

Advances in non-hygienic applications of superabsorbent hydrogel materials

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Abstract Superabsorbent polymers (SAPs) are organic materials with lightly crosslinked three-dimensional structure possessing high to very high swelling capacity in aqueous media. These are in fact the most commercially successful members of the hydrogel family. The SAP production for personal care products (baby diapers and feminine incontinence products) accounts for about 80% of the overall hydrogel production. Research during the past 30 years, although not affected the commercial status of SAPs, has led to more and more understanding of superabsorbent structures, their properties, and potential uses. Beyond the hygienic use, the SAPs have found very wide applications from the agricultural formulations to pharmaceutical dosage forms. Since hygiene applications of SAPs are very well established and well reviewed, this article reviews and highlights the SAP applications in other sectors, such as in agriculture, pharmaceuticals, separation technology, fibers/textiles, water-swelling rubbers, soft actuators/valves, electrical and construction.

Introduction

Hydrogels are macromolecular networks of hydrophilic polymer chains, with the ability to absorb aqueous fluids. In contact with the aqueous medium, the hydrogels swell to the extent, which is mainly determined by the hydrogel network crosslink density. Hydrogels, in general, are highly crosslinked and are made of less hydrophilic monomers, such that their absorption capacity is very low. Superabsorbent polymer (SAP) hydrogels, on the other hand, are generally based on ionic monomers and are lightly crosslinked; therefore, they display an exceptional capacity of water absorption [1]. While swelling or absorption capacity of general hydrogels in water is less than 100% (1 g/g), the SAPs can imbibe as much water as about 1,000–100,000% (10–1,000 g/g) [2].

With the initial and successful use of hydrogels in contact lenses, the hydrogel applications are now widespread [3–6]. Hydrogels are currently used as scaffolds in tissue engineering, where they may contain cells to repair defective tissues. Environmentally sensitive hydrogels can sense the changes in pH, temperature, or the concentration of metabolite, so that they can release their load as a result of such changes. Hydrogels that are responsive to specific molecules (e.g., glucose or antigens) can be used as biosensors and as controlled-release delivery systems for bioactive agents and agrochemicals.

The SAP hydrogels with the ability to absorb urine and blood are used in hygiene products such as in baby diapers and feminine incontinence products, and they account for most of the commercial SAP use. Since there are several review papers on hygienic use of the SAP hydrogels, this article attempts to cover non-hygienic applications of SAPs.

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The SAP history and market

Since acrylic acid and divinylbenzene were first polymerized in an aqueous medium in 1938 [1], it took about a decade to witness the first generation of hydrogels with a successful commercial use. These hydrogels displayed a swelling capacity of up to 40–50% and were mainly based on hydroxyalkyl methacrylate and related monomers with similar structures. They were used in development of contact lenses which marked a revolution in ophthalmology [7]. Alkaline hydrolysis of starch-*graft*-polyacrylonitrile (SPAN) led to the first commercial SAP. The product, HSPAN, was developed in the 1970s at the Northern Regional Research Laboratory of the US Department of Agriculture [6]. High price and poor mechanical properties of this product were major factors of its early commercial failure. The commercial production of the first fully synthetic SAP began in Japan in 1978 for use in feminine products. Further developments led to the use of SAP hydrogels in diaper products in Germany and France in 1980. In 1983, low-fluff diapers (contained 4–5 g SAP) were marketed in Japan. This was followed shortly by the introduction of thinner superabsorbent diapers in other Asian countries, the US and the Europe. The SAPs with better wet strength ability could successfully replace the bulkier cellulose fluff, and hence thinner diapers were produced [3]. As a result, the SAP hydrogels caused a huge revolution in the personal health care industries in just over 10 years.

In late 1990, the world production of the SAP resins was more than one million metric tons and major manufacturers were Amcol (Chemdal), Stockhausen, Hoechst, Sumitomo, Sanyo, Colon, Nalco and SNF Floerger [8]. According to the European Disposables and Nonwovens Association (EDANA) [9], the total SAP production in 2005 approached to around 1,483,000 million metric tons; 42% in Asia (mostly by Nippon Shokubai, San-Dia Polymers and Sumitomo Seika Chemicals), 33% in the North America (by Degussa, BASF, Dow and Nippon Shokubai), and 25% in Europe (mostly by Degussa and BASF).

Preparation of absorbent core for ultra-thin high-absorbent sanitary napkins has recently been developed using superabsorbent fiber and viscose fiber [10]. As a result, a new generation of hygienic superabsorbent, Safe and Natural Absorbent Polymer (SNAP), has been introduced to the market [11]. SNAPs are totally natural with no residual monomer, and are rapidly biodegraded in the environment. However, they possess lower absorbency and higher price compared to their fully synthetic counterparts.

The SAP literature

The first book to cover the fundamentals of the synthetic hydrogels was published in 1990 [3]. From commercial

prospective, the first of such literature prepared by the Stanford Research Institute, SRI, which covered the acrylic-based SAPs [12]. Synthetic methods and properties of hydrogel networks [13], as well as synthetic, semi-synthetic, and biopolymeric hydrogel materials have been reviewed [14]. In an article published in 1994 [5], Ricardo Po critically surveyed the water-absorbent polymers from the patent perspective. Buchholz has elaborated the uses of superabsorbents based on crosslinked, partially neutralized poly(acrylic acid) and graft copolymers of starch and acrylic acid [15]. In another review, the synthesis of the crosslinked acrylic acid-co-sodium/potassium acrylate has been described with some details on the production methods [7]. Meanwhile, a more comprehensive book on the synthetic SAP materials was published in 1998 [1]. Fibers and textiles with high water absorbency characteristics are covered in “Absorbent Technology”, published in 2002 [16].

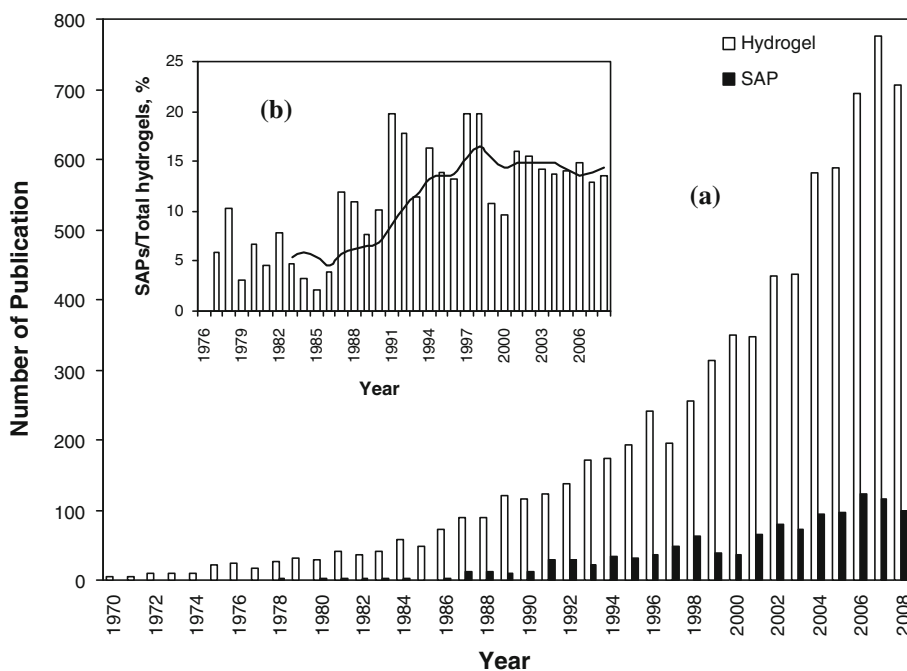
The chemistry and physics of agricultural hydrogels were reviewed by Kazanskii and Dubrovskii [17]. Bouranis et al. [18] have reviewed the synthetic polymers as soil conditioners. Superabsorbents obtained from shellfish waste have also been reviewed [19]. There are also certain reviews on the superabsorbent products based on polysaccharides and proteins [20], and those based on graft copolymers of acrylic acid and gelatinized starch [21]. In one review, a reader can find several practical methods for testing and evaluation of SAP materials [2].

Figure 1 exhibits the number of publications (periodical research journal papers, patents, etc.) in the area of SAPs when compared to those in general hydrogel area in the past 30 years. A growing trend of activities related to the SAP materials is highlighted, particularly since 1990.

SAP classes and uses

Depending on the backbone charges, the SAPs may be categorized to non-ionic, ionic, ampholytic, and zwitterionic [8]. In this regard, the majority of the commercial SAPs contain negative backbone charges, so they are anionic. They are also classified based on the type of monomer units used in their chemical structure, e.g., crosslinked polyacrylates or polyacrylamides, and hydrolyzed cellulose-polyacrylonitrile (PAN) or starch-PAN graft copolymers [5, 8]. When the term “superabsorbent” is used without specifying its type; it generally implies the most conventional types of SAPs, i.e., the copolymers of an acrylic salt either with acrylic acid (AA) or with acrylamide (AM). Based on their sources, the SAPs are often divided into synthetic (petrochemical-based) and natural. The natural-based SAPs are those based on polysaccharides and polypeptides (proteins).

Fig. 1 Growing trend of publications (periodical research journal papers, patents, etc.) in the area of hydrogels and SAPs in past three decades as of July 2009 (data obtained through Google-Scholar (a) number of publications for hydrogels (excluding SAPs) (white) and for SAPs only (black). (b) Percentage of SAP-to-total hydrogel publications exhibiting an average trend (black line). Note: The internet search was accordingly made using *hydrogel* and *superabsorbent* keywords occurred “in the title of the article”



Most recently, protein- and homopoly(amino acid) based super-swelling hydrogels have been reviewed [22]. The SAPs can also be categorized based on their fields of application, e.g., hygienic and agricultural hydrogels. Figure 2 shows classification of SAPs with applications beyond the hygiene sector.

Medical and pharmaceutical uses

In medicine, biocompatible SAPs may be used to remove the body fluids during surgery. Sannino et al. [23] reported the biomedical application of a cellulose-based SAP for imbibing body fluid in the treatment of edemas. The hydrogels are based on carboxymethylcellulose sodium salt (CMC) and hydroxyethylcellulose (HEC), chemically crosslinked with divinylsulphone. The sorption capacity of these polyelectrolyte hydrogels was found to be very sensitive to the ionic strength and pH of the external solution, which was a key parameter for the application under investigation. The hydrogel biocompatibility studies show that the gel can be considered as an alternative to diuretic therapies in those pathologic conditions in which edemas occur [24]. Biocompatible sodium salt of CMC, HEC, and polyethyleneglycol (PEG) with various molecular weights were used to prepare orally administrable hydrogels with the ability to absorb large amount of water [24]. Hollow and flexible crosslinked microcapsules of soybean protein were produced to obtain maximum plasma absorption of approximately 2000% [25]. The presence of residual unreacted protein inside the microcapsules was believed to be the main osmotic driving force. SAP microparticles were

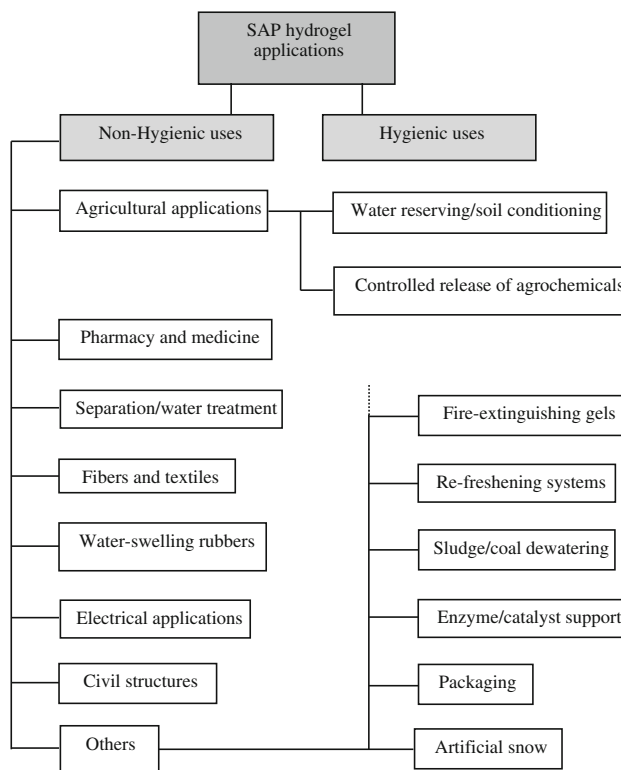


Fig. 2 A classification for SAP hydrogel applications

used safely in transarterial embolization (TAE) treatment of arteriovenous malformations (AVM). TAE treatment with use of the particles was found to be suitable for certain symptomatic AVMs. Histologically, the SAP microspheres could penetrate the intralesional vessels and conformed to

the vessel lumen, resulting in tight vessel occlusion [26]. This initial experience suggests that embolization with use of the SAP particles leads to extensive tumor necrosis of large nodular HCC, sparing the use of chemotherapeutic agents [27]. Bland embolization of HCC using SAP microspheres has also been investigated [28]. The intracerebral injection of a high-capacity SAP was performed to study the functions of hypothalamic areas in controlling the female productive cycle [29]. In another research, clinical evaluation of transcatheter arterial embolization with SAP microspheres has been reported for hypervascular metastatic bone tumor of the pelvis [30].

