Superabsorbent Polymer Materials:
A Review

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A B S T R A C T

Superabsorbent polymer (SAP) materials are hydrophilic networks that can absorb and retain huge amounts of water or aqueous solutions. They can uptake water as high as 100,000%. Common SAPs are generally white sugar-like hygroscopic materials, which are mainly used in disposable diapers and other applications including agricultural use. This article reviews the SAP literature, background, types and chemical structure, physical and chemical properties, testing methods, uses, and applied research works. Due to variability of the possible monomers and macromolecular structure, many SAP types can be made. SAPs are originally divided into two main classes; i.e., synthetic (petrochemical-based) and natural (e.g., polysaccharide- and polypeptide-based). Most of the current superabsorbents, however, are frequently produced from acrylic acid (AA), its salts, and acrylamide (AM) via solution or inverse-suspension polymerization techniques. The main synthetic (internal) and environmental (external) factors affecting the acrylic anionic SAP characteristics are described briefly. The methods for quantifying the SAP practical features, i.e., absorption capacity (both load-free and under load), swelling rate, swollen gel strength, wicking capacity, sol fraction, residual monomer, and ionic sensitivity were discussed. The SAP applications and the related research works, particularly the hygienic and agricultural areas are reviewed. Meanwhile, the research findings on the effects of SAP in soil and agricultural achievements in Iran, as an arid country are treated as well. Finally, the safety and environmental issues concerning SAP practical applications are discussed as well.

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INTRODUCTION

Hydrophilic gels that are usually referred to as hydrogels are networks of polymer chains that are sometimes found as colloidal gels in which water is the dispersion medium [1]. In another word, they are water absorbing natural or synthetic polymers (they may contain over 99% water). Hydrogels have been defined as polymeric materials which exhibit the ability of swelling in water and retaining a significant fraction (>20%) of water within their structure, without dissolving in water [2-4]. They possess also a degree of flexibility very similar to natural tissue due to their large water content.

The applications of hydrogels are grown extensively [3-6]. They are currently used as scaffolds in tissue engineering where they may contain human cells in order to repair tissue. Environmental sensitive hydrogels have the ability to sense environmental stimuli, such as changes of pH, temperature, or the

concentration of metabolite and then release their load as a result of such a change. Hydrogels that are responsive to specific molecules, such as glucose or antigens can be used as biosensors as well as in drug delivery systems (DDS). These kinds of hydrogels are also used as controlled-release delivery devices for bio-active agents and agrochemicals. Contact lenses are also based on hydrogels.

Special hydrogels as superabsorbent materials are widely employed in hygienic uses particularly disposable diapers and female napkins where they can capture secreted fluids, e.g., urine, blood, etc. Agricultural grade of such hydrogels are used as granules for holding soil moisture in arid areas.

Absorbing versus Superabsorbing Materials

The hygroscopic materials are usually categorized into two main classes based on the major mechanism of water absorption, i.e., chemical and physical absorptions. Chemical absorbers (e.g., metal hydrides) catch water via chemical reaction converting their entire nature. Physical absorbers imbibe water via four main mechanisms [8]; (i) reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts); (ii) physical entrapment of water via capillary forces in their macro-porous structure (e.g., soft polyurethane sponge); (iii) a combination of the mechanism (ii) and hydration of functional groups (e.g., tissue paper); (iv) the mechanism which may be anticipated by combination of mechanisms of (ii) and (iii) and essentially dissolution and thermodynamically favoured expansion of the macromolecular chains limited by cross-linkages. Superabsorbent polymer (SAP) materials fit in the latter category, yet, they are organic materials with enormous capability of water absorption.

SAPs as hydrogels, relative to their own mass can absorb and retain extraordinary large amounts of water or aqueous solution [2,3]. These ultrahigh absorbing materials can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). Visual and schematic illustrations of an acrylic-based anionic superabsorbent hydrogel in the dry and water-swollen states [7] are given in Figure 1.

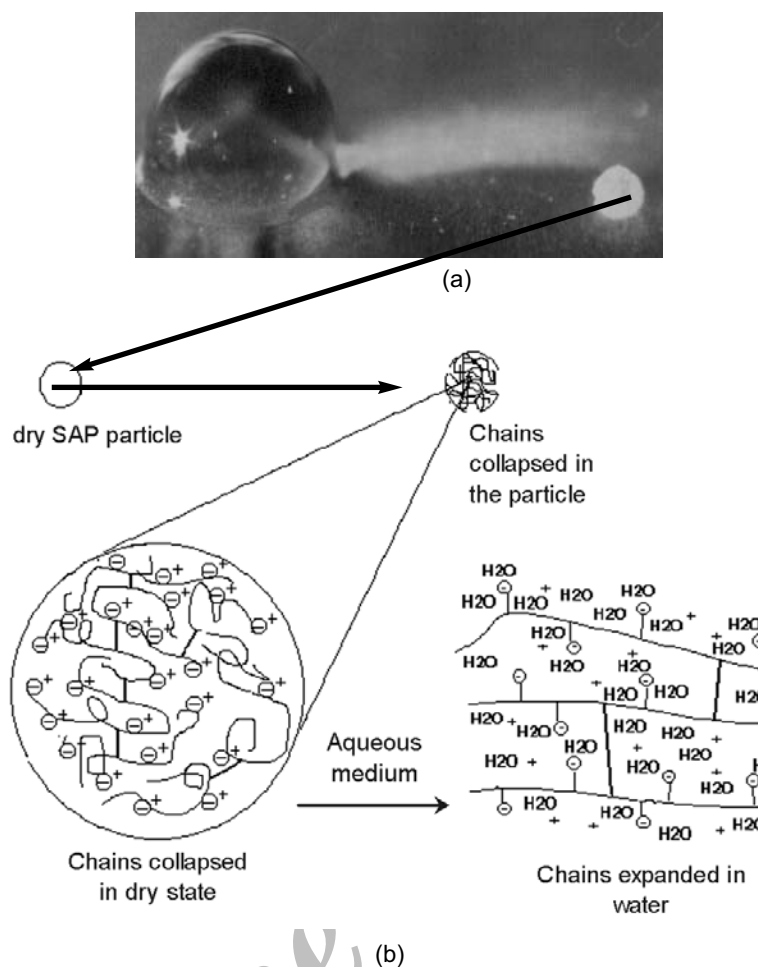Commercial SAP hydrogels are generally sugar-

Figure 1. Illustration of a typical acrylic-based anionic SAP material: (a) A visual comparison of the SAP single particle in dry (right) and swollen state (left). The sample is a bead prepared from the inverse-suspension polymerization technique. (b) A schematic presentation of the SAP swelling.

like hygroscopic materials with white-light yellow colour. The SAP particle shape (granule, fibre, film, etc.) has to be basically preserved after water absorp-

Table 1. Water absorbency of some common absorbent materials [2] in comparison with a typical commercial SAP sample.

Absorbent Material	Water Absorbency (wt%)
Whatman No. 3 filter paper	180
Facial tissue paper	400
Soft polyurethane sponge	1050
Wood pulp fluff	1200
Cotton ball	1890
Superab A-200[a]	20200

[a] Agricultural SAP produced by Rahab Resin Co., Ltd., Iran [9].

tion and swelling, i.e., the swollen gel strength should be high enough to prevent a loosening, mushy, or slimy state. This is a major practical feature that discriminates SAPs from other hydrogels.

Traditional absorbent materials (such as tissue papers and polyurethane foams) unlike SAPs, will lost most of their absorbed water when they are squeezed. Table 1 compares water absorptiveness of some common absorbent materials [2] with a typical sample of a commercially available SAP [9].

History and Market

The synthesis of the first water-absorbent polymer goes back to 1938 when acrylic acid (AA) and divinylbenzene were thermally polymerized in an aqueous medium [2]. In the late 1950s, the first generation of hydrogels was appeared. These hydrogels

were mainly based on hydroxyalkyl methacrylate and related monomers with swelling capacity up to 40-50%. They were used in developing contact lenses which have make a revolution in ophthalmology [10].

