absorption capacity of protein-based SAPs, which means transferring less hydrophilic functional groups to stronger hydrophilic groups. Ethylenediaminetetraacetic dianhydride (EDTAD) and CA have been proved useful regent to transfer hydroxyl or amine groups to more hydrophilic carboxyl groups [283–285,294–296]. Using this method, taking soy protein (SPI) as an example, when the EDTAD/SPI mass ratio was 0.15, the absorption capacity of SAPs after chemical functional is 30% higher than that of native SPI-based SAPs [283].

Bifunctional diamines and aldehydes are the reagents most commonly used to cross-link protein-based materials [264,271–276]. *N,N'*-methylene bis-(acrylamide) (MBA) and glutaraldehyde (GA) are the representatives of each type (Fig. 19). MBA, which are frequently used to cross-link polyacrylates or polysaccharide-based SAPs, is also an excellent reagent to construct the network of protein-based absorbent materials with the grafted AA pendant units [34,109,185,292,300–302]. As an inexpensive and low-toxic cross-linker [297–299,303–305], GA in particular is known to effectively cross-link polypeptide chains, providing a fast reticulation reaction in proteins [297,306,307]. A suggested cross-linking reaction given by glutaraldehyde is shown in Fig. 19, but although glutaraldehyde is reported to be highly reactive, it is also known that

Table 6
Summary of composition and properties of protein-based SAPs.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
AA/AM grafted onto collagen/Na-MMT composite	MBA	KPS	950	NA[b]	[185]
AA/AM grafted onto gelatin/Na-MMT composite		APS	316	NA	[292]
Sodium acrylate/HEA grafted onto collagen		APS	360	NA	[293]
AA grafted onto hydrolyzed canola protein		Sodium bisulfite and KPS	448	NA	[109]
AA grafted onto modified chicken feather protein (MCFP)		KPS	NA	NA	[34]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all cases.
[b] NA means not available or not applicable.

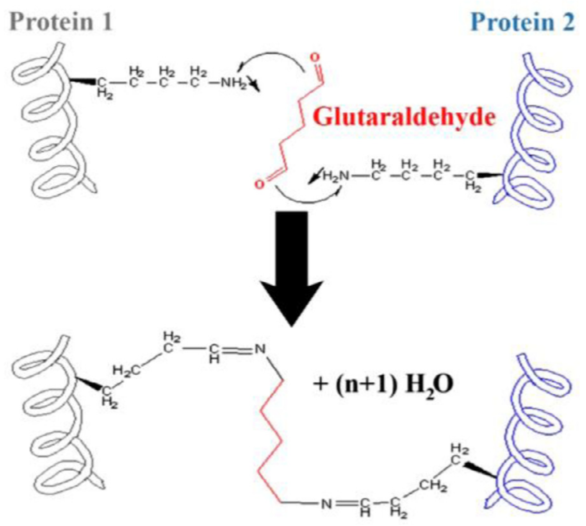


Fig. 19. Cross-linking of protein through the lysine group using GA. [291], Copyright 2019. Reproduced with permission from American Chemical Society.

its reactivity mostly targets specific amino acid groups, e.g. lysine. Because the acylation of proteins occurs mainly through the lysine group, a balance in the extents of acylation in the protein must be considered when using GA as the cross-linking agent.

In general, protein-based SAPs do not show excellent absorption capacity in comparison with other natural polymer-based SAPs. The reason is expected to relate to the relatively low concentration and the low strength of the hydrophilic groups. Therefore, proteins have not been studied to the same extent as polysaccharides counterpart, and just a few studies have been reported concerning the grafting of synthetic monomers onto protein-based materials or their composites [34,109,185,292,293]. Even though, the heterogeneity of proteins together with their abundant availability and unique properties create new opportunities for the production of relatively inexpensive multifunctional protein-based SAPs [291].

10. Homo poly(amino acid)-based SAPs

A poly(amino acid) is a polymer composed of amino acids as monomeric units, with hydrophilic groups such as -COOH and/or -NH_2 as pendant groups which can absorb water. Due to their excellent biodegradability, poly(amino acid)s are frequently used in biological applications such as tissue engineering and drug delivery. Not only the intrinsically present pendant functional groups, exhibiting a high affinity to water, but also the possibility to use these pendant groups for further chemical modification with hydrophilic grafts, makes this type of polymers suitable for SAP applications.

10.1. Structural characteristics and biodegradation properties of homo poly(amino acid)s

Different from the natural proteins composed of different α-amino acid units, homo poly(amino acid)s consist of only one kind of amino acid residue, but these are rarely found in nature. Only three kinds of homo poly(amino acid)s are found in nature, *viz.* poly(aspartic acid), poly(glutamic acid), and poly(ε-lysine) (Fig. 20), meaning that thesecan be synthesized by microbiological or natural chemical processes.