Plugs, hemostatic, or other medical devices have been designed using freeze-dried SAP hydrogels [31]. The device may be introduced into body to implant or to seal a puncture or other passage through tissue.

SAPs have also been used to develop drainage to absorb body fluids [32]. The bags are lightweight, compact, and easy carrying without backflow, independent of its position. Another invention deals with surgical drape with SAP for fluid management [33]. It includes a sheet configured for covering at least a portion of the patient.

Polyacrylate SAP hydrogel has been employed as a wound dressing core covered with a non-adherent knitted polypropylene fabric, TenderWet, which was found to be a better alternative to other methods of debridement. Micro-organism absorption properties of the polyacrylate debridement have been studied by Bruggisser [34]. In vitro data showed that the hydrogel dressing attracted and retained micro-organisms and reduced the number of viable germs.

SAPs with antibacterial activity have been prepared by Lee and Huang [35]. Superabsorbents containing silver nanoparticles were prepared from sodium acrylate, *N*-vinyl pyrrolidone–Ag⁺ complex and methylenebisacrylamide by inverse suspension polymerization. The Ag⁺ ions in the gels are reduced to Ag nanoparticles in the presence of vitamin C. The water absorbencies for the gels containing 1–10 ppm silver were lower than that of Ag-free gels (1016 g/g water). The study on the antibacterial effect (*Candida albicans*) of the hydrogel showed that the inactivation efficiency of the hydrogel could be increased with increase in the silver content and reached 90% (after 2 h) for the SAP sample containing up to 10 ppm Ag.

In the field of pharmaceuticals, a class of SAPs (i.e., superporous hydrogels, SPHs) was invented by Park and co-workers [36]. The SPHs were originally intended for gastric retention applications [37–39]. The SPHs, hydrogels with pore sizes in the range of 100 μm and larger, are different from SAPs in a sense that swelling rate of SPHs is independent of the hydrogel size [40]. The very fast swelling property of the SPHs is due to an increased capillary of the interconnected pore structure [41]. Figure 3 shows the morphology of a typical SPH sample.

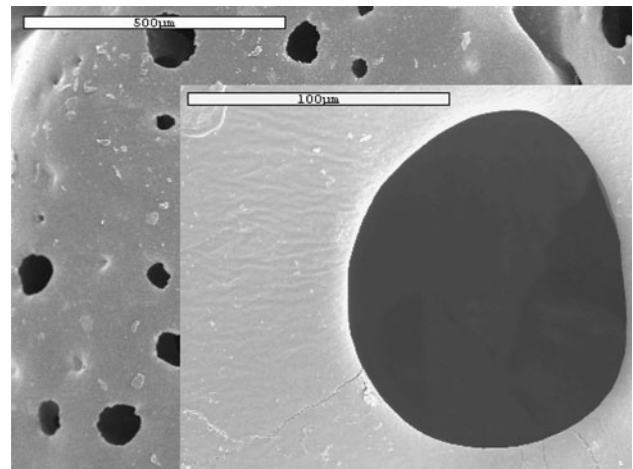


Fig. 3 Morphology of a typical superporous hydrogel (SPH) with an average pore size of about 70 μm

The SPHs have been essentially designed for prolonging the retention of the drug in the stomach or in the intestine. The pH-responsiveness of poly(AM-*co*-AA)-based SPHs was investigated by Gemeinhart et al. [42]. Effect of compression on the SPH swelling was also studied [43]. A method of coating the SPH surface with a layer of an amphiphilic block copolymer, poly(ethylene glycol-*b*-tetramethylene oxide), has been introduced to control the swelling kinetics of SPHs in aqueous solutions [44]. Hydrophilic poly(ethylene glycol) (PEG) grafts were introduced into SPHs to enhance the equilibrium water absorption rate to as fast as 20 s. These PEG-grafted SPHs may be useful for certain bioapplications where a fast swelling kinetics is critical [45].

Thermosensitive SPHs were also synthesized using *N*-isopropylacrylamide (NIPAM) and acrylamide (AM). Upon increase in temperature from 10 to 65 °C, the SPH made of 9:1 ratio of NIPAM/AM was shrunken from its fully swollen state (36 cm³) to the collapsed state (6.5 cm³) in 72 s. It swelled to 36 cm³ in 78 s when the temperature was reduced down to 10 °C [46]. These typical fast responsive hydrogels may find applications in the pharmaceutical and biomedical areas.

SPHs, because of their porous structure and high absorption capacity, yet suffer from poor mechanical strength. To generate strong and elastic polyacrylamide SPHs, an experimental design, based on L-18 Taguchi matrix, was used to examine the influence of formulation ingredients on a variety of aspects of gel formation during the synthesis [47]. However, the mechanical weakness was mainly overcome by development of the second-generation SPH composites (SPHCs) and the third-generation SPH hybrids [48]. The gastric retention property of the prepared SPH composites has been tested in dogs both in fasted and

in fed states. The SPH composites were placed in a hard gelatin capsule for oral administration [37]. It was indicated that the SPH composites possess the desirable properties for gastric retention including fast swelling, super-swelling, and high mechanical strength (Fig. 4a). As a result, these provided the basis for the development of effective and durable gastric retention devices [37, 38, 48].

SPHCs have been reviewed by Park et al. [49]. Recently, Demirtas et al. [50] have synthesized and characterized polyacrylamide-based SPHCs containing hydroxyapatite. The compressive modulus for the SPHC was found to be 6.59 N/mm^2 as opposed to 0.63 N/mm^2 for the non-composite SPH. The cytocompatibility toward fibroblasts was confirmed using L929 fibroblasts. Because

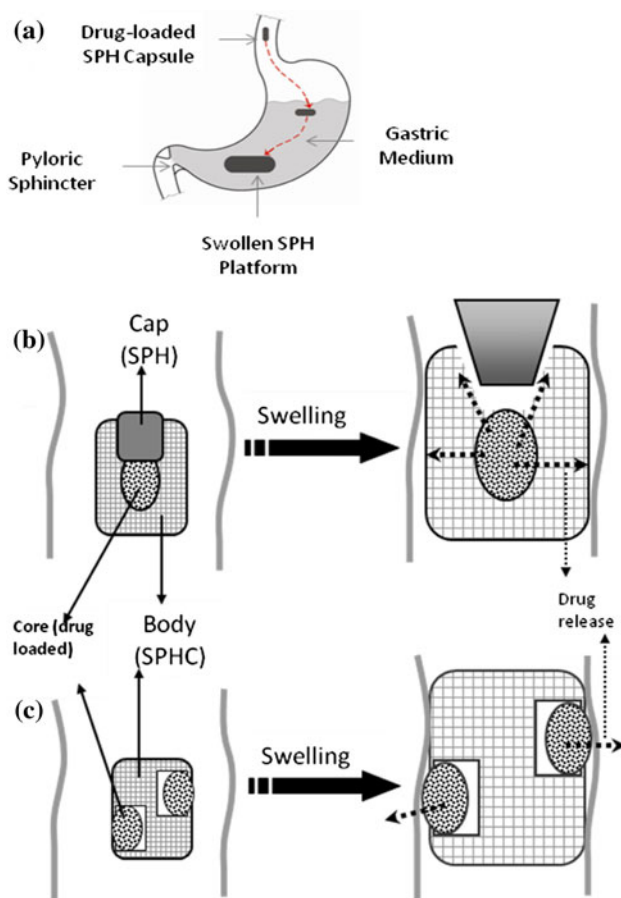


Fig. 4 Superporous hydrogel-based oral drug delivery. **a** Transit of SPH-based drug-loaded gastroretentive capsule in stomach. The swollen platform (larger than the pyloric sphincter) persists against harsh stomach medium and contractions. The SPH-based shuttle systems designed for controlled peptide drug delivery to intestine: **b** core inside the conveyor system consists of the drug contained microparticles including the peptide. Drug is released from the core after removing the cap due to its more and faster swelling than the core; **c** core outside the conveyor system contains a mixture of the drug and lactose which are pressed to minitablets. Drug is released after swelling and attachment the system to intestinal wall

of their enhanced mechanical property, these SPHs have a potential application in scaffolds for bone tissue engineering.

Most recently, the potential of SPH scaffolds based on PEG diacrylate for in vivo cellular infiltration and vascularization has been shown [51]. The neovascularization and limited fibrotic response have suggested that the SPH architecture may be conducive to cell survival and rapid vessel development.

The SPHs and SPHCs can provide the basis for the development of effective and durable gastric retention devices [48]. For instance, varieties of SPH-based oral peptide delivery systems have been developed. Dorkoosh et al. prepared optimized SPH and SPHC formulation, and characterized them using NMR spectroscopy [52]. The hydrogels were used to develop two different controlled delivery systems for peroral administration of peptide and protein drugs for site-specific mechanical fixation at the gut wall and with specific release patterns [53]. These so-called shuttle systems keep the dosage form at the site of drug absorption by mechanical interaction of the dosage form with the intestinal membranes. The focus of these novel systems is to achieve a “double phase time-controlled release profile” [54] and to target the dosage form into the desired site(s) of the intestinal tract [55]. The in vitro characteristics of these polymers showed a promising time-controlled release profile for a model drug [53]. As shown in Fig. 4b and c, the drug carrier system can accommodate the drug either in its center or at its surface. With the former, drug is released followed by the SPH swelling while with the latter the drug is directly released to the intestine tissue after SPH is completely attached into the intestine wall.

The capability of SPH and SPHC polymers were evaluated ex vivo for their potential to enhance the transport of model compounds of different molecular weight, across the porcine intestine [56]. Moreover, the possible damaging effects of SPH and SPHC polymers on the intestinal epithelium, the ability of these polymers for mechanical fixation in a segment of the intestine, and the effects of the hydrogels on paracellular drug permeability and cytotoxicity were investigated in Caco-2 cell monolayers [57]. Release characteristics of a few protein drugs including busferelin, octreotide, and insulin from these hydrogels [58], intestinal absorption of human insulin in pigs [59], in vitro evaluation of intestinal absorption of desmopressin [60], mechanism of opening the paracellular tight junctions using SPHs in Caco-2 cell monolayers [61], peroral absorption of octreotide in pigs [62], and the retention of SPHC in the intestinal tract of man [63] have been studied.

It was shown that orally administered insulin in combination with SPH and SPHC is absorbed through the gastrointestinal tract in its biologically active form. This was demonstrated by suppression of endogenous insulin

secretion [64]. Polnok et al. [60] have shown that AcDiSol[®] (crosslinked sodium carboxymethylcellulose) can optimize the properties of the SPHs as peroral carrier of the peptide drugs. It was established in vitro that these delivery systems with and without TMC (*N*-trimethyl chitosan; a quaternized ammonium salt of chitosan) as additional absorption enhancer can improve the transport of desmopressin across porcine intestinal membranes via opening the tight junctions and increasing the drug concentration at the surface of the mucosal epithelium. Peroral peptide and protein delivery systems including SPH/SPHC have been reviewed by Dorkoosh et al. [65].

The superporous superabsorbents have expanded their applications in the pharmaceutical sector. For example, poly(acrylic acid) SPH microparticles were used as super-disintegrant in fast-disintegrating tablets [66]. Another research team introduced Carbopol, a commercial poly(acrylic acid) gel, into the SPH structure to improve its mucoadhesive and swelling characteristics [67].