The first commercial SAP was produced through alkaline hydrolysis of starch-graft-polyacrylonitrile (SPAN). The hydrolyzed product (HSPAN) was developed in the 1970s at the Northern Regional Research Laboratory of the US Department of Agriculture [6]. Expenses and inherent structural disadvantage (lack of sufficient gel strength) of this product are taken as the major factors of its early market defeat.

Commercial production of SAP began in Japan in 1978 for use in feminine napkins. Further developments lead to SAP materials being employing in baby diapers 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 superbasorbent diapers in other Asian countries, US and Europe. Because of the effectiveness of SAPs, nappies became thinner, as the polymer mainly replaced the bulkier cellulose fluff that could not retain much liquid under pressure [3]. As a result, SAP caused a huge revolution in the personal health care industries in just over ten years.

In late 1990, the world production of the SAP resins was more than one million tons. The greatest SAP manufacturers are the Amcol (Chemdal), Stockhausen, Hoechst, Sumitomo, Sanyo, Colon, Nalco, and SNF Floerger Companies [8]. According

Figure 2. World SAP producer capacities estimated for 2005 according to the last data from EDANA [11].

to European Disposables and Nonwovens Association (EDANA) [11], the total production in 2005 approached to around 1,483,000 tons; 623,000 tons in Asia (mostly by Nippon Shokubai, San-Dia Polymers and Sumitomo Seika Chemicals), 490,000 tons in the North America (by Degussa, BASF, Dow and Nippon Shokubai), and 370,000 tons in Europe (mostly by Degussa and BASF). Specialty markets for SAPs have also been developed in agriculture, sealants, air-fresheners, toys, etc. Figure 2 shows the worldwide SAP production distribution.

In the Middle East, SAP production was started around 2004 by Rahab Resin Co., an Iranian private sector company, under the license of Iran Polymer and Petrochemical Institute (IPPI) [9].

Literature Review

Several papers have been published to review SAP hydrogel materials, each with own individual outlook. As a general framework, synthetic methods and properties of hydrogel networks were reviewed [12]. Synthetic, semi-synthetic and biopolymeric hydrogels were also briefly reviewed [13]. Chemistry and physics of agricultural hydrogels were reviewed by Kazanskii and Dubrovskii [14]. Bouranis et al. have reviewed the synthetic polymers as soil conditioners [15].

Superabsorbents obtained from shellfish waste have also been reviewed [16]. Ichikawa and Nakajima have reviewed the superabsorptive materials based on the polysaccharides and proteins [17]. A review profile of water absorbing resins based on graft copolymers of acrylic acid and gelatinized starch was presented by Athawale et al. [18].

Buchholz has elaborated the uses of superabsorbents based on cross-linked, partially neutralized poly(acrylic acid) and graft copolymers of starch and acrylic acid [19]. In another review, the synthesis of cross-linked acrylic acid-*co*-sodium/potassium acrylate has been described. The solution and suspension polymerization techniques used for preparing the acrylate superabsorbents have been discussed in detail [10].

In a unique article published in 1994, Ricardo Po [5] critically surveyed the water-absorbent polymers in accordance with the patent literature. Within an industrial production viewpoint, a useful profile has
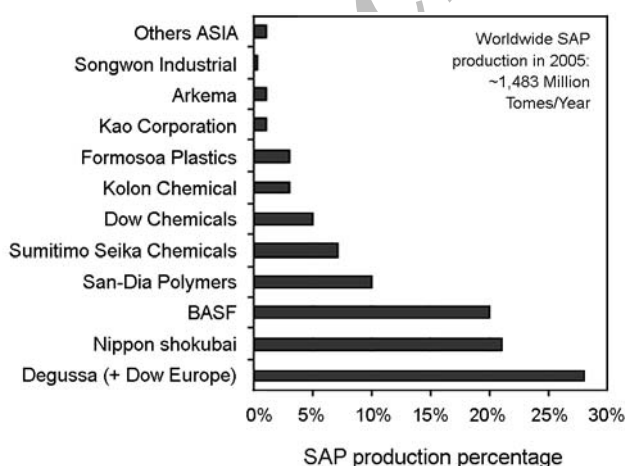
been published about acrylic SAPs by the Stanford Research Institute, SRI [20].

Two valuable books on the synthetic SAP materials were published in 1990-1998 [2,3] and the fundamental phenomena dealing with the synthetic hydrogels were reflected very clearly [3]. In 2002, another valuable book was published, focused mainly on the fibres and textiles with high water absorbency characteristics [21].

In spite of the foresaid reviewing sources, to the best of our knowledge, there is no other published review with a comprehensive perspective on SAP hydrogels. The present article represents a different outlook; it gives an account of all types of SAP materials with a practical viewpoint from structure to usage, based on either the current literature or our long experience on these materials. The main target is appraisal the SAPs to be useful for either academies or industries. Meanwhile, a very beneficial section related to the practical methods of the SAP testing and evaluation has also been included in the analytical evaluation section.

SAPs TYPES AND PREPARATION

Classification

Resembling the hydrogel family, the SAPs can also be classified based upon different aspects. SAPs may be categorized to four groups on the basis of presence or absence of electrical charge located in the cross-linked chains [8]:

1- non-ionic

2- ionic (including anionic and cationic)

3- amphoteric electrolyte (ampholytic) containing both acidic and basic groups

4- zwitterionic (polybetaines) containing both anionic and cationic groups in each structural repeating unit

For example, the majority of commercial SAP hydrogels are anionic. SAPs are also classified based on the type of monomeric unit used in their chemical structure, thus the most conventional SAPs are held in one of the following categories [5, 8]:

(a) cross-linked polyacrylates and polyacrylamides

(b) hydrolyzed cellulose-polyacrylonitrile (PAN)

or starch-PAN graft copolymers

(c) cross-linked copolymers of maleic anhydride

However, according to original sources, SAPs are often divided into two main classes; i.e., synthetic (petrochemical-based) and natural. The latter can be divided into two main groups, i.e., the hydrogels based on polysaccharides and others based on polypeptides (proteins). The natural-based SAPs are usually prepared through addition of some synthetic parts onto the natural substrates, e.g., graft copolymerization of vinyl monomers on polysaccharides.

It should be pointed out when the term "superabsorbent" is used without specifying its type, it actually implies the most conventional type of SAPs, i.e., the anionic acrylic that comprises a copolymeric network based on the partially neutralized acrylic acid (AA) or acrylamide (AM).

Main Starting Materials

Variety of monomers, mostly acrylics, is employed to prepare SAPs. Acrylic acid (AA) and its sodium or potassium salts, and acrylamide (AM) are most often used in the industrial production of SAPs (discussed later).

The AA monomer is inhibited by methoxyhydroquinone (MHC) to prevent spontaneous polymerization during storage. In industrial production, the inhibitor is not usually removed due to some technical reasons [2]. Meanwhile, AA is converted to an undesired dimer that must be removed or minimized.

The minimization of acrylic acid dimer (DAA) in the monomer is important due to its indirect adverse effects on the final product specifications, typically soluble fraction and the residual monomer. As soon as AA is produced, diacrylic acid (β-acryloxypropionic acid) is formed spontaneously in the bulk of AA via a sluggish Michael-addition reaction [2]. Since temperature, water content, and pH have impact on the rate of DAA formation, the rate can be minimized by controlling the temperature of stored monomer and excluding the moisture [22]. Increasing water concentration has a relatively small impact on the DAA formation rate. Nevertheless, the rate roughly doubles for every 5ºC increase in temperature. For example, in an AA sample having 0.5% water, the dimerization rate is 76 and 1672 ppm/day at 20ºC and 40ºC, respectively. DAA, however, can be hydrolyzed in alkaline

media to produce AA and β-hydroxypropionic acid (HPA). Since the latter is unable to be polymerized, it remains as part of the SAP soluble fraction. Fortunately, alkaline media used conventionally for AA neutralization with NaOH favours this hydrolytic reaction. For instance, in an 80% neutralized AA, the dimerization rate at 23ºC and 40ºC has been determined to be 125 and 770 ppm/day, respectively [2].

DAA can also be polymerized to go into the SAP network. It may be then thermally cleaved through a retro-Michael reaction in the course of heating in the drying step of the final product. As a result, free AA will be released and causes the enhancement of the level of residual monomer.