The structure of poly(aspartic acid) in its natural form contains only α-blocks which means there is only α links between two repeating units (Fig. 20). Poly(aspartic acid) can also be synthesized by two chemical pathways: a. by a peptide chemical procedure, b. by a thermal polymerization process. For the former one, uniformly directed α- or β-poly(aspartic acid) with different molecular weight can be produced. For the latter one, usually poly(aspartic acid) sodium salt with both α-blocks and β-blocks (two repeating units are β-linked) is produced. Because of its excellent biodegradability and the high density of negatively charged carboxylic groups, which is higher than in poly(glutamic acid) and poly(ε-L-lysine), Poly(aspartic acid) is an ideal substitute for the non-biodegradable poly(anionic) SAPs, e.g. poly(acrylic acid) [308].

In 1937, poly(glutamic acid) was first discovered by Erdös et al. [309] during their study on the capsular substance of the pathogen *Bacillus anthracis*. Poly(glutamic acid) exhibits an extraordinary high water absorbency [310]. In addition, it has high affinity to metal ions [311] such as Ca^{2+}, Cu^{2+}, and Fe^{3+}. Therefore, poly(glutamic acid) can be potentially used as flocculant or absorber in bioremediation or water purification applications.

Poly(ε-lysine), an L-lysine homo poly(amino acid), is water soluble and biodegradable like the other two homo poly(amino acid)s mentioned above. Poly(ε-lysine) and its derivatives have been of interest in the past few years for many industrial applications such as in food, medicine, environment, and so on.

It has been reported these three homo-poly(amino acid) can be degraded into corresponding monomers by different enzymes via different mechanisms. Detailed information can be found in the mini review published by Obst et al. [312].

10.2. Preparation and properties of homo poly(amino acid)-based SAP

Although all these three naturally occurring homo poly(amino acid)s are water soluble, modification of them is necessary to get the required high water absorbing and retaining ability for SAP applications. These SAPs can be prepared by two methods: (i) The

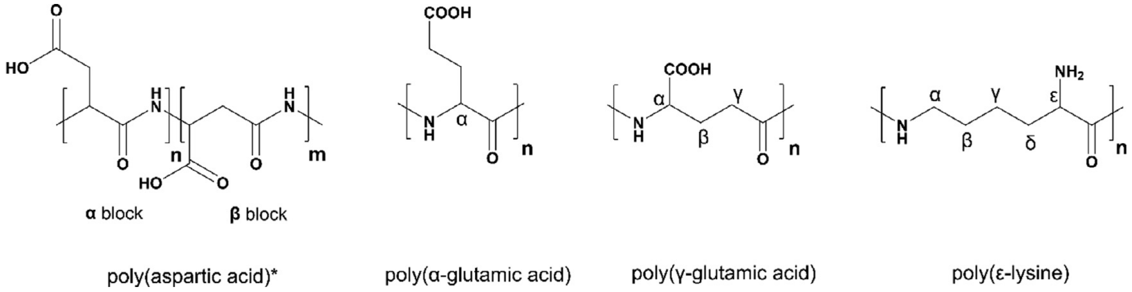


Fig. 20. Repeating units of poly(aspartic acid), poly(α-glutamic acid), poly(β-glutamic acid), and poly(ε-lysine); *naturally occurring poly(aspartic acid) consists of only α blocks while synthetic poly(aspartic acid) may consist of both α and β blocks.

homo poly(amino acid) can be cross-linked directly to get a 3D structure; (ii) The homo poly(amino acid) can be mixed with polyacrylates to form a stable structure which is called interpenetrating polymer network (IPN). There are two methods to cross-link the homo poly(amino acid)s: a. chemical cross-linking; b. irradiation cross-linking. SAPs cross-linked by irradiation show a better water absorbing ability than chemically cross-linked systems because of the porous structure produced by the irradiation method [313].