Natural compounds, such as carbohydrates, have also been studied in preparation of superporous SAPs. Chen and Park [68] prepared superporous crosslinked network of sucrose hydrogels (sucrogels). Followed by introducing double bonds into sucrose via reaction with glycidyl acrylate, the acrylated sucrose was polymerized and was made porous by incorporating a porogen into the polymerization mixture. The fast swelling sucrogel SAPs could be used in various applications, including controlled drug delivery. Park et al. [69] prepared glyoxal-crosslinked chitosan and glycol chitosan SPHs utilizing a freeze drying or gas blowing technique and evaluated them for gastric retention application.

Omidian et al. [70] developed a SPH hybrid with superior mechanical and elastic properties. They polymerized acrylamide in the presence of a water-soluble alginate polymer as well as a chemical crosslinker. Then, the alginate part of the semi-interpenetrated hydrogel was ionically crosslinked to generate a fully interpenetrated network possessing resilience and a rubbery property in its fully water-swollen state. Omidian et al. [71–73] have reported several approaches to reinforce SPHs.

Similarly, incorporating polyacrylonitrile into the SPH structure has resulted in enhanced mechanical property up to 50 times higher than of the control SPH [74].

Yin et al. [75] prepared poly(AA-*co*-AM)/*O*-carboxymethyl chitosan interpenetrating polymer networks (SPH-IPNs) and evaluated their sensitivity toward the pH, ionic strength, and temperature stimuli. With insulin as a model drug, polymer–protein interaction was detected. Precise tests, such as in situ lactate dehydrogenase assay and morphological study on rat intestine, confirmed that the SPH-IPNs are desirably biocompatible. These distinct properties suggested that the SPH-IPNs could be developed

as an attractive peroral delivery vehicle for peptide and protein drugs [75]. Beneficial properties for insulin absorption using SPH-IPNs as an oral delivery carrier has been investigated [76]. Cytotoxicity and genotoxicity of SPH-IPNs were studied as well [77]. The study shows no evidence of induced cell apoptosis or DNA breakage or increased micronucleus incidence in mouse bone marrow. Therefore, the SPH-IPN was preliminarily considered to be biocompatible and might be a safe carrier for protein drugs. In addition, using the HPLC method, residual AA, AM, and glutaraldehyde in the SPH-IPN were quantified as 1.4, 2.0, and below 0.2 ppm, respectively. The biocompatibility of the SPH-IPN can partially be accounted for in terms of a very low concentration of reactive low molecular weight monomer and crosslinker.

Poly(vinyl alcohol) (5 w/w%) has been shown to be very effective in improving the mechanical strength of the swollen semi-IPN SPHs prepared from 3-sulfopropyl acrylate potassium salt (SPA), acrylic acid, and PEG diacrylate [78]. The mechanical strength of the fully swollen hydrogel in a pH 1.2 HCl medium was found to be over 200 g/cm². The optimal swelling and mechanical properties of this formulation suggest its potential as gastroretentive delivery system.

Kim and Park [79] prepared an SPH based on poly(AM-*co*-AA)/polyethylenimine (PEI) semi-IPN. High mechanical strength was provided by the entanglement associated with the highly branched structure of PEI and charge attraction between PEI and AA. However, as a strong polycation, the PEI does not seem to be suitable for peroral drug-delivery systems due to its certain cytotoxicity.

A full-IPN superporous hydrogel containing sodium alginate (IPN-SPH_{Alg}) was recently synthesized by cross-linking the sodium alginate with calcium ions after the SPH formation [80]. The effects of the full-IPN on the structure morphology, swelling behavior, and mechanical strength were investigated. No significant cell or mucosal damage was caused by the SPH superabsorbent. Fast swelling, good mechanical properties, pH sensitivity, and biocompatibility suggest the use of IPN-SPH_{Alg} as a controlled delivery carrier.

Hydrogel networks containing psyllium husk, a medicinally important natural polysaccharide and acrylic polymers have been prepared for developing controlled drug delivery devices. The abrupt swelling increase (e.g., from 1400 to 5000%) by changing the swelling medium indicated the smart behavior of the network. Due to its pH sensitivity, it has a potential to be used as colon-specific drug delivery carrier [81].

Polyacrylate/polyaniline hybrids [82] and poly(acrylamide-aniline) interpenetrating polymer networks (IPNs) [83] were synthesized by a two-step aqueous polymerization method. The conductivity of the hybrid and IPN was

measured to be 2.33 and 25.28 Ms cm⁻¹, respectively. While being thermosensitive, the conductive superabsorbent hydrogels displayed an anomalous release mechanism.

There has also been considerable interest in utilizing crosslinked-CMC and other natural-based SAPs as tablet disintegrants [84]. The hydrogel in its powder form is mixed with the other excipients and compressed to a tablet which, upon contact with water or acidic solution, rapidly expands to aid in disintegration of the tablet [60]. Compared to traditional starch and starch derivatives [85], the crosslinked CMC reduces the disintegration rate and increases the dissolution rate. Tablets containing superabsorbent may soften at high humidity and may add instability concern to the moisture-sensitive drugs.

SAPs containing nanofiber hydrogels were prepared by electrospinning technique and they might be suitable in drug delivery and wound care applications (see “Fibers/textiles”).

Innovations have been published in numerous patents on the medical applications of SAPs. Riesinger described a wound care article including a layer of SAP and a foam layer [86]. A medical device for use in the treatment of urinary disorders including a SAP material has been disclosed [87].

Rahmouni et al. have introduced a misuse preventative system of controlled release pharmaceutical formulation, including a SAP material as a core. When crushed and exposed to an aqueous medium, the SAP material present in the core swells to encapsulate the microparticles, which remains substantially intact; so, retarding the release of the pharmaceutically active agent. Using the misuse preventative, release formulation is controlled to deliver a pharmaceutically active agent to a mammal, e.g., a human [88].

SAPs have been used to make improved wound dressing, comprising an absorbent layer including one or more absorbent and/or SAP materials; a porous, non-stick layer or film and overlying, a wound-facing surface of the absorbent layer such that a portion of the non-stick layer extends beyond the length and width of the absorbent layer; a protective cover layer [89].

A process for manufacturing wound dressing has been invented that efficiently absorbs fluid from wounds and can easily be released from the wound without disrupting the wound surface. The dressing comprises a layer of film bonded to a fibrous absorbent web containing a mixture of a particulate SAP and a hydrocolloid [90].

A medical compress for use in treating chronic wounds includes a non-woven textile fabricated from air laid fibers containing a SAP material. The superabsorbent material is enclosed by a knitted mesh which can be formed to the shape of the wound. An irrigation solution is preferably contained by the compress to keep the wound irrigated and to encourage healing [91].

Hobson et al. have disclosed methods for production of an anhydrous, hydrophilic wound dressing, containing a SAP polymer and an antimicrobial agent. The anhydrous nature allows it, when applied to a wound site, to absorb wound fluid and slowly release its water-soluble active microbial agent into the wound [92].

A process for production of cellulosic materials having high water-retention capacity has been described which are suitable for the production of hygiene products, baby or disposable diapers, sanitary towels, tampons, incontinence articles, absorbent patches, wound dressings, strappings, bandages, absorbent cloths, moisture-absorbing clothing, bed matting, filter materials or filters, packaging materials, or cable sheathings [93].

A nano-silver wound dressing has been produced consisting of a skin contact layer made of hydrophilic cloth and directly contacting a wound on the surface of the skin, a disinfecting (or bactericidal) antitoxic layer made from activated charcoal cloth impregnated with nanocrystalline silver, a blood absorbing and styptic layer made of a SAP non-woven cloth, an isolation layer made of a composite fabric with fine pore size and an elastic bandage for fixing a main body on the site of wound [94].

Timmermans has disclosed production methods of wound dressings with the ability to absorb large amounts of wound fluids and water. For this purpose a SAP fiber was used, preferably consisting of polyacrylonitrile. The absorptive power of this fiber was obtained by saponification of surface molecules of the fiber. Through this, the core of the fiber will remain inviolable and the stability of the fiber is ensured [95].

A superabsorbent foam that carries graphical symbol on its surface was produced by polymerizing a foamed monomer mixture that contains an inorganic solid in a mold that carries graphical symbols on inner surface [96].

Fibers/textiles

The final form of a superabsorbent material, i.e., powder, granule, film or fiber, is determined by its application. An auxiliary feature of a superabsorbent material is that the aqueous fluid can be retained even under application of an external pressure. Such powders may usually be dispersed in multilayer non-woven webs of cellulosic and other textile fibers to provide absorbent pads. Even greater fluid holding capacity can be achieved when the SAP is in the fiber form.

The cellulose fibers are modified by esterification or etherification and, in many products, by controlled grafting of other hydrophilic polymers. A typical example of superabsorbent fibers is a crosslinked acrylate copolymer, partially neutralized to the sodium salt, which is now commercially available as Oasis[®] [97].

Due to wicking effect of the thinner fibers, non-woven webs and pads containing SAP fiber offer a faster fluid uptake than those containing powders [98]. SAP fibers are predominantly designed for towels and pads for hygienic and surgical uses. Sweat-absorbing inlays have been developed by incorporating SAP fibers to needled hot-pressed non-wovens [99]. The composition of 33% Oasis 102 (SAP fibers), 33% polyethylene terephthalate (PET fibers for transferring liquid), and 34% polypropylene (PP binding non-woven during hot pressing) was found to be an optimized composition. Compared to the cotton knits, traditionally used in the production of underwear, the product swelling capacity is almost four times higher as characterized by a liquid sorption technique. Sannino et al. [100] invented yarns with sweat absorption ability by incorporating SAP hydrogel inside the yarn itself, and eventually to release a perfume, which was previously absorbed inside the hydrogel. According to the invention, such a product after washing and drying can be used repeatedly. Moreover, the hydrogel is able to take the perfume of the washing soap in and, to retain it for a long time and finally to release it slowly.

In order to determine the role of SAP fibers in parallel non-woven interlinings, a series of dampness perception tests and a special humidity sensor as well as a static thermal resistance test device was used [101]. It was shown that dampness perception and fiber hygroscopicity were interrelated. The positive role of hygroscopic fibers in preserving thermo-insulating properties as well as “dry feeling” at high water content was also confirmed.

In another function, SAP acrylic fiber (acryorb) was spun into ring, rotor, and yarns, which were knitted to terrysock fabrics [102]. The quality of these fabric samples was evaluated and compared with that of terrysock fabric knitted from cotton ring yarn. The acryorb yarns acted well upon knitting, and the fabrics displayed better appearance and handle compared to the cotton fabric. The acryorb terrysock fabrics offered higher water absorption, water retention, drying capability, and air permeability than that of cotton fabric.

Electrospun nanofibers are made when electrostatic forces overcome the surface tension of a polymer solution, causing an electrically charged jet to be ejected; as the jet travels through the air, the solvent evaporates, leaving behind an electrically charged fiber, which can be collected in the form of a non-woven sheet [103]. Upon addition of superabsorbent to a polymer solution containing an elastomer, the mixture is electrospun, producing nanofibers in which the SAP particles are held in place using nanoscale elastic fibers. The water absorption capacity was found in the range of 400–5000%. Samples containing 0–70% superabsorbent reached essentially their maximum absorbency within 5 s. The excellent strength and elasticity of

the wet samples make these structured hydrogels ideal for many uses, including wound care, drug delivery, and sanitary goods [103].

The idea of making fibers out of hydrophilic monomers, such as AM, seems to be very motivating since the surface area per unit mass will increase enormously from granular to fibrous shape structures. Ali has recently reported a new generation of super-absorber ultra-fine PAM fibers (as PAM/PAN hybrid nano-fibrous fabric) by electro-spinning [104]. As theory and experiments suggest, the electro-spun PAM/PAN hybrid due to its very high surface/mass ratio can potentially be used in applications such as irrigation systems, diapers, napkins, etc.