On laboratory scales, however, number of monomers such as methacrylic acid (MAA), methacrylamide (MAM), acrylonitrile (AN), 2-hydroxyethylmethacrylate (HEMA), 2-acrylamido-2-methylpropane sulphonic acid (APMS), N-vinyl pyrrolidone (NVP), vinyl sulphonic acid (VSA) and vinyl acetate (VAc) are also used.

In the modified natural-based SAPs (i.e., hybrid superabsorbents) trunk biopolymers such as cellulose, starch, chitosan, gelatin and some of their possible derivatives e.g., carboxymethyl cellulose (CMC) are also used as the modifying substrate (polysaccharide-based SAPs section).

The bifuntional compound *N,N'*-methylene bisacrylamide (MBA) is most often used as a water soluble cross-linking agent. Ethyleneglycole dimethacrylate (EGDMA), 1,1,1-trimethylolpropane triacrylate (TMPTA), and tetraalyloxy ethane (TAOE) are known examples of two-, three- and four-functional cross-linkers, respectively.

Potassium persulphate (KPS) and ammonium persulphate (APS) are water soluble thermal initiators used frequently in both solution and inverse-suspension methods of polymerization (discussed in the snap shot section of production processes). Redox pair initiators such as Fe^{2+}-H_2O_2 (Fenton reagent) and APS-sodium sulphite are also employed particularly in the solution method.

Synthetic SAPs
The greatest volume of SAPs comprises full synthetic or of petrochemical origin. They are produced from the acrylic monomers, most frequently acrylic acid (AA), its salts and acrylamide (AM). Figure 3 shows
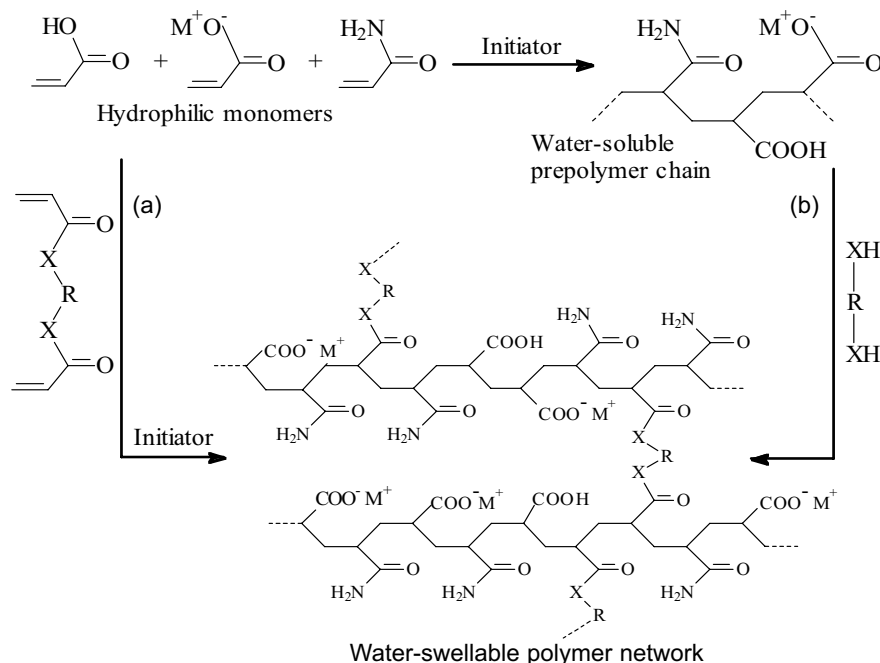

Figure 3. Chemical structures of the reactants and general pathways to prepare an acrylic SAP network: (a) Cross-linking polymerization by a polyvinylic cross-linker, (b) Cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. R is often CH_2 or another aliphatic group. M stands for the sodium or potassium cations [7]. X= O, NH.

two general pathways to prepare acrylic SAP networks, i.e., simultaneous polymerization and crosslinking by a polyvinylic cross-linker, and cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. More discussions on the synthetic SAPs are provided in the related sections.

Polysaccharide-based SAPs

Although the majority of the superabsorbents are nowadays manufactured from synthetic polymers (essentially acrylics) due to their superior price-to-efficiency balance [2,5,9], the worlds firm decision for environmental protection potentially support the ideas of partially/totally replacing the synthetics by "greener" alternatives [17].

Carbohydrate polymers (polysaccharides) are the cheapest and most abundant, available, and renewable organic materials. Chitin, cellulose, starch, and natural gums (such as xanthan, guar and alginates) are some of the most important polysaccharides.

Generally, the reported reactions for preparing the polysaccharide-based SAPs are held in two main groups; (a) graft copolymerization of suitable vinyl monomer(s) on polysaccharide in the presence of a cross-linker, and (b) direct cross-linking of polysaccharide.

In graft copolymerization, generally a polysaccharide enters reaction with initiator by either of two separate ways. First, the neighbouring OHs on the saccharide units and the initiator (commonly Ce^{4+}) interact to form redox pair-based complexes. These complexes are subsequently dissociated to produce carbon radicals on the polysaccharide substrate via homogeneous cleavage of the saccharide C-C bonds. These free radicals initiate the graft polymerization of the vinyl monomers and cross-linker on the substrate.

In the second way of initiation, an initiator such as persulphate may abstract hydrogen radicals from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone. Due to employing a thermal initiator, this reaction is more affected by temperature compared to previous method.

The earliest commercial SAPs were produced from starch and AN monomer by the first mentioned method without employing a cross-linker. The starch-*g*-PAN copolymer (SPAN) was then treated in
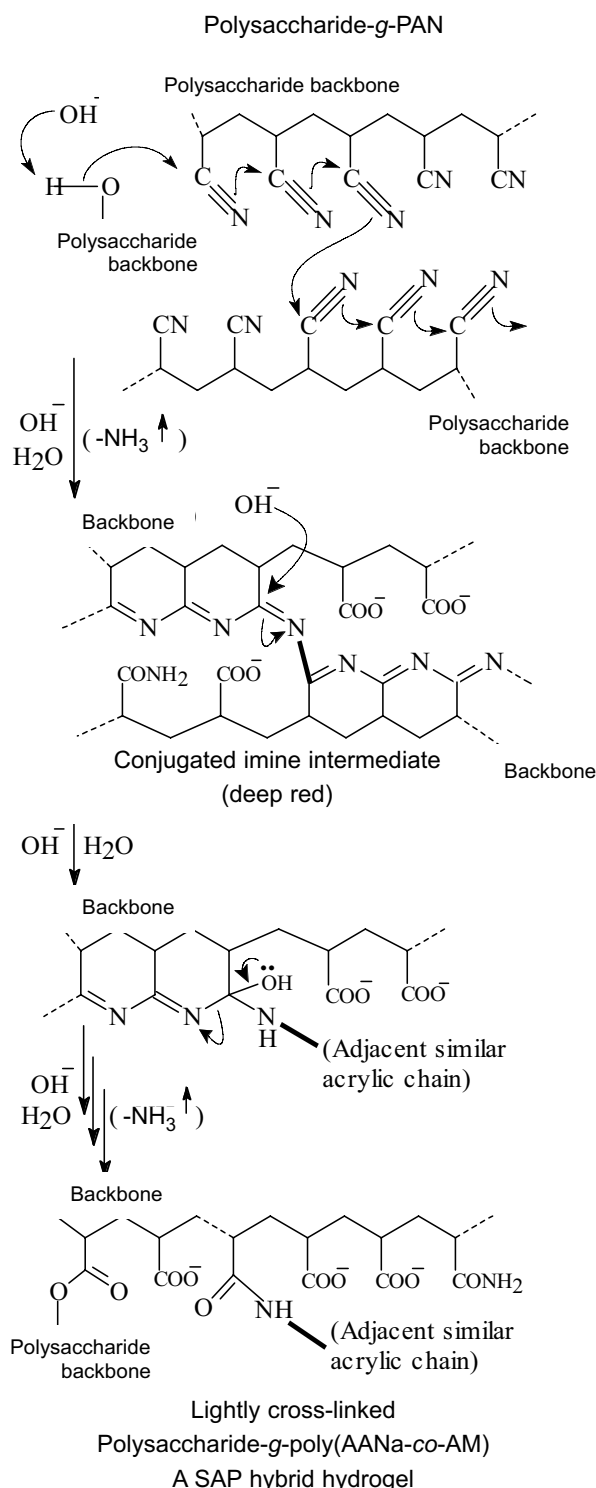