In the first preparation method (i), it has been frequently reported that lightly cross-linked homo poly(amino acid) showed excellent water absorbing property. Poly(aspartic acid) was cross-linked with PEG-diepoxide at different temperatures and reaction times [314]. It was observed that, the lower the cross-linking temperature, reaction time and molecular weight of PEG-diepoxide, the better the water absorbency was. The maximum water absorbency could reach up to 1100 g distilled water/g SAP and 70 g 0.9% NaCl solution/g SAP. Tan et al. [315] chose 1,6-hexamethylene diamine as cross-linker to produce poly(aspartic acid) SAPs. The produced SAPs showed comparable water absorbency (about 700 g distilled water/g SAP) with the PEG-diepoxide cross-linked ones. Similar to poly(aspartic acid), both α- and γ-poly(glutamic acid) (Fig. 20) could be chemically cross-linked to produce SAPs. It has been reported that several difunctional cross-linkers such as diisocynates, dihalogenoalkanes, cystamine, cysteine and diamino-PEG are appropriate to produce poly(glutamic acid)-based SAPs [316–319]. However, the average water absorbency ($\sim$300 g distilled water/g SAP) of these materials is lower than those produced from poly(aspartic acid) due to their relatively lower density of the negatively charged carboxylic groups in the backbone. In addition to chemical cross-linking, it has also been reported that poly(glutamic acid) and poly(ε-L-lysine) could be cross-linked under irradiation. Kunioka [320] used 19 Gy or a high doseof γ-irradiation to cross-link the poly(glutamic acid). The water absorbency is very high (3500 g distilled water/g SAP) while the mechanical properties are very poor. He also proposed a cross-linking mechanism by intermolecular combination between free radicals generated on the -CH_2- carbons via γ-induced cleavage of C–H bonds [320]. In addition, he claimed this SAP is biodegradable but unfortunately did not perform any biodegradation study on this. Similarly, lightly cross-linked poly(ε-lysine) has been produced by γ-irradiation cross-linking [321]. The swelling capacity is 20–180 g distilled water/g SAP.

In the second preparation method (ii), there is only one example showing a composite of poly(amino acid) and polyacrylates forming an interpenetrating polymer network. Tan et al. [322] produced a kind of salt-, pH-, temperature-sensitive SAP from acrylic acid and poly(aspartic acid) under redox initiating system ($K_2S_2O_8$, K_2SO_3, TEMEDA, 33 °C, 6 h). The maximum water absorbency was about 160 g distilled water/g SAP. A detailed comparison of the various properties of homo poly(amino acid)-based SAPs is summarized in Table 7.

11. Alginate-based SAPs

11.1. Structural characteristics of alginate

Alginates, salts of alginic acid, are naturally occurring anionic polymers, usually refined from brown seaweeds. The chemical structure of alginates consists of linear copolymers of β-(1–4) linked D-mannuronic acid (M block) and β-(1–4)-linked L-guluronic acid (G block) units (Fig. 21). Because of their good biocompatibility, low toxicity and low cost, alginates have been extensively investigated for applications in biomedical and industrial fields [323]. Among all kinds of alginates, sodium alginate is the most commonly used one, especially for drug delivery. It is worth noting that the inherent hydrophilicity of alginate makes it an excellent gel-forming compound, capable of holding large amounts of water (about 6 g water/g alginate in a fiber form) [324], which endow it a potential wound dressing material. The abundant free hydroxyl and carboxyl groups (or -COO^- in alginate salts) in alginate (salt) molecules can be easily cross-linked by multivalent cations (e.g. Ca^{2+}) or multifunctional chemical cross-linkers (e.g. glutaraldehyde) [325]. In addition, vinyl moieties like acrylic acid can also be conveniently introduced on alginates via graft copolymeriation. All these characteristics of alginates make it a promising renewable and biodegradable substrate for SAPs application.

11.2. Preparation and properties of alginate-based SAPs

As illustrated above, carboxyl groups along the backbone of alginate can be cross-linked by divalent metal ions such as Ca^{2+}, Mg^{2+}, which belongs to ion cross-linking. It has been reported [326] that sodium alginate fibers cross-linked by Ca^{2+} shows super swelling property and the water absorbency is determined by the content of Ca^{2+} (percentage of calcium ions to total metal ions). When content of calcium ions is 76.5%, the fiber shows maximum water absorbency (about 25 g distilled water/g SAP).

Hydrophilic groups in the backbone of alginate also make it possible to graft copolymerize with vinyl monomers such as acrylic monomers including acrylic acid and acrylamide. Multifunctional cross-linkers can cross-link the copolymer and generate a stable 3D network which can function as a SAP. Bassioni et al. [327] cross-linked poly(acrylamide) and sodium alginate using ^{60}Co γ- radiation to produce a pH-sensitive SAP which has a highest absorbency of 22 g liquid/g SAP at pH 11.0. Manjula et al. [328] synthesized a sodium alginate-based SAP from acrylamide, methacrylamide, N-isopropylacrylamide and sodium alginate by using MBA as the cross-linker for drug release application. The maximum water absorbency is about 30 g distilled water/g SAP. In order to enhance the water absorbing ability, vinyl monomers with stronger hydrophilic groups instead of carboxyl group, such as sulfonate group, can be utilized for the production of alginate-based SAPs, as shown in an example that 2-acrylamido-2-methylpropane sul-

Table 7
Summary of composition and properties of homo poly(amino acid)-based SAPs.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
Poly(aspartic acid)	PEG-diepoxide	NA	1100	NA[b]	[314]
	1, 6-Hexamethylene diamine		700		[315]
Poly(glutamic acid)	Diamino PEG		300		[308]
	γ-Irradiation		3500		[320]
Poly(ε-lysine)	γ-Irradiation		20–180		[321]
Poly(aspartic acid), AA	MBA	$K_2S_2O_8$, K_2SO_3, TEMEDA	160		[322]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all cases.
[b] NA means not available or not applicable.