Natural fiber composites have been prepared by grafting *n*-butyl acrylate (BA) onto chemically modified pineapple leaf fiber (PALF) using a complex-initiating system without and with additives of sodium silicate (SS) and *N,N'*-methylenebisacrylamide (MBA), as crosslinking agent. The chemically modified PALF, crosslinked PALF-*g*-poly(BA) copolymer, and (crosslinked PALF-*g*-poly(BA))/SS composites were characterized. Study shows that the composites offer a higher water uptake capacity than the copolymers, which makes it suitable as a natural superabsorbent fiber. Compared to the copolymer, the composite superabsorbent shows lower biodegradability in both sludge water and soil [105].

Poly(acrylonitrile-*co*-AA) with high acid content were synthesized and converted to fine fibers by solution spinning in DMF-water system, drawn in coagulation bath, and annealed at 120 °C for 2 h [106]. The fibers were evaluated for pH response behavior, mechanical stability, and retracting stresses. The fiber displayed a swelling capacity as high as 3300–3700% and it possessed high stability against swelling–deswelling cycles, lower thermal shrinkage, good mechanical property during swelling and higher retracting forces during deswelling. These results indicate that the copolymer with enriched block architecture (confirmed by NMR) could possibly form segregated domain structure with acrylic acid domains, facilitating the pH response while acrylonitrile domains enhancing the mechanical property. This approach may be more attractive than chemically crosslinked gel rods in producing artificial muscles with faster response and good mechanical properties.

Water absorbency of textile products has been developed for protection and enhancement of environment. Pre-seeded erosion control blanket, Coirsorb and Brecodrain, aimed, respectively, at arresting erosion, enhancing moisture retention capacity of soil, and recovering useful land from marshy areas, have been developed from ecofriendly and biodegradable jute and coir fibers [107].

Superabsorbents have been used in fabrication of packaging for shipment of heat sensitive materials.

Continuous web of SAP rolls is advanced into the hydration module which comprises a dip tank or spray system to provide an adequate supply of hydrating fluid to the SAP. The impregnated web was then conveyed through a freezing chamber where the fluid freezes [108].

Manufacturing of laminates of SAPs, for water and aqueous liquids absorption, and layers of a plastic foam and/or latex foam has been described. The laminates can be used in several applications; in hygienic articles, as components in natural or artificial soils, as insulating material for pipes and ducts, primarily for cables and constructional elements, as liquid-absorbing and liquid-storing component in packaging materials and as a part in garments [108–111].

Superabsorbents are used in food packaging to preserve aqueous liquids. Jonas et al. [112, 113] described fabrication of a SAP containing packaging for foodstuff.

Manufacture of packages, for instance semi-rigid foam product trays without any need for discrete registration, has been described by Belina and Miller [114]. The package includes a continuous strip coated with SAP powder particles for collecting and retaining exuded fluids in conjunction with structurally supportive packages such as food product trays. Superabsorbents, such as crosslinked carboxymethylcellulose (CMC), were introduced as the superabsorbent powder.

Manufacture of a container including an absorbent material has been described by Brander and D'Ablaing [115]. The storage container includes a tray having a base and side walls for retaining fluids exuded from stored food. A SAP material is placed into the reservoir below the cover to absorb and retain the exuded fluids.

Earmuffs are objects that cover ears for protection. A superabsorbent non-woven has been used in a moisture absorbing cover for an earmuff [116].

Agricultural uses

Human life is entirely connected to food, food depends highly on agriculture, and agriculture is absolutely indebted to water. Taking into account the water imbibing characteristics of SAP materials, the potential of their applications in the agricultural fields has increasingly been investigated to alleviate certain agricultural problems. In such applications, water absorbency and retention are essentials. In arid areas, e.g., the use of SAP in the sandy soil (macroporous medium), to increase its water-holding capacity, seems to be one of the most important means to improve the quality of plants [117]. The SAP particles may be taken as “miniature water reservoirs” in soil. Water will be removed from the reservoir upon the root demand through osmotic pressure difference.

The SAP use for agricultural applications has shown encouraging results. The certain advantageous of SAP use

in this field can generally be mentioned as follows [2, 118, 119]:

- reducing irrigation water consumption and the death rate of plants
- increasing the available water in the soil which enables the plants to survive longer under water stress
- reducing the evapotranspiration rate of the plants
- inducing a much higher growth rate
- reducing compaction tendency and increasing the soil aeration and microbial activity
- preventing erosion and water runoff
- improving fertilizer retention in the soil and, thus, increasing the fertilizer efficiency as well as preventing the contamination of the underwater sources
- binding heavy metals and mitigating their action on plants
- mitigating the effects of salinity
- water-retaining materials in the form of seed additives (to aid in germination and in seedling establishment), seed coatings, and root dips, etc.

The SAPs are not yet affordable to be used in vast cultivation of strategic plants such as wheat and corn. However, their high costs are going to be overshadowed progressively by the benefits of SAP amendment to soils.

There are many reports available on the SAP synthesis for agricultural purposes. In an early publication, Kazanskii and Dubrovskii [17] reviewed the methods of superabsorbent gel synthesis, measurements and treatment of their properties, as well as their effects on soil and on the plant growth. According to the authors, the thermodynamic approach used to describe the swelling behavior of polymer networks proves to be quite helpful in modeling the hydrogel efficiency as a water-absorbing additive. Huttermann [118] has recently reviewed the SAP applications focusing on the ecochemical aspect.

Water reserving and soil conditioning

Among the human problems originated mainly from imbalanced illogical human activities, the water shortage and the desertification are extremely serious for many regions of the world (~30% of the total solid lands). The ecological restoration of these lands is a major challenge for mankind since they are the only option left for increasing the amount of arable land and producing food for the ever growing worldwide population. One common feature of these degraded lands is the fact that their organic soil matter is degraded as well. A solution for the restoration of these lands could be the application of SAPs to these soils. Since SAPs are hydrophilic and contain carboxylic groups, they can be taken as artificial humus. This enables them to bind cations and water; so

they have the following advantages for the restoration of degraded lands.

SAPs have effectively been used as a soil amendment in the horticulture industry to improve the physical properties of soil in view of increasing their water-holding capacity and/or nutrient retention of sandy soils. SAPs potentially influence the soil permeability, density, structure, texture, water evaporation, and infiltration rates of water through the soils. Particularly, as mentioned above, the hydrogels reduce irrigation frequency and compaction affinity, avoid erosion and water runoff, and increase the soil aeration and microbial activity [120]. According to Azzam, a SAP can act as a reclaimer-ameliorator material that imparts almost all the properties of arable lands to sandy soils and hydroponic substrates [121].

Depending on the type, age, and characteristics of the plant as well as the characteristics of the soil and environmental circumstances, such as temperature and irrigating water, different techniques and different SAP concentration are utilized. In planting, e.g., 0.05–0.1% of dry SAP is used in soil or with the seeds and agrochemicals [8]. In forestry, SAP is used in tree transplanting and seedling. Superabsorbent is spread over the surface of the tree roots to prevent them from drying out in the transportation process. Japan has been carrying out a 5-year soil improvement project in Egypt. In the draught area of northeast China, the SAP composite has been employed to plant sugar beet, soybean, rice, etc. The field experiments showed that the superabsorbent increased the production of beet, soybean, and rice [122].

Generally, the SAP materials used in the agriculture are polyelectrolyte gels often composed of acrylamide (AM), acrylic acid (AA), and potassium acrylate (KA). Therefore, they swell much less in the presence of monovalent salt and can collapse in the presence of multivalent ions [2, 123, 124]. These ions are naturally existed in the soil or introduced through fertilizers and pesticides. In saline media, however, the uptake capacity is yet as high as 30–60 g/g depending on the ionic strength of the aqueous medium. Effect of the environmental conditions; such as pH and various salt solutions, on the water absorption of polyacrylamide (PAM)/poly(potassium acrylate)-based SAPs has been studied [125].

Radiation-induced crosslinking of polyacrylamide (PAM), poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), and potassium polyacrylate (PAAK) has been investigated individually and in PAM binary systems for potential use in agricultural fields [120]. A PAM/PAAK copolymer possessing porous structure and fast swelling capacity was also prepared by mixing the hydrogel components with a gas-forming agent, i.e., ammonium carbonate. Such hydrogels have been studied for improving the physical and water-retention properties of sandy soil for

agricultural purposes. The effect of different types and amounts of hydrogels added to sandy soil on the emergence, vegetative growth, and wilting time of corn (*Zea mays*) plants has been investigated. The average plant height, leaf width, total dry weight, corncob production, and wilting time are improved as more SAPs are used. Results suggest that the PAM/PAAK hydrogels improve the sandy soil properties for cultivation due to their high water absorption capacity, reduced plant watering, and enhanced water retention in soil [120].

To study the potential of SAP for water storage in a ground (Haouz, an area of Marrakesh, South of Morocco), the optimal proportions of polymer and soil was evaluated to achieve maximum retention of water [126]. The effect of certain ions, which are naturally present in the ground or are introduced by the means of manure and pesticides as well as the pH, has been studied. The polymer in the ground increases the water absorption capacity of the soil, saves water, decreases the irrigation frequency, and reduces the water loss by evaporation and infiltration.

SAPs as soil conditioners were developed to aid plant establishment and growth in drought-prone growing media. For instance, the effects of a starch copolymer and a PAM copolymer on the establishment and growth of lettuce and barley were investigated [127]. The crops were grown under limited irrigation on a coarse sand substrate. The interval between field capacity and the onset of wilting was increased 300% in the presence of SAPs. Water use efficiency and dry matter production also responded positively to the SAP use.

SAPs synthesized by graft copolymerization of AA and AM onto starch via gamma-irradiation and PEG as a crosslinking agent were studied [128]. It was shown that the water absorbency of these SAPs depended mainly on the conductivity of water. The water retention of sand and soil was enhanced using the SAPs. Effects of these SAPs on the seed germination and growth of young plants were also investigated.

The effect of a commercial SAP (Stockosorb K 400) at 0.04–0.4% concentration on the survival of *Pinus halepensis* seedlings in a sandy soil during water stress was studied. Use of highest SAP concentration was shown to enhance the drought tolerance of the seedlings growing on this substrate to a great extent [129].

Poly(AA-ethyl acrylate-vinyl acetate) (PAEVA superabsorbent) as 0.1–0.5% solution has been shown to stimulate germination and growth of soybean in Petri dishes, pot, and field experiments, both at 11 and 25 °C. PAEVA reduced water uptake in initial hours of imbibitions. It depressed development of seed microorganisms and reduced water evaporation from soil substrate [130].

It has been shown that SAPs could clearly increase the nodulation of two actinorhizal plant species [131]. Nodules

on the roots of the plants that were inoculated with Frankia in the polymer slurry were distributed throughout the entire root system, instead of being concentrated near the root collar. When amended with SAPs, actinorhizal plants inoculated with 5–10-fold lower titers of Frankia exhibited early growth and nodule numbers equal to or greater than those plants inoculated with standard titers without polymers.

Superabsorbents based on poly(AM-sodium acrylate-calcium acrylate), poly(AM-potassium acrylate-magnesium methacrylate), and poly(AM-calcium methacrylate-hydroxyethyl methacrylate) have been prepared and their effects on water retention of soil and the growth of bean and sunflower plants have been reported [132].

SAPs derived from guar gum, a naturally occurring polysaccharide, with a special emphasis on its use as a soil additive have been reported [133]. Recently, a superabsorbent composite based on PAA/sodium humate was synthesized via crosslinking graft copolymerization of AA on sodium humate micropowder. The effect of the SAP composite on the growth of corn was reported [134].

Extensive research has been done to assess the effectiveness of the commercially available SAPs in the agricultural field. Abedi-Koupai et al. [135] have evaluated the SAP effect on either soil water retention or on the indices of plant. They examined the effect of superabsorbent on water retention of three kinds of soils in the Isfahan region (Isfahan province, Iran).

The use of SAP for ornamental plants has recently been studied. In this regard, the growth indices of *Cupressus arizonica* under reduced irrigation regimes in the field and on the soil water-retention curve in a laboratory was investigated [136].

SAP hydrogels have also been evaluated for artificial cultivation of edible products such as mushroom. Sook et al. [137] prepared a superabsorbing hydrogel via crosslinking polymerization of AM and allyl sulfonate salt followed by alkaline hydrolysis. They examined the effect of the SAP medium on mycelial growth and sporophore production of edible mushrooms. They concluded that proper hydrated polymer gel concentration for sporophore production of *Pleurotus sajor-caju* and *Hericium erinaceus* were 2 and 2–2.5 g/cm³ medium, respectively. The desirable hydrated polymer gel and puffed rice hull concentration for sporophore production of *Flammulina velutipes* was concluded to be 2 g/cm³ medium and 10% (v/v), respectively.