Figure 4. The mechanism of in-situ cross-linking during the alkaline hydrolysis of polysacchride-g-PAN copolymer to yield superabsorbing hybrid material.

alkaline medium to produce a hybrid SAP, hydrolyzed SPAN (H-SPAN) while an in-situ cross-linking
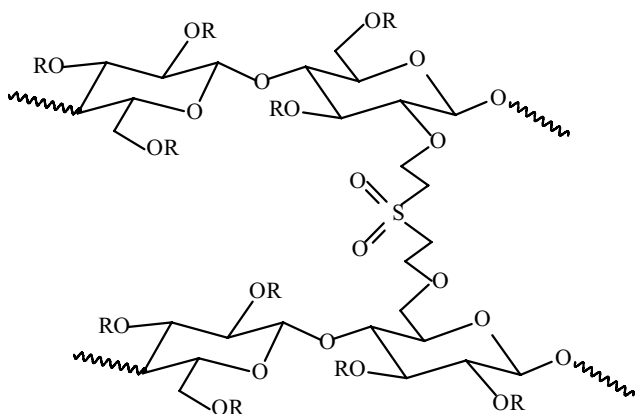
Figure 5. Typical cellulose-based SAP prepared via direct cross-linking of sodium carboxymethyl cellulose (CMC; R= H, COO⁻Na⁺) or hydroxyethyl cellulose (HEC; R= H, CH_2CH_2OH) [24].

occurred simultaneously. This fascinating approach (Figure 4) has been employed to convert various polysaccharides into SAP hydrogel hybrids [23].

In the method direct cross-linking of polysaccharides, polyvinylic compounds (e.g., divinyl sulphone, DVS) or polyfunctional compounds (e.g., glycerol, epichlorohydrine and glyoxal) are often employed [13,23]. $POCl_3$ is also used for the cross-linking. Figure 5 exhibits the structure of valuable CMC- and hydroxyethyl cellulose (HEC)-based SAPs prepared by Saninno et al. [24]. Most recently, they have also synthesized fully natural SAP hydrogels via cross-linking of the cellulosics by citric acid [25].

Poly(amino acid)-based SAPs

Dissimilar to polysaccharide-based hydrogels, relatively fewer works have been reported on the natural-based SAP hydrogels comprising polypeptides as the main or part of their structure. Proteins from soybean, fish, and collagen-based proteins are the most frequently used hetero-polypeptides for preparation of proteinaceous super-swelling hydrogels.

The most important research programme of the protein-based SAPs has been conducted by Damodaran et al. [26-35] working in the Department of Food Science, University of Wisconsin, Madison, USA. They converted soy and fish proteins to SAP through modification by ethylenediamine tetraacetic dianhydride (EDTAD) in the first stage. EDTAD has

low toxicity because the only reactive group introduced into the network is the carboxyl group, and lysyl residues of the protein that can be modified with EDTAD in a relatively fast reaction. They often used the soy protein isolate (SPI) for the modification. The modified product was prepared by extraction of defatted soy flour with water at pH 8 at a meat-to-water ratio of 1:10 [26].

In the second stage, the remaining amino groups of the hydrophilized protein are lightly cross-linked by glutaraldehyde to yield a hydrogel network with superabsorbing properties. The SAP was capable of imbibing 80-300 g of deionized-water/g of dry gel after centrifugating at 214 g, depending on the extent of modification, protein structure, cross-link density, protein concentration during the second step, gel particle size, and environmental conditions such as pH, ionic strength, and temperature [26].

The EDTAD-modified soy protein SAPs are reported to be highly pH sensitive. It also exhibits reversible swelling-deswelling behaviour when the swollen gel is alternatively exposed to 0.15 m NaCl, and deionized water [26,32].

Some patents have also been disclosed, investigating extensively on the preparation and properties of the SAPs based on the soy protein isolate [32,33]. The inventors have specified that similar approaches can be used on other proteins such as leaf (alfalfa) protein, microbial and animal proteins and those recovered from food-processing wastes.

Following the introduction of a large number of hydrophilic groups into fish protein (FP) concentrate by modification with EDTAD, the proteins are reported to be cross-linked by sulphhydryl-disulphide interchange reaction between the endogenous sulphhydryl groups (-SH) and -S-S- bonds to produce a SAP network [28]. The swelling capacity of a 76% EDTAD-modified FP is reported to be 540 g/g at 214 g, assumed to be dependent on pH and ionic strength of the swelling media, similar to what observed for EDTAD-modified SPI hydrogels [26,27,32,34]. When glutaraldehyde (GA) was employed as a cross-linker, the SAP swelling ability was diminished to 150-200 g/g, whereas the gel rigidity was enhanced. Therefore, these SAPs are preferred to be used for water absorption under pressure in real applications, such as diapers.

Proteins can also be modified by either polysaccharides or synthetics to produce hybrid hydrogels with super-swelling properties. For instance, the researchers have studied the water swelling property of binary polymer networks (frequently as interpenetrated polymer networks, IPNs) of modified proteins with some water-soluble, hydrophilic, biodegradable, and non-toxic polymers, e.g., modified soy protein, gelatin, sodium carboxymethyl cellulose (CMC), poly(ethylene glycol) (PEG), poly(vinyl alcohol), guar gum, chitosan, and carboxymethyl chitosan [30, 35-40].

Collagen-based proteins including gelatin and hydrolyzed collagen (H-collagen; very low molecular weight products of collagen hydrolysis) have been used for preparing SAP materials. For example, gelatin-*g*-poly (NaAA-*co*-AM) hydrogel has been synthesized through simultaneous cross-linking and graft polymerization of AA/AM mixtures onto gelatin [41]. The hybrid hydrogels in 0.15 mol salt solutions show appreciable swelling capacity (e.g., in NaCl 38 g/g, and in CaCl$_2$ 12 g/g). The SAP hydrogels exhibit high sensitivity to pH, thus swelling changes may be observed in a wide range of pH 1-13.

H-collagen was also graft copolymerized with AA [42] , binary mixtures of AA and AM [43], AM and AMPS [44], AA and AMPS [45,46], AM and methacrylic acid (MAA) [47], and AA and hydroxyethyl acrylate (HEA) [48] for preparation of SAP hybrid materials.

Homo-poly(amino acid)s of poly(aspartic acid)s, poly(*L*-lysine) and poly(γ-glutamic acid)s have also been employed to prepare SAP materials. In 1999, Rohm and Haas Company's researchers reported lightly cross-linked high MW sodium polyaspartates with superabsorbing, pH- and electrolyte-responsiveness properties [49]. They used ethylene glycol diglycidylether (EGDGE) as a cross-linker. Polyethylene glycol diglycidylether (PEG-diepoxide) with different MWs has also been employed to synthesize biodegradable poly(aspartic acid) hydrogels with super-swelling behaviour [50]. To enhance the swelling capacity, several hydrophilic polymers (i.e., starch, ethyl cellulose, carrageenan, PAM, β-cyclodextrin, and CMC) were incorporated into the hydrogels (after or before the hydrolysis step) to attain modified SAP composites [51].

Super-swelling hydrogels based on poly(γ-glutamic acid), PGA, has been prepared by cross-linking reactions via both irradiation [52-54] and chemical approaches [55-61]. Similar to PGA, highly swollen hydrogels based on *L*-lysine homopolymer have been also prepared simply by γ-irradiation of their aqueous solutions [52-54,62].

SAPs PROPERTIES DETERMINATION FACTORS

SAP Technical Features
The functional features of an ideal SAP material can be listed as follows [8]:
- The highest absorption capacity (maximum equilibrium swelling) in saline
- Desired rate of absorption (preferred particle size and porosity) depending on the application requirement
- The highest absorbency under load (AUL)
- The lowest soluble content and residual monomer
- The lowest price
- The highest durability and stability in the swelling environment and during the storage
- The highest biodegradability without formation of toxic species following the degradation
- pH-neutrality after swelling in water
- Colourlessness, odourlessness, and absolute non-toxicity
- Photostability
- Re-wetting capability (if required)

The SAP has to be able to give back the imbibed solution or to maintain it; depending on the application requirement (e.g., in agricultural or hygienic applications).