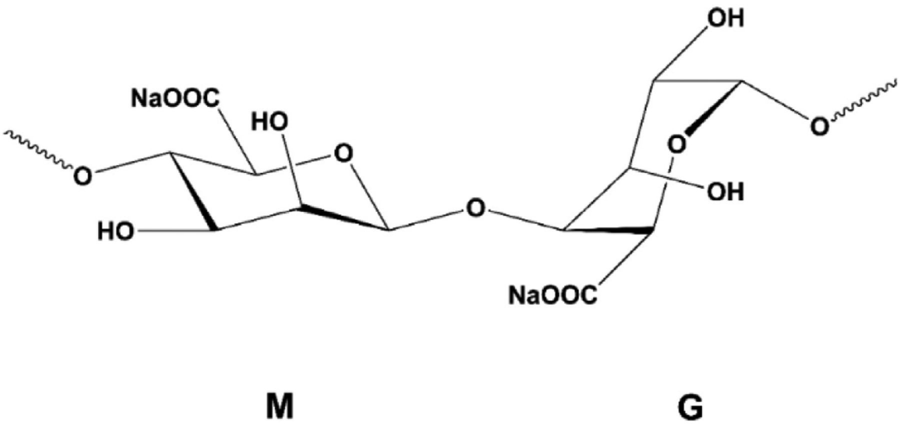


Fig. 21. Repeating units of sodium alginate; M units represent D-mannuronic acid and G units represent L-guluronic acid.

Table 8
Summary of composition and properties of homo poly(amino acid)-based SAPs.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
Alginate	Calcium ion	NA	25	NA[b]	[326]
Acrylamide, sodium alginate	^{60}Co γ- Radiation	NA	22		[327]
Acrylamide, methacrylamide, N-isopropylacrylamide and sodium alginate	MBA	APS	30		[328]
2-Acrylamido-2-methylpropane sulfonic acid, acrylamide, sodium alginate			560		[329]
Acrylic acid, Alginate, sodium humate			1380		[330]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all cases.
[b] NA means not available or not applicable.

fonic acid and acrylamide were graft copolymerized with alginate to make a SAP for drug delivery application [329]. A remarkable water absorbency of 560 g distilled water/g SAP was obtained in this case.

Attempts have also been made by creating alginate blends or composites including alginate, alginate graft copolymers or other macromolecules. Wang et al. [330] produced an alginate-based SAP composite from alginate-g-poly(acrylic acid) and sodium humate by using MBA as the cross-linker. The authors stated that a remarkably high water absorbency of 1380 g distilled water/g SAP was achieved when 10 wt% sodium humate was included. A detailed comparison of the properties of this type of SAPs of varied compositions is summarized in Table 8.

Lee et al. [331] demonstrated the relationship between the type of cross-linking and cross-linker and the properties of SAPs including mechanical and swelling properties. The authors concluded that the hydrophilic molecules such as PEG segments used as (biodegradable) cross-linker could compensate the partial loss of the hydrophilic character of the SAP due to cross-linking. This can provide guidance for the production of SAPs with high water absorbency by using hydrophilic (and preferably biodegradable) molecules as cross-linker instead of more hydrophobic molecules such as MBA.

Teh et al. [332] investigated the microbial degradability of an alginate-based SAP incorporated with additional acrylic acid, acrylamide and itaconic acid units. After the SAP was incubated in vegetable farm soil for 40 days, a weight loss of 82.8% was observed indicating a sufficient biodegradability of this material. Since the author did not indicate the chemical composition, we assume that such a high weight loss is ascribed to the alginate-based components of this material and that the acrylic/itaconic acid-based part is not degrading which has a consequence that the biodegradability of whole SAPs is reduced.

12. Other natural polymer-based SAPs

Carrageenan (CG) is a high molecular weight linear polysaccharide existing in the cell walls of red algae, which is consisted of repeating galactose units and 3,6-anhydrogalactose joined by alternating α-(1,3) and β-(1,4) glycosidic links. The global production capacity of CG is around 60,000 tons/year [333]. Current applications of CG hydrogels are mainly for drug delivery, immobilization of enzymes and pharmaceuticals [334].