SAPs have also been evaluated and used in landscaping, turf establishment nurseries, and interiorscaping [138]. Irrigational water consumption of turf is huge, especially in the hot and dry climates due to either surface evaporation or infiltration. A research was recently conducted in Tehran on the effect of a commercial SAP (Superab A200) on the

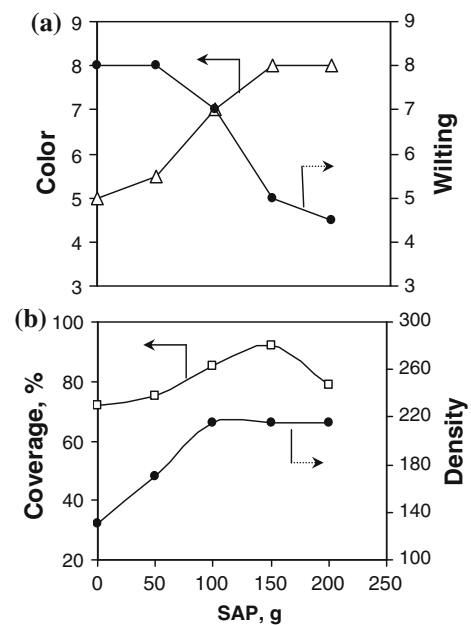


Fig. 5 Commercial SAP (Superab A200) influence on the sport turf characteristics based on the NTEP standard: **a** color and wilting, and **b** coverage and density [2]

characteristics of sport turf [2]. Figure 5 shows, based on the NTEP standard (The National Turfgrass Evaluation Program), the turf density, color intensity, and coverage percentage increases, while its wilting level substantially decreases in the presence of SAP.

The effect of commercial SAPs levels and different drought stress levels on growth and yield of olive plants and forage corn have been investigated [139]. Moreover, the effect of food element-enriched SAP in low-water-treated hydroponic substrates was studied as well [2]. SAP materials have shown excellent influence on decreasing casualties (up to 30%) in the productive process of the olive sapling [2].

Research shows that that SAP hydrogels could highly improve physical properties of horticultural substrates, such as bark, perlite, peat, and their mixtures [140]. An increase of the applied SAP doses from 2 to 6 kg/m³ resulted in an improvement of substrate properties when compared to the control with no SAP. The results showed that it was feasible to add SAPs as an additive to horticultural substrates to highly improve the conditions for the plant development and growth.

In arid and semiarid regions, wind erosion and stretch of sand dunes are major problems that may be solved via chemical stabilization [141]. SAP hydrogels can be utilized to promote simultaneous mechanical and biological sand stabilization. In a research on the soil samples from Ardestan area (Isfahan province, Iran), Jafarzadeh et al. [142] investigated the SAP needed together with irrigation

in biological consolidation of sand dunes using two kinds of suitable desert plants, i.e., *Haloxylon aphyllum* and *Smirnovia iranica*. They comparatively evaluated composition of clay mulch for mechanical stabilization of sand dunes.

The effectiveness of SAPs in biotechnical protection systems has also been established [143]. In earth structures, there are zones where only capillary water suspends in humus layer. In such places there is not enough water during the summer, which causes plants to wither and, as a result, to lose their protective functions. Such problems can be encountered, for instance, in upper parts of slopes, in soil dams and embankment drainage systems, in protection structures made of gabions and consolidated with vegetation. SAP containing geocomposites placed in the root zone could improve the situation, because of SAP ability to retain water, which can be later used by plants during a draught period. Apart from increasing the water reserves for plants, the SAP can also reduce the run-off during heavy rains.

In one study using starch-based SAP [144], the plant pathologists suggested that the SAP combination successfully increased bacterial aggressiveness, which could either be used to promote the ability of biological agents to control weedy plants or to increase the robustness of saprophytic epiphytes against competition from potentially harmful microbes.

Muthiah et al. have disclosed processes for coating the surface of substrates, such as a sheet, film, foam, fiber, with a curable liquid resin or solution of a curable resin, attaching a SAP powder to such resin, and then curing the resin to form a coated superabsorbent product. The coated product was utilized for water and nutrient retention in combination with irrigation, erosion control, to direct plant root growth, and to clean up standing water and petroleum spills. In another patent, Anderson and Miller [145] have disclosed the use of aqueous SAP composition to improve the water retention of soil and to increase the open time of cement.

Controlled release systems for agrochemicals

In view of the current growing trend of food programs, the use of chemicals, such as fertilizers and pesticides, is acceptable, and a significant increase in the agrochemical demand is predicted. However, the effect of pesticides and fertilizers on surface water and groundwater quality is becoming a concern. Agrochemicals may be carried along with the water that moves downward from the surface until they eventually reach the groundwater (leaching). Slow release formulations are outstanding alternatives to the conventional solution-based formulations, because active materials are released at a slow and constant rate over an

extended period of time. Consequently, less frequent applications are required and plants are able to take up the agrochemicals without waste caused by leaching [146]. In this regard, an ideal fertilizer, e.g., should be able to provide essential nutrients and should preferably have reasonable water holding capacity. Furthermore, it should be eco-friendly and affordable [147].

The SAP hydrogels can be designed to work as a controlled release system by favoring the uptake of some nutrient elements, holding them tightly and delaying their dissolution. Thus, the plant can still access some of the fertilizers, resulting in improved growth and performance rates [123, 124, 148, 149]. On the other hand, SAPs in agriculture can be used to aid in germination and seedling establishment, seed coatings and root dips, and for immobilizing plant growth regulator or protecting agents for controlled release [120].

About 40–70% of the applied urea fertilizer is lost to the environment, causing serious environmental pollution. Slow release technology is useful in increasing the efficiency of highly soluble fertilizers, like urea, as well as in reducing environmental pollution. The fertilizer can be simply loaded onto the hydrogel via immersing the polymer in the fertilizer solution [150]. Addition of fertilizer into the polymerization medium of monomers, such as sodium acrylate, is another method for preparing controlled release fertilizer in laboratory scale [151].

A SAP system for slow-releasing of nitrogen fertilizer was prepared via solution polymerization of AA and maleic anhydride in the presence of urea. To improve slow release and water-retention properties, the product was surface-crosslinked with trihydroxymethyl propane glycidol ether. The nitrogen content of the optimally synthesized system was 28.5%, and the water absorbencies were found to be ~900 and 180 g/g in distilled water and in tap water, respectively [152]. A similar partially neutralized AA-based system was prepared by inverse suspension polymerization in the presence of urea [124]. The N content of optimized system was 22.7%, and the absorption capacities were ~965 g/g in distilled water and 185 g/g in tap water. A possible slow release mechanism was proposed and the release rate constant and the diffusion coefficient of urea in the hydrogel were determined. The results showed that these products could effectively improve the utilization of fertilizer and water resources.

Liang and Liu [153] conducted an inversion suspension polymerization to prepare a coated nitrogen fertilizer with slow nitrogen release and water retention. It is composed of a crosslinked PAA/organo-attapulgite (outer coating), urea–formaldehyde (UF) (inner coating), and urea granule (core). The tap water absorbency and N content of the product was 80 g/g and 28.3%, respectively. Another slow-release system containing 33.6% nitrogen was prepared

based on crosslinked PAA-containing urea (the outer coating), polystyrene (the inner coating), and urea granule (the core) [154]. The outer coating regulated the nitrogen release rate and protected the inner coating from damage. The slow-release property of the product was investigated in water and in soil. It was found that polystyrene percentage, temperature, and water absorbency had a significant influence on the release of nitrogen, whereas the pH had no effect.

Another core/shell structured system has been prepared based on poly(AA-co-AM)/kaolin SAP to simultaneously improve the utilization of fertilizer and water resource [155]. Its core was potassium silicate in an alginate matrix, and the shell was SAP composite. The product contained 26.6% K_2O and 10.4% SiO_2 . Release characteristics of potassium and silicon from the system in soil and water-retention capacity of the soil were also investigated. A non-Fickian diffusion mechanism of nutrient release was proposed, and the release rate factor K , the release exponent n , and the diffusion coefficient D of nutrients in the system was calculated.

A series of poly(AA-co-AM)/kaolin SAP composites were prepared by aqueous solution copolymerization of partially neutralized AA and AM in the presence of kaolin nanopowder, which was synthesized to act as a release carrier of urea fertilizer [156]. The composite was swollen in an aqueous solution of urea to load urea, and the effect of urea concentration on the swelling was investigated. It was found that the urea loading could be adjusted by urea concentration in the swelling medium, and the urea diffusion coefficient could be regulated by changing the concentration of crosslinking agent, kaolin AM, and the neutralization degree of acrylic acid. Additionally, temperature and ionic strength of the release medium may also affect the urea release process. These conclusions could provide a theoretical basis for the diffusional behavior of urea from a SAP matrix.

A series of amphoteric, poly(AA-co-diallyldimethylammonium chloride) SAPs with different molar ratios of anionic groups to cationic groups were prepared to investigate the controlled release of agrochemicals [157]. Various factors, including the solution pH, the concentrations of different salt solutions, and the temperature, were studied. The dynamic parameters of hydrogels at different temperatures suggested that diffusion was Fickian at lower temperatures, whereas non-Fickian diffusion prevailed at higher temperatures. A copolymer hydrogel with a low anionic-group/cationic-group ratio showed a higher swelling capacity in water and higher salt tolerance.

Zhan et al. [158] prepared a SAP product with a slow-release phosphate fertilizer via esterification of polyvinyl alcohol (PVA) and phosphoric acid. The optimally prepared product contained P content of 31.2% (calculated as

P_2O_5). They also studied water-retention property and phosphate slow-release mechanism of the product. A slow-release fertilizing system was also prepared via crosslinking polymerization of AA and potassium acrylate in the presence of water-soluble granular phosphorus fertilizer KH_2PO_4 under microwave irradiation (300 W, 5–7 min) [159]. It was found that the rate of release, its pattern and reproducibility could be governed by a proper choice of the several control parameters, such as the initiator and crosslinking agent concentrations.

A controlled release system of nitrogen, phosphorus, and potassium compounds fertilizer having a core/shell structure with the water-retention capability was also prepared via inversion suspension polymerization by Liang et al. [160]. Its core was urea formaldehyde and polyphosphate potassium fertilizer, and the shell was poly(AA-co-AM)/kaolin SAP composites (Fig. 6). The absorption capacity and the N, P, and K contents were measured as 91 g/g (in tap water), 11.3%, 21.1% (shown by P_2O_5), and 8.6% (shown by K_2O), respectively. The swelling rate, slow release, and water-retention properties of the system were also investigated.

A new type of chitosan-coated NPK compound fertilizer with controlled-release and water-retention capability was recently prepared by Wu et al. [161] via inverse suspension polymerization. It possessed a three-layer structure; core was water-soluble NPK fertilizer granule, the inner coating was chitosan and the outer coating was poly(AA-co-AM) SAP hydrogel. In the optimally synthesized product, N, P, and K elements were measured to be 8.06%, 7.98% (shown by P_2O_5), and 8.14% (shown by K_2O), respectively. They also prepared a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention properties [148]. This system contained PAA/diatomite-urea (the outer coating), chitosan (the inner coating) and water-soluble granular fertilizer NPK (the core). The product contained 8.47% potassium (shown by K_2O),

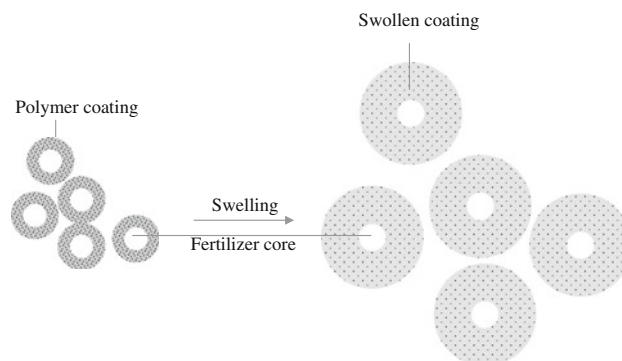


Fig. 6 A typical NPK controlled release fertilizer system with core/shell structure based on SAP hydrogel before (*left*) and after (*right*) swelling in water

8.51% phosphorus (shown by P_2O_5), and 15.77% nitrogen. They investigated the water-retention property of the product and the slow release behavior of N, P, and K fertilizers.