Obviously, it is impossible that a SAP sample would simultaneously fulfil all the above mentioned required features. In fact, the synthetic components for achieving the maximum level of some of these features will lead to inefficiency of the rest. Therefore, in practice, the production reaction variables must be optimized such that an appropriate balance between the properties is achieved. For example, a hygienic SAP must possess the highest absorption rate, the lowest re-wetting and the lowest residual monomer. In contrary, for an agricultural SAP the

Table 2. Effect of the main synthetic (internal, structural) factors affecting SAP material properties [8][a].

Variation in synthetic factor[b]	Absorption capacity	Absorption rate	Swollen gel strength or AUL	Soluble fraction
Increase in crosslinker concentration	-	-	+	-
Increase in initator concentration	+	-	-	+
Increase in monomer concentration	-	+	-	+
Increase in reaction temperature	+	-	-	+
Increase in particles porosity	×[c]	+	-	-+
Surface cross-linking	-	-+	+	-+

[a] + = increasing, - = decreasing, +- = varied, depending on the reagents and/or techniques employed. [b] Each factor is considered under a constant value of the rest factors. [c] Some authors have reported absorption enhancement, however, no absorption rise has to be logically observed if more accurate methods are employed for swelling measurement, e.g., centrifuge method.

absorption rate is not much necessary; instead it must acquire higher AUL and lowest sensitivity to salinity.

Reaction Variables
According to the voluminous research on the acrylic anionic SAP literature [2-6,8,10,14,18,41-48] the most important reaction variables affecting the final properties are as follows:

(a) Cross-linker type and concentration

(b) Initiator type and concentration

(c) Monomer(s) type and concentration

(d) Type, size, and amount of inorganic particles incorporated (if any)

(e) Polymerization method

(f) Polymerization temperature

(g) Amount and type of the surfactant used

(h) Stirrer/reactor geometry and rate of stirring

(i) Porosity generating method or the amount and type of the porogen (if used)

(j) Drying; its method, temperature, and time

(k) Post-treatments such as surface cross-linking to enhance the swollen gel strength

Each of the above mentioned variables has its own individual effects on the SAP properties. However, to optimize a process, a set of variables having the most special effects on the desired SAP product should be taken into consideration.

Effect of "Synthetic Parameters" on Properties
Employing fixed type of reactants, the acrylic SAP properties are affected by the main synthetic factors abstracted in Table 2 [8]. Many researchers have studied the effects of the preparative reaction vari-

ables on the SAP characteristics. These table contents have been actually extracted from numerous published works [2-6, 63-86].

Additionally in recent years, researchers have partially focused on SAP composites [69,78,87-91] and nanocomposites [92-94] to improve particularly the mechanical and thermal properties of the hydrogels.

Effect of "Environmental Parameters" on Properties
The SAP particle physical specifications (e.g., size and porosity) as well as the swelling media also greatly affect their properties. These physical and environmental factors, particularly for acrylic anionic SAPs, have been studied widely by many researchers [2-6, 63-94]. Table 3 summarizes the results of plenty published works on the conventional SAPs properties [8].

PRODUCTION PROCESSES: A SNAP SHOT

Acrylic acid (AA) and its sodium or potassium salts, and acrylamide (AM) are most frequently used in the SAP industrial production. AM, a white powder, is pure enough to be often used without purification. AA, a colourless liquid with vinegar odour, however, has a different story due to its ability to convert into its dimer (sub-section main starting materials). In this regard, the DAA level must be minimized to prevent the final product deficiencies, e.g., yield reduction, loss of soluble fraction, residual monomers, etc. Due to the potential problems originating from the inherent nature of AA to dimerize over time, manufactur-

Table 3. Effect of physical and environmental (external) factors on behaviour of the conventional anionic SAP materials [8] [a].

Factor[b]	Absorption capacity	Absorption rate	Swollen gel strength or AUL	Soluble fraction
Increase in Particle size	×[c]	-	+	×
Increase in Porosity	×[c]	+	-	×
Increase in Ionic Strength of Medium	-	-	-+	×
Increase in Temperature of Medium	×	+	×	×
Photo-/Bio-degradation	+	-	-	+
pH > 7	+	+	-+	×
pH < 7	-	-	-+	×

[a] += increasing, - =decreasing, × = non-effective, +- = depending on the other various factors. [b] Each factor is considered under a constant value of the rest factors. [c] Lower particle size and higher porosity are usually reported as factors that increase the swelling capacity. However, the capacity should not to be actually influenced by the particle size and porosity, if the absorption capacity is accurately measured by more precise methods, e.g., centrifuge method.

ers work properly with AA, such as timely order placement, just-in-time delivery, moisture exclusion, and temperature-controlled storage (typically 17-18ºC). In the laboratory scale syntheses, however, AA is often distilled before use, to purify and remove the impurities including the inhibitor and DAA.

AA salt solutions are usually produced by slow addition of appropriate solution of a desired metal hydroxide (NaOH or KOH) to cooled AA while stirring mild. The temperature of this extremely exothermic neutralization reaction must be precisely controlled to prevent undesired polymerization.

As mentioned before, the SAP materials are often synthesized through free-radically-initiated polymerization of acrylic monomers. The resins are prepared either in aqueous medium using solution polymerization or in a hydrocarbon medium where the monomers are well-dispersed. These different methods are briefly discussed in the following sections.

Some additional treatments, such as modified gel drying methods [2,64,72] and, particularly, surface cross-linking [2] and porosity generating techniques [2,64,68,70] are important approaches for altering and fine-tuning the SAP morphology and physico-chemical properties.

Solution Polymerization
Free-radical initiated polymerization of AA and its salts (and AM), with a cross-linker is frequently used for SAP preparation.

The carboxylic acid groups of the product are partially neutralized before or after the polymerization step. Initiation is most often carried out chemically with free-radical azo or peroxide thermal dissociative species or by reaction of a reducing agent with an oxidizing agent (redox system) [5,19]. In addition, radiation is sometimes used for initiating the polymerization [2-5].

The solution polymerization of AA and/or its salts with a water-soluble cross-linker, e.g., MBA in an aqueous solution is a straight forward process. The reactants are dissolved in water at desired concentrations, usually about 10-70%. A fast exothermic reaction yields a gel-like elastic product which is dried and the macro-porous mass is pulverized and sieved to obtain the required particle size. This preparative method usually suffers from the necessity to handle a rubbery/solid reaction product, lack of a sufficient reaction control, non-exact particle size distribution [95,96], and increasing the sol content mainly due to undesired effects of hydrolytic and thermal cleavage [72]. However, for a general production of a SAP with acceptable swelling properties, the less expensive and faster technique, i.e., solution method may often be preferred by the manufacturers.

Inverse-Suspension Polymerization
Dispersion polymerization is an advantageous method since the products are obtained as powder or microspheres (beads), and thus grinding is not

required. Since water-in-oil (W/O) process is chosen instead of the more common oil-in-water (O/W) the polymerization is referred to as "inverse-suspension". In this technique, the monomers and initiator are dispersed in the hydrocarbon phase as a homogenous mixture. The viscosity of the monomer solution, agitation speed, rotor design, and dispersant type mainly govern the resin particle size and shape [2-6].

Some detailed discussions on heterophase polymerizations have already been published [97,98]. The dispersion is thermodynamically unstable and requires both continuous agitation and addition of a low hydrophilic-lipophilic-balance (HLB) suspending agent. The inverse-suspension is a highly flexible and versatile technique to produce SAPs with high swelling ability and fast absorption kinetics [99]. A water-soluble initiator shows a better efficiency than the oil-soluble type. When the initiator dissolves in the dispersed (aqueous) phase, each particle contains all the reactive species and therefore behaves like an isolated micro-batch polymerization reactor [100]. The resulting microspherical particles are easily removed by filtration or centrifugation from the continuous organic phase. Upon drying, these particles or beads will directly provide a free flowing powder. In addition to the unique flowing properties of these beads, the inverse-suspension process displays additional advantages compared to the solution method. These include a better control of the reaction heat-removal, ab initio regulation of particle-size distribution, and further possibilities for adjusting particle structure or morphology alteration [99].