The use of CG for producing superabsorbent materials in hygienic products has also gained increasing attention in recent years. Salimi et al. [335] introduced a new CG-based hydrogel hy-

Table 9
Summary of composition and properties of natural material-based SAPs, not containing cellulose, chitosan, starch or protein.

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
Poly(AA/AM)/SH composite	MBA	APS	800–1200	NA[b]	[153]
AA grafted onto *k*-Carrageenan/celite composite		APS	335–343	NA	[32]
AA grafted onto *k*-Carrageenan		APS	789	NA	[336]
AA/HEA/sodium acrylate grafted onto carrageenan		APS	295	NA	[335]
AA/AM/DMDAAC grafted onto wheat straw		KPS,$(NH_4)_2Ce(NO_3)$	133.76	NA	[106]
AA grafted onto alginate/alumina composite		APS	2000	NA	[62]
AA/AM grafted onto SA/humic acid composite		APS	228	19.3% degradation after 90 days in soil	[30]
Poly(AA/AM)/WMCAA composite		KPS	1548; 72 (saline solution)	NA	[337]
Poly(sodium acrylate/sodium p-styrenesulfonate)/SA/Attapulgite composite		APS	535	NA	[338]
AA/styrene grafted onto SA/Illite/smectite mixed-layer clay composite		APS	810; 86 (saline solution)	NA	[14]
AA grafted onto CMPWS		APS	417; 45 (saline solution)	NA	[7]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all cases.
[b] NA means not available or not applicable.

brid based on CG, acrylic acid, sodium acrylate and 2-hydroxyethyl acrylate. The obtained product exhibited high water absorption (217 g distilled water/g SAP) and absorbency under load (about 40 g 0.9% NaCl solution/g SAP at 0.3 psi pressure), which are relevant for use in baby diaper and feminine personal care absorbent products. Pourjavadi et al. [336] grafted the acrylic acid (AA) unit onto a kappa-carrageenan (κC) in the presence of a cross-linking agent (MBA) and a free radical initiator (ammonium persulfate). The Maximum absorption capacity of the optimized product was found to be as high as 789 g distilled water/g SAP. Wang et al. [32] also reported a SAP produced from CG, sodium alginate and acrylic acid for slow release fertilizer applications. The absorption capacity of this material was around 350 g distilled water/g SAP.

In addition to the polymer classes mentioned before, several other natural polymers, for instance, alginate, sodium alginate, waste material cultured Auricularia Auricula etc., are also the potential candidates for developing renewable SAPs. Their composition and water absorbing properties are shown in Table 9.

13. Bio-based and polycondensate-based synthetic SAPs

Even though most of the SAPs are produced from synthetic polymers (essentially acrylics) for their superior price-efficiency balance [63,95], the trend for replacing these synthetic, non-biodegradable products with “greener” alternatives is becoming increasingly clear. As discussed in the previous sections, although natural polymer-based SAPs can offer excellent biodegradability, application of these materials remains to be restricted from the difficulties encountered during the functionalization process. The large amount of hydrophilic groups (e.g. –OH, $-NH_2$, –NH–CO–) of such natural polymers are perfect to offer a high hydrophilicity, however, their aggregating structures, especially the existence of dense hydrogen bonding in the bulk structure restrict them from a large size expansion when exposed to water, or the degree of such change is not as significant as required for SAPs.

Recently, some innovative approaches have been reported in the direction of synthetic SAP systems by utilizing bio-based monomers. Among the known bio-based building blocks, itaconic acid (IA) and citric acid (CA) are highly promising bio-based monomer candidates. IA has a structure rather similar to acrylic acid, which perfectly contains a double bond and two carboxylic acid group (Fig. 22). Since 2004, IA has been selected as one of the twelve top platform molecules by the United States Department of Agriculture (USDA), which can be derived from lignocellulosic sugars [339]. Nowadays, biological synthesis of IA has been successfully launched industrially by using glucose as the starting material via fermentation processes where the filamentous fungus *Aspergillus Terreus* [340], is known to be the working microorganism. CA, which has three carboxylic and one hydroxyl group in its molecular structure, is another well-known bio-based monomer with a global annual production of over 2000,000 tons [341,342]. Aside from being renewable and have low cost and low toxicity, this building block is featured by the presence of three carboxylic groups, which apparently makes this an excellent candidate to build the SAP material via polycondensation reaction and to afford a product with one pendant hydrophilic acid group in each repeating unit when the region-selectivity is well controlled during polymerization. This pendant carboxylic group can further serve as the reaction site for cross-linking to form 3D networks [343].