Guo et al. [162] prepared a slow-release fertilizer with superabsorption and moisture preservation using carboxymethyl starch, AA, ammonia, urea, diammonium phosphate, etc. The analysis results showed that the product contained 22.6% nitrogen element and 7.29% phosphorous (shown by P_2O_5) element. Its tap water absorbency was about 85 g/g. The slow release mechanism of both N and P in water was also investigated. The researchers also developed a type of slow-release N fertilizer using SAP to improve the utilization of fertilizer and water resource at the same time [163]. The coatings were formed by the inverse phase polymerization technique.

A slow-release membrane-encapsulated urea fertilizer was also prepared using crosslinked starch (the first layer), AA and AM (the second layer; AM), ammonia, borax, urea (the third layer) [164]. The tap water absorbency and N content of the product were measured to be 80 g/g and 26.74%, respectively.

Recently, Talaat et al. [165] reported a new process design features of a multi-component fertilizing starch-acrylic SAP with relevant techno-economic indicators. After preparation of hydrolyzed starch-g-polyacrylonitrile (H-SPAN) superabsorbent with N content of 2.1%, the authors simply produced a fertilizing base as a mixture composed of 65–70% corn starch, 28–33% urea, and 2% of other ingredients as conventional salts. The product (ESRF) was prepared via sequential addition and mixing of the ingredients followed by controlled drying and size reduction procedures, and it contained certain amounts of N (14%), P (5.6 mg/g), K (9 mg/g), and Zn (0.65 mg/g). A fertilizing slow release blend (HESRF) was developed by appropriate mixing of H-SPAN and ESRF (ratio 1:5). A plant with a capacity of 10 metric tons per day is estimated to produce HESRF product with an approximate price of 770\$/ton. It is perceived that the economics of the production can be considerably improved if cheap substrates such as waste food grains and other polysaccharide sources are used.

Preliminary agricultural experiments using in house pots showed an excess of seed or grain yield for faba bean and wheat crops by about 80 and 116%, respectively, as compared to the normal fertilizing treatment. It was shown that the added cost due to the application of HESRF (i.e., ~108\$/acre) was surpassed by the benefits obtained through the increased crop yield [165].

The general release mechanism of gel-based controlled release fertilizers involves water penetration into dry mixtures of fertilizers and gel-forming polymers, such as SAPs [166]. Several authors have reviewed agricultural

controlled release devices including hydrogel-based systems [146, 147, 167].

Super-swelling hydrogels based on AM-crotonic acid [168, 169] and AM-itaconic acid [170] were prepared via gamma-radiation polymerization. The relationship between the swelling process and the releases of water-soluble agrochemicals, i.e., NH_4NO_3 , KNO_3 , $(NH_4)_2SO_4$, and sodium 2,2-dichloropropionate (Dalapon; a herbicide) was investigated in details. In addition to fertilizers, other agrochemicals (e.g., herbicides and pesticides) may also be formulated into the hydrogel-based controlled release systems. For example, controlled release of mosquitocides from Culigel[®] PAM/polyacrylate SAP granules in an aquatic environment could be regulated by mixing inert ingredients into the pesticide formulation during the granule manufacturing [171]. Release profiles of organophosphate larvicides, growth regulators and larvicidal *bacilli* can be tailored to specific mosquito control requirements by altering the type and/or concentration of a dispersant complex.

SAP-pesticide formulations have been prepared and evaluated for prolonged insect control. Organophosphate chlorpyrifos or insect growth regulator or both were evaluated against German cockroaches [172, 173]. The research suggested that joint-action disquiets could provide simultaneous control of mixed population of nymphs and adults.

Pellets, with partially hydrogenated vegetable oil, talc, and a starch-based SAP, were used to formulate *Bacillus sphaericus*. This formulation improved the residual activity against *Culex* spp. larvae in large and small plots, including polluted water [174].

A suspension of starch-based SAP particles was combined with a liquid fertilizer solution to use as fertilizer for soil amendments [175]. Methods of production and application of a superabsorbent based on starch graft copolymers, having particle sizes useful for agricultural applications, have been disclosed by Doane and Doane. The superabsorbent applied to field crops provided excellent anti-crusting properties, increased seed germination and stand, increased crop growth, increased yields, and reduced water requirements [176].

Separation and water treatment

SAPs are ionic three-dimensional networks capable to uptake many molecular and ionic species. In addition to the absorption of water and aqueous fluids, SAPs can adsorb cationic dyes and metals and remove them from the solution. For example, Bajpai and Johnson [177] synthesized and characterized hydrogels based on AM and sodium acrylate with respect to their swelling behavior and structural parameters and models. The swollen gels

demonstrated a sharp volume phase transition when placed in the solutions of divalent ions, i.e., Ni^{2+} and Ba^{2+} , thus proving their potential to remove toxic divalent ions from their aqueous solutions via divalent–monovalent ion-exchange mechanism.

Guilherm et al. [178] described the sorption percentage of Pb^{2+} and Cu^{2+} (as high as 60–80% at pH 5.0) from an aqueous environment using a SAP matrix made of an acrylic-modified Arabic gum copolymerized with AA and AM. Metal-absorption tests, upon sequential pH variation, indicated that the SAP had pH-sensitivity for the absorption of the metals from solution, attributed to the functional ionic groups ($-\text{COOH}$) present in the AA and the gum segments. The authors found that both the interaction and the main effects of the pH and the initial concentration of metal solution on absorption percentage of the metals were statistically significant.

Another biopolymer-based SAP was synthesized via crosslinking copolymerization of partially neutralized AA onto the hydrolyzed collagen. The Taguchi method was employed for optimizing the synthesis reaction [179]. The sorption capacity of the hydrogel toward bivalent metal ions was evaluated to be considered as a chelating hydrogel for water treatment.

A novel crosslinked poly (AA-*co*-Kryptofix-22-DM) SAP containing pendant group of diazacyclooctadecane crown ether was synthesized and characterized [180]. Sorption capacity of the SAP was investigated for heavy metal ions (i.e., Pb^{2+} , Cu^{2+} , Cr^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} , and Ni^{2+}) at different pH values using Freundlich and Langmuir isotherms.

Recently, SAP nanocomposite hydrogels based on AM and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) sodium salt and clay were synthesized via in situ copolymerization in aqueous solution [181]. The hydrogels were used to remove heavy metal ions ($\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$) from aqueous solution in competitive and non-competitive conditions. The effects of time and pH of the initial metal ion solution on the adsorption capacity were investigated, and selectivity properties of the samples were evaluated. It was found that incorporation of a low amount of clay (10 wt%) into the polymer structure could increase the heavy metal ion adsorption capacity of the sample. It was concluded that the AM-AMPS/clay nanocomposites could be used as novel type, fast-responsive and high capacity sorbent materials in heavy metal removing processes.

Synthesis, characterization, and swelling behavior of *N*-vinylpyrrolidone-AA-AMPS hydrogels by UV-curing technique have been reported [182]. The SAP hydrogels were used for the separation of $\text{Cd}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Fe}(\text{III})$ ions from their aqueous solutions. The influence of the uptake conditions, such as pH, time, and initial feed

concentration on the metal ion binding capacity of hydrogel was also tested. The selectivity of the hydrogel toward the different metal ions tested was in the order of $\text{Cd}(\text{II}) > \text{Cu}(\text{II}) > \text{Fe}(\text{III})$. It was observed that the specific interaction between metal ions and ionic comonomers in the hydrogel could affect the metal binding capacity of the hydrogel. The recovery of metal ions has also been investigated in acid media.

Many efforts have been made to remove textile dyes from the wastewater. Batch adsorption kinetics of seven cationic dyes (namely, Methylene Blue, Safranin T, Rhodamine B, Crystal Violet, Malachite Green, Brilliant Green and Basic Fuchsin) from an aqueous solution onto a commercially available SAP has been reported [183]. The adsorption of dyes reaches equilibrium in 60–90 min. Equilibrium isotherms and intra-particle diffusion rate constants were measured for single component systems. It was found that uptake of dyes on the SAP followed the Langmuir and Freundlich isotherm models. It was also found that photocatalytic regeneration of the spent SAP using UV/ TiO_2 is more effective when compared to the conventional methods. Furthermore, the regenerated SAP exhibited 90% efficiency for subsequent adsorption cycle with Methylene Blue and Safranin T aqueous solutions. Janus Green B (a cationic textile dye) was also reported to be highly adsorbed by poly(AA-AM) super-swelling hydrogels [184].

Kasgoz and Durmus [185] prepared an AM-AMPSNa/clay SAP nanocomposite with 10 wt% montmorillonite (MMT) to be used in dye removal. Swelling properties and kinetics of the hydrogel samples were investigated in water and aqueous solutions of the Safranin-T and Brilliant Cresyl Blue (BCB) dyes. It was found that the clay incorporation increased the adsorption capacity and rate. Adsorption capacity values of the hydrogel nanocomposite were found to be 484.2 and 494.2 mg/g for Safranin-T and BCB dyes, respectively. The dye adsorption by the nanocomposite was completed in 10 min while the clay-free hydrogel adsorbed dyes approximately in 90 min. It was found that the adsorption kinetics of hydrogel nanocomposite followed a pseudo-second-order model.

Chitosan-*g*-PAA/MMT nanocomposite SAPs were reported by Wang et al. [186] to be used for removing methylene blue. The adsorption behavior of the so-called superadsorbent gels showed that the adsorption kinetics and isotherms was in good agreement with a pseudo-second-order equation and the Langmuir equation, respectively. The maximum adsorption capacity of the nanocomposite containing 30 wt% clay at the ratio of 7.2:1 was found to be 1859 mg/g. The desorption studies revealed that the SAP has the potential for regeneration and reuse.

Crosslinked starch-*g*-PAA and poly(AA-*co*-AM) were synthesized, and were mixed with inorganic coagulants of

aluminum sulfate hydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$, calcium hydroxide $[\text{Ca}(\text{OH})_2]$, and ferric sulfate $[\text{Fe}_2(\text{SO}_4)_3]$ in a proper ratio to form complex polymeric flocculants (CPFs) [187]. The color reduction by the CPFs was tested with both synthetic wastewater and selected wastewater samples from textile industries. Starch-*g*-PAA/ $\text{Ca}(\text{OH})_2$ CPF could reduce the synthetic direct dye and the industrial wastewater by 74 and 18%, respectively. Chemical oxygen demand, residual metal ion concentrations, pH, and turbidity of the wastewater were also investigated and the potential use of the complex polymer flocculants for textile wastewater treatment was elaborated.

The removal of methylene blue (MB) in water with a SAP composed of polyacrylate, polyacrylamide, and modified Arabic gum was investigated [188]. The maximum absorption capacity was found to be 48 mg/g of SAP. In a procedure with an individual solution of orange II, an opposite effect was observed; the hydrogel only absorbed water, resulted in a solution richer in orange II. The orange II concentration in solution increased about 50 times (relative to the initial concentration). In another experiment using an aqueous mixture of orange II and NIB, the SAP absorbed the MB exclusively.

Highly swollen AM/AMPS hydrogels and AM/AMPS/bentonite composite hydrogels were prepared by free radical solution polymerization in the presence of ethylene glycol dimethacrylate (EGDMA) [189]. Sorption experiments of water-soluble monovalent cationic dye, such as Lauths violet “LV (Thionine)” were performed. Some swelling kinetics and diffusion parameters were found. Water and LV diffusion into hydrogels was found to be of non-Fickian character. The influence of the AMPS content on the dye sorption was examined.

SAPs can also be employed for selective absorption of water from oil–water emulsions [190]. *Psyllium* has been functionalized with AM using hexamethylene tetramine as a crosslinking agent under gamma irradiation or chemical initiation. *Psyllium-g*-PAM was then used to remove water from different water–oil emulsions. The hydrogel was found to be selective in its absorption and maximum absorption of water was found to be 3020% [191].