ANALYTICAL EVALUATION

This section contains the SAP testing methods that are very useful in a practical point of view for academic and industrial analysts.

Free-absorbency Capacity
Generally, when the terms swelling or absorbency are used without specifying its conditions; it implies uptake of distilled water while the sample is freely swollen, i.e., no load is put on the testing sample. There are several simple methods for the free-absorbency testing which are dependent mainly on

the amount of the available sample, the sample absorbency level, and the method's precision and accuracy.

Tea-bag Method
This method is the most conventional, fast, and suitable for limited amounts of samples (W_0= 0.1-0.3 g) [63,75-86]. The SAP sample is placed into a tea-bag (acrylic/polyester gauze with fine meshes) and the bag is dipped in an excess amount of water or saline solution for one hour to reach the equilibrium swelling. Then excess solution is removed by hanging the bag until no liquid is dropped off. The tea bag is weighed (W_1) and the swelling capacity is calculated by eqn (1). The method's precision has been determined to be around ±3.5%.

$$S_e = (W_1-W_0)/W_0 \qquad (1)$$

Centrifuge Method
The centrifugal data are more accurate than the tea-bag method and are occasionally reported in patents and data sheets [2, 4, 6, 101]. Thus, 0.2 g (W_1) of SAP is placed into a bag (60×60 mm) made of non-woven fabric. The bag is dipped in 100 mL of saline solution for half an hour at room temperature. It is taken out, and then excess solution is removed with a centrifugal separator (3 min at 250 g). Then, weight of bag (W_2) is measured. The same stages are carried out with an empty bag, and the weight of bag (W_0) is measured. The swelling capacity is calculated by the eqn (2).

$$S_e = (W_2-W_0-W_1)/W_1 \qquad (2)$$

Since the inter-particle liquid is noticeably removed by this method, the measured values are often more accurate and lower than those obtained from the tea-bag method values.

Sieve Method
SAP sample (W_1, g) is poured into excess amount of water or a solution and dispersed with mild magnetic stirring to reach equilibrium swelling (0.5-3 h depending on the sample particle size). The swollen sample is filtered at desired time through weighed 100-mesh (150 μm) wire gauze (sieve). Then it is

dewatered carefully and rapidly using a piece of soft open-cell polyurethane foam (by repeated rubbing under the gauze bottom and squeezing the foam) until the gel no longer slips from the sieve when it is held vertical [65-71,95,96,100,102]. The quantitative figures of swelling can be calculated by eqn (3).

$$S_t = [(A_t + B) - (B + W_1)]/ W_1 \qquad (3)$$

where, S_t = swelling at time t; g/g (gram of absorbed fluid per gram of polymer sample)
A_t = weight of water-absorbed polymer at time t; g
B = weight of the sieve; g

This method, also called filtering and rubbing method [7], needs a large amount of sample (1-2 g). The method's standard deviation has been determined to be around ±2.1% [102].

Absorbency Under Load (AUL)
The absorbency under load (AUL) data is usually given in the patent literature and technical data sheets by industrial SAP manufacturers [101]. When the term AUL is used without specifying its swelling media; it implies an uptake of 0.9% NaCl solution while the testing sample is pressurized by some loads (often specified to be pressures 0.3, 0.6, or 0.9 psi). A typical AUL tester is a simple but finely made device including a macro-porous sintered glass filter plate (porosity # 0, d=80 mm, h=7 mm) placed in a Petri dish (d=118 mm, h=12 mm). The weighed dried SAP sample (0.90±0.01g) is uniformly placed on the surface of polyester gauze located on the sintered glass. A cylindrical solid load (Teflon, d=60 mm, variable height) is put on the dry SAP particles while it can be freely slipped in a glass cylinder (d=60 mm, h=50 mm). Desired load (applied pressure 0.3, 0.6, or 0.9 psi) is placed on the SAP sample (Figure 6).

Saline solution (0.9% NaCl) is then added when the liquid level is equal the height of the sintered glass filter. The whole set is covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen particles are weighed again, and AUL is calculated using the following equation [73]:

$$AUL(g/g) = \frac{W_2 - W_1}{W_1} \qquad (4)$$

(a)
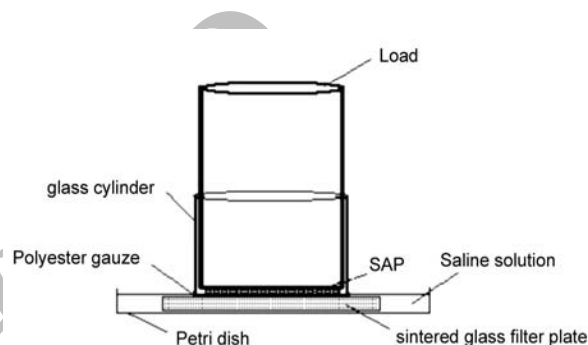
(b)

Figure 6. A typical AUL tester picture (a) and various parts (b) [8].

Where, W_1 and W_2 denote the weight of dry and swollen SAP, respectively.

The AUL is taken as a measure of the swollen gel strength of SAP materials [73,103].

Wicking Capacity and Rate
An originating simple test has been suggested by pioneering researchers Fanta and Doane [104] to quantify the wicking capacity (WC) of SAP materials with conventional physical appearance, i.e., sugar-like particle.

Thus, SAP sample (W_1= 0.050±0.0005 g) is added to a folded (fluted) filter paper cone prepared from an accurately tared circle of 9 cm Whatman 54 paper. The cone was lightly tapped to settle the sample into the tip, and the tip of the cone is then held for 60 s in a 9 cm Petri dish containing 25 mL of water. Water wicks up the entire length of the paper in a minute. Excess water is then allowed to drain from the paper by contacting the tip for 60 s with a circle of dry filter paper on a square of absorbent towel. The

weight of wet paper plus swollen polymer is determined (A), and the absorbency of the sample in g/g is then calculated after correcting for the weight of dry paper and the amount of water absorbed under identical conditions by the paper alone in the absence of sample (eqn 5). Each test is preferred to be repeated 3-5 times and the results are averaged.

$$WC = (A-B-W_1)/W_1 \qquad (5)$$

where, B is wet paper without polymer.

Assuming a monotonous absorption for the duration of 60 s, an estimation of wicking rate (g/g.s) of the SAP may be obtained by dividing the WC value by 60.

Swelling Rate
Vortex Method
The vortex method, the most rapid and simple way to evaluate the SAP swelling rate, is often employed in R&D and technical laboratories [8]. Water or saline solution (50.0 g) is poured in a 100 mL beaker and its temperature is adjusted at 30ºC. It is stirred at 600 rpm using a magnetic stirrer (stirrer bar length 400 mm). Superabsorbent sample (mesh 50-60, W_0= 0.50-2.0 g) is added and a stopwatch is started. The time elapsing from the addition of SAP into the fluid to the disappearance of vortex (t_{vd}, sec) is measured. This swelling rate (SR, g/g.s) is calculated by eqn (6).

$$SR = (50/W_0)/t_{vd} \qquad (6)$$

Swelling-time Profile
The profiles of swelling vs. time is obtained via separating swelling measurements of sample absorbed desired fluid at consecutive time intervals. Either, tea-bag, centrifuge, or sieve methods can be used for the measurements depending on the amount of the available sample and the desired precision. Typically, several 2 L Erlenmeyer flasks containing distilled water or desired solution are labeled and SAP sample (e.g. 1.0 g, 50-60 mesh) is poured into each flask and is dispersed with mild stirring. At consecutive time intervals (e.g., 15, 30, 45, 60, 90, 120, 180, 300, 600, 1800 s), the absorbency of the sample is measured by sieve method [7]. A typical profile is shown in Figure 7.
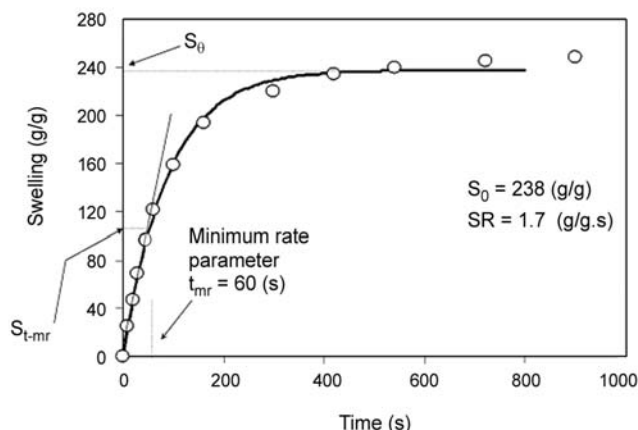

Figure 7. Representative curve for swelling kinetics of a hybrid SAP sample in distilled water [75].