It is interesting to understand the possibility of utilizing both monomers for SAP synthesis. As shown in Fig. 22, both radical polymerization and polycondensation can be conducted for IA for such a purpose. In the case of free radical polymerization, usually only low to medium molecular weight (M_w=1000–200,000 g/mol) poly(itaconic acid) (PIA) can be produced, even after a long reaction time [343–346], because of the relatively low reactivity of IA [347,348]. The vinyl group of IA faces a much larger steric hindrance compared to acrylic acid due to the existence of the pendent $-CH_2COOH$ group. To overcome this issue, some researchers have demonstrated the radical copolymerization of IA with additional acrylate-based monomers for obtaining high MW copolymers, which are therefore only partially bio-based (unless the acrylates are bio-based as well, which could become reality soon). For instance, Hamshary and Karadag et al. prepared such a system by using sodium persulfate or *N, N, N’, N’*-tetramethylenediamine (TMEDA) as initiator or under gamma radiation [349,350]. It was found that the amount of residual monomer (e.g. the toxic acrylamide) was extremely low at the end of the copolymerization when a dose of 2.00 kGy gamma radiation was used, and the cross-linking reaction between acrylamide and itaconic acid was fairly complete, affording almost a full gelation of the system [350]. The absorption capacity of this IA-based SAP, however, was fairly low ($\sim$ 9–21 g distilled water/g SAP), which is far inferior to the acrylate-based SAPs. This finding may seem a bit unexpected, given the fact that the main chains of IA-based (co)polymers made by free radical polymerization strongly resemble those of the polyacrylates-based ones and also have quite similar COOH contents. Another similarity of radically-polymerized IA-based (co)polymers is the presence of non-biodegradable, highly stable carbon-carbon bonds in their main chain, and hence like the polyacrylates are presumably non-biodegradable. In a separate re-