The detoxification of agro-industrial effluents using SAPs is an innovative process. For instance, olive mill wastewater (OMW) constitutes a major environmental problem in Mediterranean countries due to the large volumes generated, the seasonality of the industry and the high content of polyphenols and organic matter. Davies et al. [192, 193] have shown that the application of SAPs could allow OMW to be used as a fertilizer. In its immobilized form, water, organic matter, and mineral content of the OMW would be available for plant nutrition.

SAPs are smart hydrogels, hence, they can potentially be employed in separation science and technology, including

bioseparation. Due to large changes in the swelling ratio, the hydrogels have been used in the separation of various molecules, including proteins [194].

Iritani et al. [195] investigated a process for concentrating dilute aqueous bovine serum albumin (BSA) solutions with SAP hydrogels. In this process, the gel swells by absorbing water only while macromolecules are excluded, thus producing a concentrated retentate. The concentration of the retentate is about 5.8 times higher than that of the feed for a dosage of dry gels of 0.63% by weight. The dynamic behavior of the concentration process was described using the equation of motion of the gel network on the basis of the kinetics of the gel swelling. The pore size of the hydrogel controlling the sieving property was estimated from the permeation rate of water through the compressed, packed bed of the swelling gels, known as the compression-permeability test. It was demonstrated that slight stirring during the concentration process was accompanied by a rapid removal of the BSA filter cake on the gel surface, leading to an efficient concentration.

A commercially available SAP from Hoechst (Sanwet IM-5000-SG) was tested to concentrate dilute solutions of BSA and to evaluate the possibility of scaling-up the process [196]. BSA was concentrated up to 3.5-times when using the appropriate polymer concentration. The recovery of protein was around 100% for concentration factors below 2.0, but decreased for higher concentration factors. As characterization study suggested, higher amounts of polymer were needed to concentrate BSA solutions with higher salt concentrations. The process performance was improved with solutions containing lower concentration of BSA (0.15–0.5 mg/mL). The concentration factor was predicted from the NaCl and polymer concentrations using a semi empirical model.

A SAP-containing membrane for CO_2 separation from a CO_2/N_2 mixture was reported [197]. The membrane is composed of an aqueous K_2CO_3 solution and a poly(vinyl alcohol)-SAP in which the aqueous solution was immobilized. This facilitated transport membrane (gel-supported membrane) worked properly when the polymer gel held sufficient amount of water. The gel-supported membrane immobilizing a 2 mol/kg of an aqueous K_2CO_3 solution worked well even under the evacuating condition for 6 months by controlling the water vapor pressure. It was concluded that the gel-supported membrane had a potential practical use to recover CO_2 from the high humid gas mixture, such as flue gas.

A hygienic grade SAP has been proposed to be used in a programmed-temperature vaporizer (PTV) injector for the introduction of large volume samples to a gas chromatography (GC) system [198]. The SAP effectiveness in the isolation of menthol and its isomers from *Mentha piperita* essential oil as well as gamma-lactones from peach

essential oil was assessed. The results proved not only the viability of using SAP in analytical procedures but also demonstrated its advantages over the adsorbent Tenax TA in attaining internal GC concentration of a sample by introducing large volumes via PTV.

There have been some patents on the applications of SAP in separation process. For instance, a water purification apparatus has been invented; including, a semi-permeable membrane and a SAP across the membrane [199].

Electrical uses

Telecommunication networks, installed in vast areas using cables, are often damaged by induced high voltage because of lightning and poor grounding of high-voltage power lines. To avoid the high voltage-induced damage to the equipment and human bodies, bar- or plate-shaped electrodes are buried in the ground (digging at the foot of a small well) to secure electrical grounding of the Telecommunication system. However, in areas formed of volcanic ash, sand, or rock (e.g., Japan) and/or hot regions, such as arid or desert areas, the resistivity of the ground is high. To reduce the resistivity (i.e., to increase the ground electrical conductivity), electrically conductive materials such as ferro-copper cyanide, silicate gel, or bentonite mixtures (e.g., bentonite–water–cement–sodium chloride with 1:1:0.1:0.1 wt ratio) are usually mixed with the pit soil. However, the ground resistance increases again due to the diffusion of the conductive species followed by contamination of the soil and underwater resources. In very hot regions, the soil dryness can also diminish the ground conductivity.

Japanese researchers proposed a method of reducing ground resistance by employing SAP hydrogels [200–202]. Either fully synthetic or semi-synthetic SAPs were found to be superior to the traditional bentonite mixture in all aspects, e.g., ground-resistance reduction (as high as 1/160), less corrosion of the metallic copper grounding electrodes, and ease of use [200]. Figure 7 displays the method of SAP-based soil treatment for reducing the ground resistance.

To support the grounding electrode, the ground resistance-reducing material was solidified with epoxy resin and the system was fundamentally evaluated in a metal box as a simulated system [201]. It was found that a maleic acid-based SAP could maintain its improved characteristics for about 10 years if the polymer degradation of 20% was allowed. For the epoxy-solidified system, it was found that the dry condition could be allowed for about 1 year during which the ground resistance can maintain its initial value if rain falls [202].

SAPs can also be used for electric cable production to stop water from entering the cable in case of damage of the outer coating. It can prevent the water from penetrating

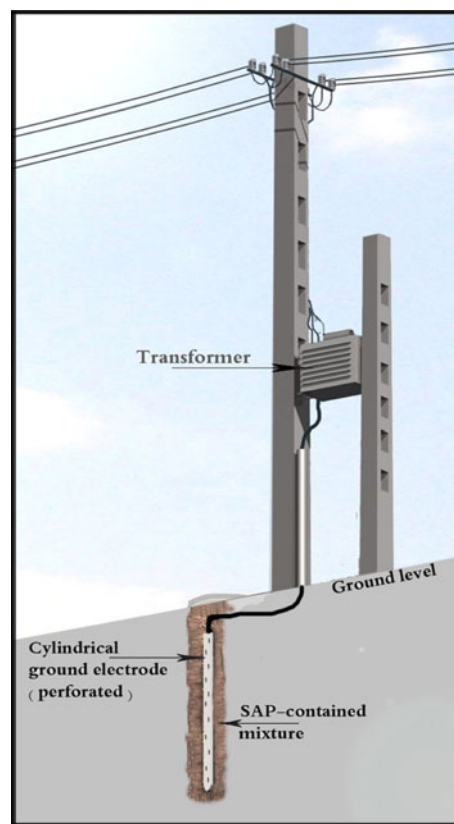


Fig. 7 SAP-based soil treatment for reducing the ground resistance

into the cable through the junction. Water-blocking tapes are widely used in communication and power cables exposed to seawater or underground water to prevent water intrusion when the coating is damaged [6]. The tapes are usually prepared by applying a dispersion of ultra-fine SAP powder onto a fabric substrate. Such tapes may be wrapped to make water blocking optical fiber cables [203].

Hogari and Ashiya [204] developed a new water-blocking optical fiber system composed of high density and high-fiber-count water-blocking optical fiber cables and water sensors by employing SAPs. The system was capable of suppressing water penetration into a cable and detecting water penetration into a cable joint. According to the inventors, the cable possess the advantageous of ease of manufacture and handling, light weight, stable transmission, and it is maintenance-free. SAP composite has been used in the cable production in China [122].

SAPs can be used as water leakage preventing material in the electric battery industry where the traditional sealing materials are a mixture of bitumen, white wax, and resin. The use of SAP solves the problem of leakage and prolongs the shelf life of the battery [122].

Innovations related to power transmission and tele-communications have been disclosed in several patents. Suzuki and Matsumoto have disclosed a method for

preparing a superabsorbent composite sheet to cover electric cables, including a bulky non-woven fabric substrate, a solid SAP, and a heat-fusible component to hold the solid SAP [205].

A water-resistance and corrosion-resistance coatings have been made of an aqueous solution of a SAP precursor onto the surfaces of the articles, like cable and curing to form a coating of the SAP [206].

SAPs have been widely used in different kinds of communications and transmission cables. Production methods of cables closure, including superabsorbent foam water blocking, have been disclosed by Arroyo et al. [207, 208]. A laminate with a superabsorbent powder was introduced to prevent the flow of water along the core and prevent freezing the cable by impregnating with an anti-freeze material [209].

A cable wrap fabric for protecting a communications cable was made of woven fiberglass yarns plied with or without low melting temperature thermoplastic yarns and superabsorbent yarns. The fiberglass yarns dissipate heat energy generated by lightning strikes or excessive thermal shocks and the superabsorbent water swellable yarns block the progression of water through the cable [210].

SAP was used for cable insulation and for the production of non-wovens. The formulation has been supplied in the form of a two-component package consisting of pre-crosslinked superabsorbent and a reactive crosslinking agent to form the product [211]. A multilayer tape, including core of SAP between two jackets has been made to protect cable. The SAP layer with a moisture content of greater than approximately 2 wt% improves the flame-retarding characteristics of the tape [212].

A layer containing SAP was used to improve the flame-retarding characteristics of cables [213]. Production of a multilayer tape containing a SAP was described by Bringuier and White to cover fiber optic cable. A mixture of two water absorbing agents was used. One of them was a mixture of two different superabsorbent substances, characterized by a very fast swelling rate to quickly block the flow of water, and the other was a high-gel strength gel to inhibit wicking [214].

SAPs have been used widely to block water flow into cables. Norris et al. described a water-blocking tape for an optical fiber cable wrapped with a synthetic fibrous non-woven tape coated with a SAP powder coating. The particles in the powder were ultra-fine to reduce micro-bending losses in the optical fiber [215, 216].

Production methods of tapes to cover cables were described by Sheu, including a core, an outer jacket surrounding the core and SAP fibers disposed between the core and the outer jacket as well as inside the core [217].

A telecommunication cable was made of a layer of wetted water-absorptive powder on the surface of a

substrate, avoiding the use of adhesives to bind the dry SAP powder. The water-absorptive powder may be adhered to the surface of the substrate element by a water-soluble adhesive material [218].

SAP-coated filaments were incorporated into telecommunications cables as a component part to achieve enhanced water-blocking functions. In this invention, the SAP particles, included homopolymers, copolymers, and/or mixtures of sodium and potassium polyacrylates, starch-grafted sodium polyacrylates, and partial sodium salts of polypropenoic acid were used. They were bound to the yarn surfaces by an alcohol-soluble nylon binder [219]. SAP powder was applied between and/or on the fiber optic ribbon stack in production of communications cable made without the use of gel or grease in the buffer tube to block water penetration [220].

Overtorn et al. [221] disclosed production of a fiber optic cable that includes optical fibers and a water-swellaable element, such as a powder-free fabric tape, which are enclosed within a buffer tube. In another patent, production of an optical waveguide was described having two layers; the first one is polyurethane foam and the second one is a water-swellaable layer. The dry insert is disposed within the tube and generally surrounds an optical waveguide [222].

Civil structures

Cement-based materials are extensively used in the civil infrastructure. Polymers as admixtures can improve the properties, particularly in relation to water absorption reduction, toughness enhancement, vibration damping and bonding strength of cement to reinforcing bars [223].

In concrete structures, appropriate curing is essential to ensure they meet their intended performance and desired durability. In conventional construction, this is achieved through external curing, applied after mixing, placing and finishing. Since the water adsorbed chemically by the cement hydration products has a specific volume less than that of bulk water, a hydrating cement paste will absorb water (~ 0.07 g water/g cement) from an available source. In fact, in high water–cement ratio (w/c) concretes, this water is often supplied by external (surface) curing. However, in low w/c ratio concretes, the permeability rapidly becomes too low to permit the effective transfer of water from the external surface to the concrete interior. This is a justification for the necessity of “internal curing”; where SAPs play a promising role. Internal curing process implies the introduction of a curing agent into concrete that will provide this additional moisture.

Internal curing (IC) refers to the process by which the hydration of cement occurs because of the availability of additional internal water that is not part of the mixing water

[224]. The additional internal water is usually supplied via two major sources. The first method uses relatively small amounts of water-saturated lightweight fine aggregates (LWA), and the second method employs SAP fine particles in the concrete [225, 226]. The internal reservoirs of LWA or SAP can be an effective means for supplying the extra curing water needed to compensate for the chemical shrinkage occurring in the cement paste during hydration. For optimum performance, the IC agent should possess high water absorption capacity and high water desorption rates [227]. It was reported that SAP-based internal curing agents were efficient in maintaining the mechanical properties of mortars, regardless the variation of external relative humidity [228].