The swelling kinetics of the SAPs can be studied by means of a Voigt-based viscoelastic model [105]:

$$S_t = S_e (1-e^{-t/r}) \qquad (7)$$

where S_t is the degree of swelling (g/g) at any moment, S_e, the equilibrium swelling, is swelling at infinite time or maximum water-holding capacity, t is the swelling time (s), and r, the rate parameter (s), is the time required to reach 0.63 of the equilibrium swelling.

The swelling values obtained from the above measurements are fitted into eqn (7), using a suitable software like Easyplot, to find the values of the rate parameters. According to Kabiri et al. [63], swelling rate (SR, g/g.s) may be defined as follows (eqn (8)):

$$SR= S_{t-mr}/t_{mr} \qquad (8)$$

Where, S_{t-mr} stands for swelling at the time related to minimum rate parameter t_{mr} (s) obtained from comparable SAP samples or SAPs prepared from a set of similar experiments (Figure 7). Actually, t_{mr} is related to the point where departure from maximum swelling rate takes place.

Most recently, open circuit potential measurement was reported to be used for tracing the swelling kinetics of super absorbents [106].

Swollen Gel Strength
The mechanical strength or modulus of swollen SAPs

is important from a practical viewpoint. The authors have recently proposed rotational rheometry to quantify the swollen gel strength of SAP materials with conventional shape, i.e., sugar-like particles [73].

Thus, the rheological measurements are performed using parallel plate geometry (plate diameter of 25 mm, gap of 3 mm) at 25°C. The strain used are chosen to be in the linear viscoelastic (LVE) range, where the G' and G'' are independent of the strain amplitude. After a strain sweep test, the test conditions for the frequency sweeps are selected to ensure that the test is really carried out in the LVE range.

The $G'(\gamma)$ function is conventionally taken for the analysis because G' curve almost falls before another curve (i.e., G). For determination of LVE, approximately 100-150 mg of dried SAP with average particle sizes of $180\,\mu$m is dispersed in 200 mL of distilled water for 30 min to reach maximum swelling. The excess water is removed and the swollen gel particles are then placed on the parallel plate of rheometer and the rheological properties are evaluated. The effect of shear strain on the measured G' and G at constant frequency ($\omega = 1$ rad/s) is evaluated. Below 0.2% deformation, $G'(\omega)$ is often independent of the applied strain i.e., LVE behaviour [107]. Therefore, G' is obtained at constant strain, over a range of frequency. A typical SAP by this time absorbs saline solution under 0.3-0.9 psi, for instance, it shows an overall storage modulus above 1000 Pa at 25°C. Most recently, Ramazani et al. [103] have explored linear relations that are active between the AUL and G' data over the rubber-elastic plateau.

Soluble Fraction

The soluble fraction (sol) is sum of all water-soluble species including non-crosslinked oligomers, HPA and non-reacted starting materials such as residual monomers. The sol content is simply measured by extraction of SAP sample in distilled water (this is why the sol is frequently referred to "extractable"). Therefore, a certain amount of the SAP sample (e.g., 0.10 g) is poured into excess amount of water and dispersed with mild magnetic stirring to reach equilibrium swelling (0.5-3 h depending on the sample particle size). The swollen sample is filtered and oven-dried. The sample weight loss easily results in the soluble fraction [8]. For a synthesized SAP, the gel content can also be obtained by the simple eqn (9). The gel content may be taken as an actual yield of the cross-linking polymerization.

$$\text{Sol(\%)} + \text{Gel(\%)} = 100 \qquad (9)$$

UV spectrometry technique has been also reported for the determination of SAP sol content [108].

Residual Monomer

In SAP materials, particularly hygienic SAPs where the residual monomer content is of very significant importance, the allowed safe level of the residual acrylic acid has dropped from over 1000 ppm to less than 300 ppm throughout the past two decades. High performance liquid chromatography (HPLC) is often taken as a preferred method to quantify the residual monomer. In this method, orthophosphoric acid solution is usually used as an extractant. During the extraction, the total residual monomer in form of either acid or salt are removed from the hydrogel network to be measured in the next step. The acrylic salt is converted to acrylic acid at the acidic pH of both the extracting and the eluting media, i.e., mobile phase (pH<3) [74].

The separation is usually performed in isocratic mode at a 1.8 mL/min flow rate and ambient temperature on an analytical column (e.g., 250×4.6 mm, 5 μm). The mobile phase is an aqueous 0.01% orthophosphoric acid [109]. The UV-vis absorbance over the 190-400 nm range is registered and the wavelength used for quantification is 200 nm.

The HPLC technique can also be employed for quantifying the residual AM in SAPs [110].

Ionic Sensitivity

To achieve a comparative measure of sensitivity of the SAP materials towards the kind of aqueous fluid, a dimensionless swelling factor, f, is defined as follows (eqn 10) [85]:

$$f = 1\text{-(Absorption in a given fluid/Absorption in distilled water)} \qquad (10)$$

Larger f value means the higher absorbency-loss of the sample swollen in salt solutions. Therefore, SAPs with lower f are usually preferred. Negative values of

f reveal that the absorbency is not decreased, but, it is increased in salt solutions. The SAP hydrogels with betaine structures exhibit such surprising behaviour [63].

USES AND APPLIED RESEARCH WORKS

Hygienic and Bio-related Areas

The most volume of SAP produced all over the world is used in disposable diapers. Therefore, most research works have been focused on hygienic grades which are usually used with fluff in diapers. As shown in Figure 8, the AUL has increased to about 30 g/g while free-absorbency has dropped to around 50 g (saline)/g (polymer) over past two decades. Because of the market requests for a thinner diaper, more SAP and less fluff is being incorporated into the diapers. This approach limits the maximum amount of SAP in a diaper to about 10 g/piece, and this is required for the AUL to be enhanced. A target for AUL of 35-40 is achievable using current technology, but it is desirable to have AUL as high as 45-50 g/g to obtain a much thinner diaper [6].

In addition to the absorbency parameters, the level of residual acrylic acid (RM, ppm) has dropped over 1000 to less than 30 ppm in 2000s. The extractable fraction (sol content) of the SAP has also decreased from ~13 to around 4% over time (Figure 8).
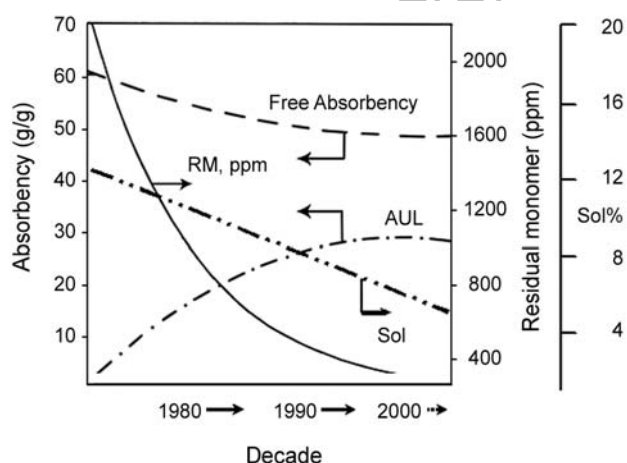

Figure 8. Trends of improvements of hygienic SAP material characteristics, i.e., free absorbency in saline, saline-absorbency under load (AUL), residual monomer (RM), and soluble fraction (sol) [6].

The efforts of manufacturers have been stressed on improving the production and engineering SAPs with higher performance, i.e., higher AUL, lower levels of RM, sol fraction and fine particles (<50 µm). Some enzymes and additives may be incorporated to prevent infection and unpleasant smell. Other hygienic applications comprise more or less similar requirements of the diaper uses.