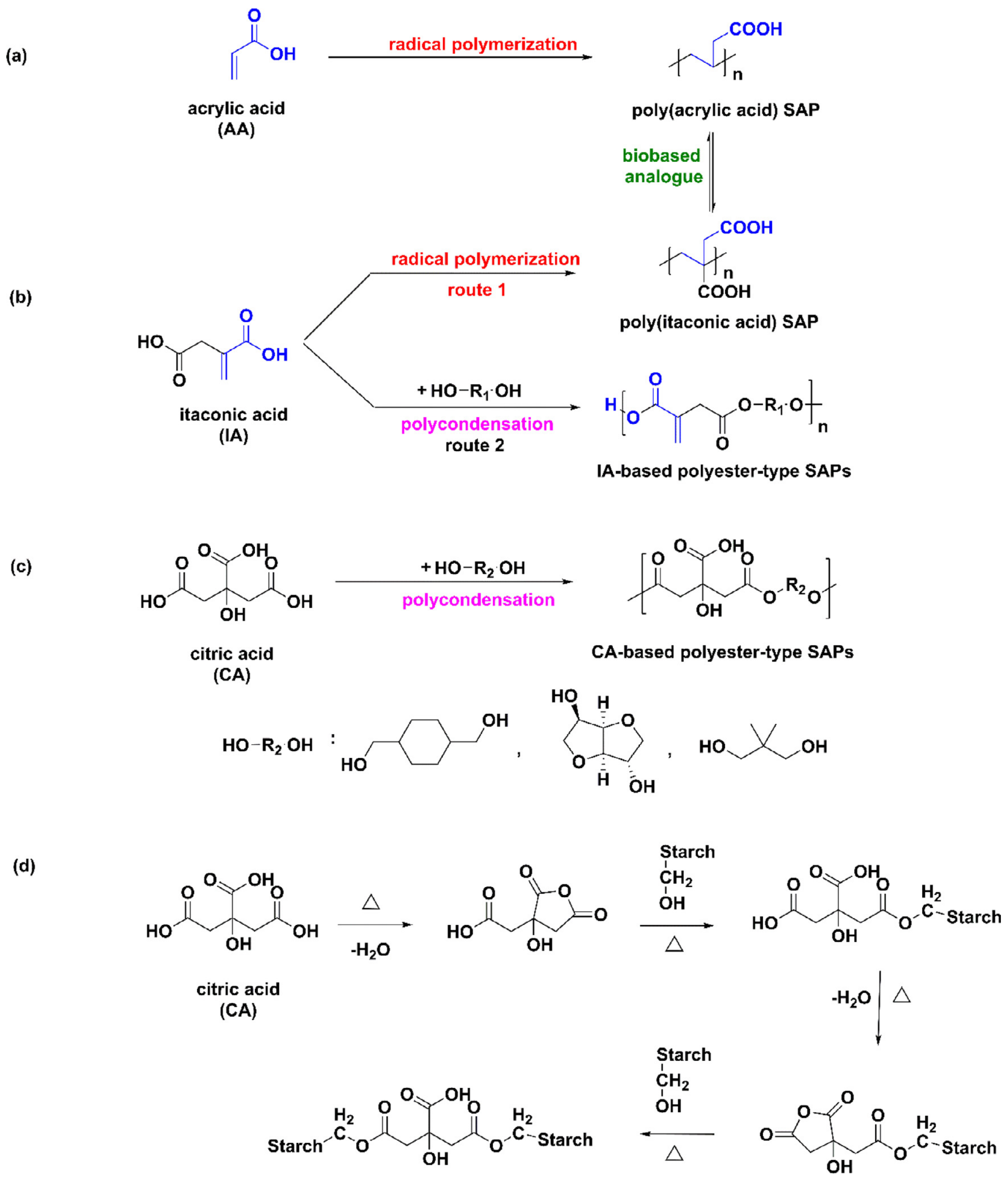


Fig. 22. (a) Structural similarity of acrylic acid and itaconic acid; (b) polymerization methods for itaconic acid, radical polymerization (above) and polycondensation (below); (c) synthesis of ester-type SAPs from citric acid. [110], Copyright 2017. Reproduced with permission from Elsevier. (d) Cross-linking reaction mechanism of starch with citric acid [343]. Copyright 2013. Reproduced with permission from Taylor & Francis Group.

port, IA was used to construct a biodegradable SAP system. However, in this report cassava starch was the main substrate, while poly(itaconic acid), together with poly(acrylamide), were grafted onto the substrate to introduce free acid groups for absorption capacity enhancement [351]. A detailed description of compositions and properties of these IA-based SAPs of section can be found in Table 10.

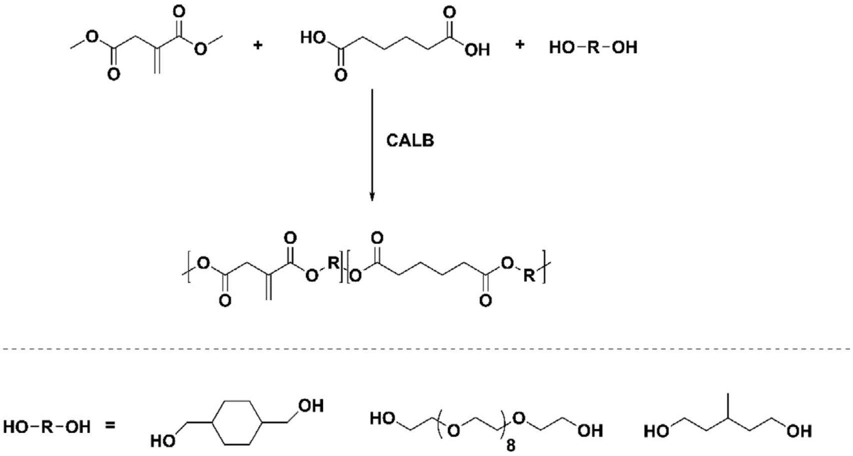
In the case of polycondensation, the unsaturated double bond in IA molecules may lead to undesired cross-linking, which leads to the formation of gel during polycondensation at elevated temperatures [352]. To avoid such undesired cross-linking side reactions, polycondensation of IA under enzymatically catalyzed conditions can be a better option. Yousaf and coworkers [353] synthesized different IA-based polyesters by this protocol in combination with a second dicarboxylic acid and trimethylolpropane (Scheme 5). This work resulted in moderate molecular weights around 12,000 g/mol. However, to the best of our knowledge, this building block has not been fully explored towards the application as a SAP system with relatively complete characterization of the crucial material properties.

CA can be utilized as monomer [110] or cross-linker [207,354–362] in the production of bio-based SAPs (Fig. 22). On one hand the multifunctional bio-based monomer CA, which is cheap, environment-friendly, nontoxic, and biodegradable, has been used for the cross-linking of natural polymers such as starch and cellulose [343,360,362]. Crosslinking proceeds via a mechanism where

Table 10
Composition and properties of SAPs containing itaconic acid (IA).

Component	Cross-linker	Initiator	Absorption capacity[a] (g/g)	Degradability	Reference
Poly(AM-co-IA)	MBA	KPS and TEMED	1.7	NA[b]	[349]
		irradiation	2.1	NA	[347]
AM/IA grafted onto cassava starch	NA	APS and TEMED	379	Partially biodegradable	[351]

[a] If not indicated specifically, absorption capacity is measured in distilled water; and the unit is g/g for all case.
[b] NA means not available or not applicable.