Benefits of internal curing include improved hydration and strength development, reduced autogenous shrinkage and cracking, decreased permeability and increased durability. The goal of internal curing is to maintain saturated conditions within a hydrating cement paste to avoid self-desiccation and the accompanying autogenous stresses and strains that may lead to early age cracking. The internal curing impact begins immediately with the initial hydration of the cement, with benefits that are observed as early as 2 days. Therefore, internal curing is especially beneficial in low w/c concretes because of the chemical shrinkage that accompanies Portland cement hydration and the low permeability of the calcium-silicate hydrates.

In concrete technology, cement matrix composites have been developed for purposes ranging from factory-fabricated pieces to the field use. Meanwhile, the development of high-performance concrete (HPC) was a noteworthy progress in the early 1980s and attention was focused on the increased strength potential of HPC. Today, however, HPC is considered to be a concrete with various properties useful for many different applications. SAP has a potential application as an admixture to improve HPC performance by acting as a water-reducing agent to eliminate the negative effect of water on the hardening of cement. It can also act as an air-entraining agent which may reduce surface tension and hence stabilize the small bubbles originating from the mixing process. Gao et al. [229] incorporated a SAP/MMT composite to an aluminate concrete to improve its compressive strength, tensile strength, and modulus. To find the optimized formulation, they derived a statistical model with three variables of the SAP content (0.2–0.5%), particle size (20–60 mesh) as well as the cement/water ratio.

Observation of the water movement from the internal reservoirs (i.e., SAP or LWA) to the surrounding cement paste during hydration has been one of the active fields of research. For instance, low-field nuclear magnetic resonance (NMR) relaxometry technique was recently employed to study water balance and pore structure

development in cementitious materials in an internal curing process employing a modified SAP [230]. The new data indicated a rapid water uptake within less than 5 min after watering the SAP/cement mixture. The re-release of the water began along with the onset of the hydration reaction, and was finished after 1–2 days depending on the SAP particle size. The water uptake of the SAP inside the cement matrix was quantified to be $\sim 2250\%$ of its dry weight.

Most recently, carboxylate- and sulfate-based polysaccharides hydrogels with superabsorbing properties were evaluated for controlled internal water release during cement hydration [231]. Gellan-based hydrogels were found to be most suitable for internal water curing during the accelerated period of cement hydration, because they offered the best mechanical stability and resistance to high pH-values compared to the other hydrogels (based on Ca- and Al-salts of alginic acid, carboxymethyl cellulose, and carrageenan).

In addition to its effective role in the internal curing process, a SAP plays a promising role to increase the freeze–thaw resistance of a high strength concrete [232]. The SAP mixture exhibited 40% less scaling than the reference mixture and showed a slight improvement of the compressive strength.

As a different application in civil engineering, methods for rapid stabilization of weak soils have been sought to support military forces worldwide. Cement and lime have been the most effective stabilizers for road and airfield applications; although, many non-traditional stabilizers have also been developed and used. The treatment of one clay with cement resulted in relatively high unconfined compressive strengths (UCS), whereas treating the same clay with quicklime and calcium carbide resulted in lower UCS. Secondary stabilizers, including sodium silicate, SAPs, a superplasticizer, and an accelerator, were unsuccessful in improvement of the UCS of a soil treated with cement, quicklime, or calcium carbide [233]. A formulation of linear anionic polyacrylamide mixed with aluminum chlorohydrate and SAP at a ratio of 6:1:1 has been applied to make helicopter landing pads that minimizes dust clouds during the helicopter operation [234]. In addition to cement admixture, SAPs have been used as sealing materials in civil engineering sector. Production of a sealing mat has been disclosed by Vogt et al., which swells under the influence of water and in which a material that is made of a superabsorber is disposed between two fleece layers. The sealing mat can be used for sealing purposes in structural and civil engineering, particularly for building tunnels [235] (see “Water-swelling rubbers”).

SAPs, like polyacrylamide or modified crosslinked poly(meth)acrylate, have been used to absorb free water in a cement slurry to form a gel, releasing the absorbed water

to the cement hydration reaction as the cement sets. The absorption of water causes the slurry to develop a solid-like structure [236]. A crosslinked SAP composition having low viscosity and high absorption capacity has been used to enhance the absorbency, to increase the humectancy and/or absorbency of a fiber matrix, to improve the water retention of soil, and to increase the open time of cement [237].

Water-swelling rubbers

Water-swellaible rubber (WSR) is a popular SAP composite and is used as a sealing material in construction applications [6]. They are usually prepared by dispersing SAP particles in common hydrophobic rubbers [238–240]. These elastomeric composites often provides the materials with sealing or caulking features preventing water leakage from pipe or block connections in civil constructions, such as subways and underwater tunnels. They were used in Euro Tunnel under the Straits of Dover and there are some examples of the segment tunnel construction for railways, subways, and highways in Japan [6]. Once rubber makes contact with water, it swells and tightly fills the spaces between the blocks to avoid water penetration.

Polychloroprene rubber (CR) was blended with additives, like precipitated silica (10–50 phr), poly(ethylene oxide) (PEO, MW 2000, 5–30 phr), and SAP (particle size 17 μm , 25–75phr) by a Banbury two-roll mill [239]. After vulcanization, a WSR is achieved in which SAP particles are well dispersed (water absorbency around 5–10 g/g).

Park and Kim [238] prepared SAP-dispersed natural rubbers using PEO (MW 100,000) and glycidyl methacrylate (GMA) as a reactive coupling agent. The size of spherical sodium polyacrylate superabsorbent particles, synthesized via inverse suspension polymerization, was in the range 76–225 μm . The equilibrium swelling in water (0.5–5.0 g/g) and dynamic swelling behavior of the prepared WSRs were considerably affected by addition of carbon black, PEO, and GMA.

Foaming WSRs based on ethylene propylene diene terpolymer (EPDM) have been prepared to enhance the swelling rate by employing a suitable foaming agent (i.e., dinitroso pentamethylenetetramine, DNPT, 2–6 phr) [240]. The SAP particle size and its initial free-swelling in water were 74–840 μm and 350 g/g, respectively. In contrast to the unfoamed WSR, the foamed WSR exhibited improved rate of swelling while its mechanical properties could be well preserved. The volume swelling ratio of the products ranged from 150 to 600% after a 20-day-swelling period.

A different approach has been reported to prepare WSRs. Lithium acrylate (LiAA) was prepared in situ in a matrix of chlorinated polyethylene (CPE) [241] or nitrile rubber [242] through the neutralization of lithium

hydroxide (LiOH) and AA in a Haake rheometer. The in situ homo- and graft-polymerization of LiAA were initiated with dicumyl peroxide (DCP) at 170 °C to produce an elastomeric vulcanizate. The effects of the LiAA content, DCP content, and LiOH/AA molar ratio on the mechanical and water-swelling properties of the vulcanizates were explored. The optimized samples exhibited a water-swelling ratio of 200–800% and a tensile strength greater than 12 MPa.

A composition of bicomponent system containing a hydrophobic polymer phase and a water-swollen SAP phase has been used to manufacture coatings, sealants, adhesives, and waterstop. The first component is an emulsion of the hydrophobic polymer; the second component comprises the SAP [243].

Other applications

Table 1 summarizes the other important applications of SAPs. Artificial snow, packaging, dewatering, and fire extinguishing systems are among the current fields of the SAP applications.

Meanwhile, very interesting innovative applications such as weather modification have been reported [244]. In this approach, a hurricane was seeded with almost 30,000 lbs of a SAP using a transport plane flying through the leading edge of the storm. Within 20 s, the SAP could achieve over 70% of its absorption capacity. The winds of the storm would continue to disperse the materials causing a form of internal flocculation disrupting the feeding nature of the storm. When presented close to the land, the storm did not have sufficient time to reform to its previous destructive strength.

SAP hydrogels have been used for preparation of solid water-equivalent radioactive standards [245]. They are also employed for water management of polyelectrolyte membrane fuel cells using different kinds of absorbent wicks [246].

Since exposure to respirable SAP dust is becoming more of a concern in a typical SAP workplace, Dow researchers employed SAPs to monitor air quality in the SAP production workplace [247]. Their technique involved exchanging the sodium of the polymer with europium and analyzing the exchanged polymer by neutron activation analysis. The technique was reported to be simple, highly sensitive, and specific to sodium polyacrylate.

A photocatalytic degradable TiO_2 /PAM composite was prepared and evaluated using methyl orange as a photodegradable target [248]. It was found that the SAP composite had good photocatalytic degradability; the composite also possessed a good reproducibility of photocatalytic degradability, which indicates its potential as a degradant for organic pollutants.

Table 1 Miscellaneous applications of superabsorbing hydrogels

| Application area | Main components | Current/potential use | References |
|--|---|---|--|
| Artificial snow | Commercial acrylic SAP (bare or properly coated) | Indoor skiing areas near Tokyo and Dubai (UAE); Toys and entertainments | [1, 5, 6, 254] |
| Packaging | Commercial acrylic SAP, hygienic grade | Absorbent airlaids in food packaging (e.g., for sorption of thin blood serum of meat), moisture absorbing pads and layers | [1, 255, 256] |
| Dewatering coal/sludge/biological slurry | Acrylic SAP and cationic reagents, poly(vinylmethylether) gel | Dewatering/concentrating fine coals, anaerobic digested and activated sludges, or microbe-rich slurries | [5, 122, 257, 258, 259] |
| Mine waste treatment | Acrylic SAP-bentonite composite | Significant potential application in acid mine tailing abatement | [122] |
| Dewatering of adulterated fuel | Commercial acrylic SAP or SAP-bentonite composite | Dewatering gasoline, diesel and non-polar solvents | [5, 122] |
| Control of flood and debris flow | Commercial acrylic SAP and permeable bags | Controlling the flood and debris destruction power | [1, 6, 260] |
| Fire extinguishing | Commercial acrylic SAP, synthetic AM-AMPS SAPs, SAP emulsions | Fire protection materials, forest fire fighting, fire retardant gels | [5, 261–263], www.thermo-gel.com |
| Oil well operation | Commercial acrylic SAP or SAP-clay composite | Reduction of water content in the crude oil, reducing lost circulation in wellbores to enhance oil recovery | [5, 122] |
| Sensors and actuators | Commercial acrylic or special SAPs, photochromic SAP | Moisture sensors, artificial muscles for robots, photo-switching | [1, 5, 6, 122, 264, 265] |
| Enzyme/catalyst | Acrylic SAP, enzyme, catalyst | Immobilization of enzymes and catalysts for production of ethanol and other chemicals | [266, 267] |
| Decoration | Self-colored and photochromic SAPs or SAP-color physical mixtures | Internal design and decorative purposes | [265, 268, 269] |
| Re-freshening systems | SAP-perfume formulations | Fragrance release systems, re-freshening tissues | [1, 5, 6, 100, 270] |

Ma et al. [249] proposed a new method to collect the size-classified fog droplets using a starch-polyacrylic SAP film. They examined the feasibility of the particle-induced X-ray emission method for the chemical analysis of the size-segregated fog droplets.

To compact Al_2O_3 ceramics, the SAP was fixed onto the surface of Al_2O_3 particles and then was injection-molded at room temperature using water as a binder [250]. The molded product was dried out at temperatures below 100 °C without cracking and then sintered.

Most recently, preparation of pure $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (30 nm) using a SAP by the thermal decomposition was reported [251]. The applicability of this nanostructure material was assessed by its catalytic effect on the Friedel–Crafts acylation reaction.

Finally, due to a well-received and attractive demonstration of SAP and glass of water, SAPs have been treated as an educational tool in advanced academic laboratories [252, 253].

Conclusion

Years of research have led to great advances in the synthesis and characterization of superabsorbent products for variety of applications. While they are proved to be an integral part of certain hygiene products, their potential of water absorption has extended their use into wide variety of applications, including agriculture, construction, electric industries, pharmaceutical, and biomedical fields. This review can be used by all scientists and researchers in other fields as a useful source to learn about the current status of the SAP materials and their applications (other than in hygiene products), through which new frontiers and products would be developed.

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