Scheme 5. Polycondensation of branched polyesters based on itaconic acid. [353], Copyright 2010. Reproduced with permission from American Chemical Society.

the two carboxylic acid groups in CA molecules form an anhydride through the loss of a water molecule [343]. Then, this anhydride reacts with a hydroxyl group on the polysaccharide to form an ester bond (Fig. 22). On the other hand, CA can be used as a comonomer in the polycondensation process for production of bio-based SAPs. Kim et al. performed a study on polyester-type SAPs (Fig. 22) by ground-up synthesis [110]. The authors conducted reactions of CA with various diols through simple melt polymerization. Post-treatment of the prepolymer by hexamethylene diisocyanate (HDI) was conducted for secondary cross-linking. The authors did not report the biodegradability of this type of SAPs and the maximum water absorption reported is only about 22 g distilled water/g SAP. However, this work is a good example showing the potential of synthesizing bio-based polycondensate-type SAPs with potential biodegradability because of the presence of many hydrolyzable ester bonds in the SAP network. Further performance enhancement towards higher water absorption capacity and good/controlled biodegradability, as well as better structural controllability by structural design, are required next steps to fully benefit from the potential advantages of biodegradable SAPs with respect to the currently popular petroleum-based and non-biodegradable synthetic SAPs, that after ending as landfill will inevitably generate persistent microplastics that may appear in our food chain.

14. Conclusions and outlook

In view of an increasing world population and an increasing higher average age, the consumption of baby diapers and adult incontinence products has also increased accordingly. Such a trend is expected to play a vital role in shaping the global superabsorbent market over the forecasted period. Nowadays, polyacrylate-based SAPs dominate the market. However they are non-biodegradable and most of them are thrown away in the nature or undergo incineration, either of which will impose a great damage to our environment. In addition, new regulations banning of the use of disposable plastic products, especially persistent microplastics-generating species (see ECHA Annex XV Restriction Report on microplastics [69]), will come into force in the (near) future. We believe that the development of biodegradable alternative SAPs can be the ultimate ecofriendly solution for tackling above issues. Along with the mentioned environmental issues, depletion of oil reserves is another big problem humans encounter. To overcome shortage of petroleum resources, utilization of renewable polymers including cellulose, starch etc. for the production of SAPs seems a good solution. Unfortunately, these natural polymer-based SAPs usually have unsatisfactory absorption capacity or too low gel strength after swelling, which limit their wide application as hygiene products.

Different from using existing macromolecules, hydrolyzable, polycondensate-type SAPs synthesized from renewable monomers stand a chance to deal with above two big problems. So far, only one example is available in literature showing that this type of SAPs may offer a feasible solution, but the reported system needs to be improved (absorption capacity: merely 22 g distilled water/g SAP) [110]. Unfortunately, the biodegradability of the reported polyester-based SAP was not investigated. The challenge is to significantly enhance the water absorption capacity of this type of SAPs. By choosing even more hydrophilic monomers and cross-linkers, keeping a very high neutralized carboxylic acid concentration, and by optimizing cross-linking density using biodegradable cross-linking units, it should be possible to produce bio-based, biodegradable SAPs.

This review, presenting a comprehensive overview of the different types of SAPs, was written to motivate both academic and industrial scientists to start working on the design of bio-based and biodegradable SAPs. In our view the group of bio-based and biodegradable polycondensate-based SAPs is the most promising and future-proof class of superabsorbent polymers, fully in line with the new upcoming legislation, aimed at avoiding the formation of persistent micro-plastics in our environment.

Till now, the so-called ‘biodegradable SAPs’ are basically produced by using the natural polymers such as cellulose, chitosan and starch as the matrix material. Introduction of additional acrylates on these substrates are unavoidable to gain sufficient water absorbing capacities. The biodegradability of them mainly come from the natural polymer part, and the pendant acrylic parts remain non-biodegradable. The total weights of these acrylates parts are generally over 50wt%. It is reasonable to assume that these products potentially can also generate microplastics once the natural polymer backbone degrades. Therefore, we believe the scientific focus should be placed on devising novel SAPs with the entire network fully biodegradable. This task is challenging in terms of how to gain a balance among a good water absorbency, sufficient mechanical properties, and a good biodegradability even at high cross-linking densities. The polycondenate type of SAPs as discussed in this review, especially those utilizing bio-based building blocks with unique chemical structures can be a promising research direction, but more innovative protocols are highly desired to bring real breakthrough in this field. Undoubtedly, the success of biodegradable SAPs is the determining step when the real biodegradable hygiene products are discussed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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