Recently, a new generation of hygienic superabsorbent named Safe and Natural Absorbent Polymer (SNAP) has been introduced to the market [111]. SNAPs are totally natural with no residual monomer therefore they are rapidly biodegraded in the environment. However, they possess lower absorbency and higher price than the full-synthetic counterparts.

Most recently, using superabsorbent fibre and viscous fibre, a method of preparing absorbent core for ultra-thin high-absorbent sanitary napkins has been presented [112].

SAPs are one of the members of the family of smart hydrogels, hence they can be potentially employed in separation science and technology, particularly bioseparation. Due to large changes in the swelling ratio, the hydrogels have been used widely in the separation of various molecules including proteins [113]. In medicine, SAPs may be used for elimination of body water during surgery, e.g., treatment of edema [24].

In the field of pharmaceutics, some superabsorbents called super-porous hydrogels (SPHs) invented by Kinam Park et al. [114] have also been developed for gastric retention applications. They are different from SAPs since SPHs swell fast, within minutes, to the equilibrium swollen state regardless of their size. The very fast swelling property is based on water absorption through open porous structure by capillary force. SPHs have been designed for controlled delivery of drugs to stomach or intestine. The poor mechanical strength of SPHs was overcome by developing the second-generation SPH composites and the third-generation SPH hybrids [115].

Agricultural Areas

The presence of water in soil is essential to vegetation. Liquid water ensures the feeding of plants with nutritive elements, which makes it possible for the plants to obtain a better growth rate. It seems to be

interesting to exploit the existing water potential by reducing the losses of water and also ensuring better living conditions for vegetation. Taking into account the water imbibing characteristics of SAP materials, the possibilities of its application in the agricultural field has increasingly been investigated to alleviate certain agricultural problems.

SAPs have been successfully used as soil amendments 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 to be comparable to silty clay or loam. SAP hydrogels potentially influence soil permeability, density, structure, texture, evaporation, and infiltration rates of water through the soils. Particularly, the hydrogels reduce irrigation frequency and compaction tendency, stop erosion and water run off, and increase the soil aeration and microbial activity [116].

In arid areas, the use of SAP in the sandy soil (macroporous medium), to increase its water-holding capacity seems to be one of the most significant 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 these reservoirs upon the root demand through osmotic pressure difference.

The hydrogels also act as a controlled release system by favouring the uptake of some nutrient elements, holding them tightly, and delaying their dissolution. Consequently, the plant can still access some of the fertilizers, resulting in improved growth and performance rates [118-121].

On the other hand, SAPs in agriculture can be used as retaining materials in the form of seed additives (to aid in germination and seedling establishment), seed coatings, root dips, and for immobilizing plant growth regulator or protecting agents for controlled release [116].

The SAPs used in the agriculture are polyelectrolyte gels often composed of acrylamide (AM), AA, and potassium acrylate. Therefore, they swell much less in the presence of monovalent salt and can collapse in the presence of multivalent ions [119] (Figure 9). These ions can be naturally provided in the soil or introduced by the use of fertilizers and pesticides [118]. In saline media, however, the uptake capacity is yet as high as 30-60 g/g (i.e., 3000-6000%).
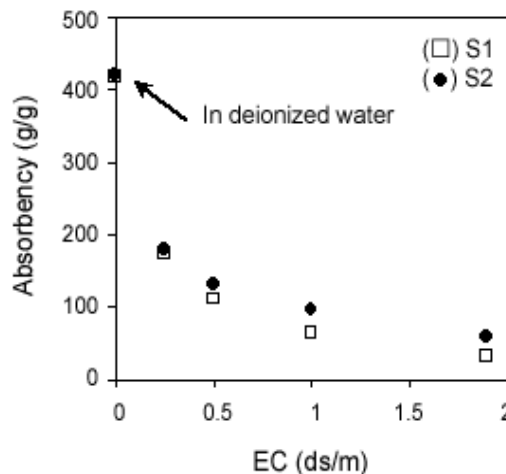
Figure 9. Representative absorbency behaviours of typical samples of agricultural SAPs (S1 and S2) swollen in deionized water and irrigative water with various salinities and electrical conductivities (ECs) [119].

There are numerous examples for the SAP assessment in the agricultural field, e.g., Abedi-Koupai et al. have experienced the SAP effect on both soil water retention and on plant indices [122]. They have evaluated the effect of superabsorbents on water retention and potentialities of three types of soils to confirm certain positive effects of the SAP on water retention of the soils.

A distinctive instance for the agricultural application of SAP has been recently practiced. Thus, the SAP effect on the growth indices of an ornamental plant (Cupressus arizonica) under reduced irrigation regimes in the field and on the soil water retention curve in a laboratory was investigated [123]. There
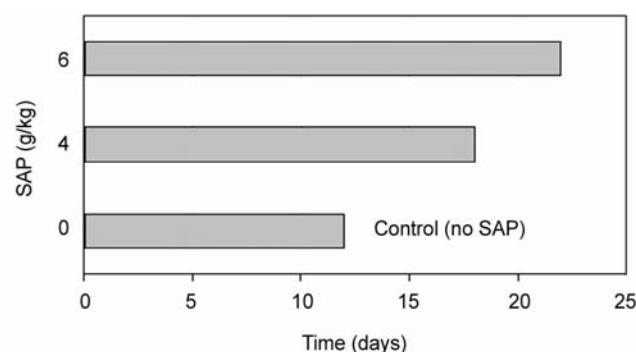
Figure 10. Number of days to reach PWP due to application of 4 and 6 g/kg Superab A200 [123].
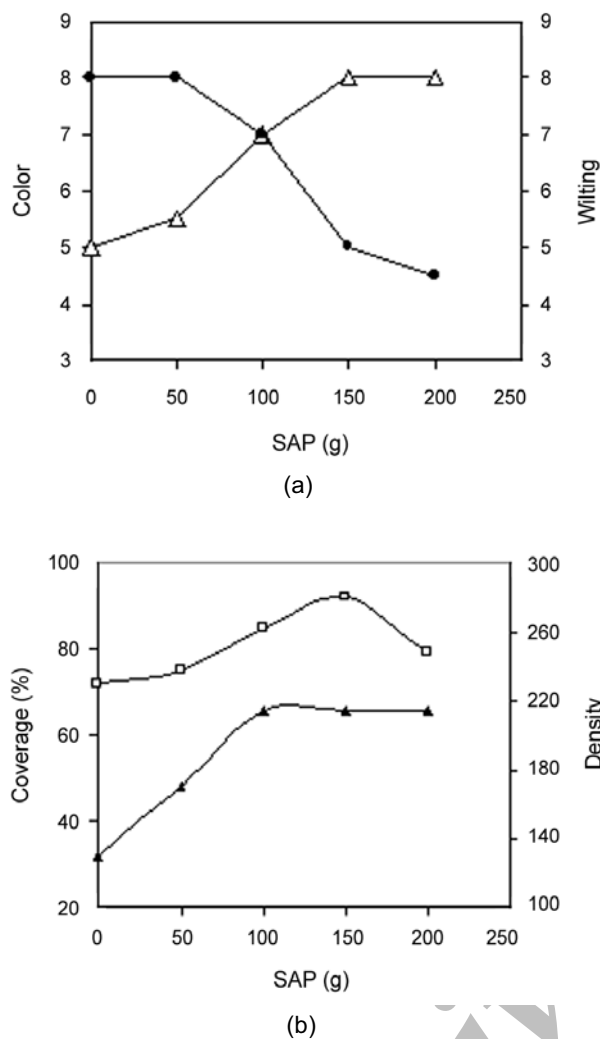
(a)

(b)

Figure 11. Effects of various amounts of SAP on the sport turf characteristics: (a) colour and wilting, and (b) coverage and density based on the NTEP standard [124].

were marked responses in the number of days to permanent wilting point (PWP) as a result of polymer application and increases in polymer concentration (Figure 10). Samples containing 6 g/kg polymer had the maximum period to reach PWP (22 days) compared to the control samples (12 days).

Additional interesting instance is a research recently conducted on the effect of SAP materials on the characteristics of sport turf. Turf is of significant importance as an inseparable part of all kinds of green spaces. Irrigation water consumption of turf is very huge, especially in the hot and dry climates due to surface evaporation and infiltration. In the research conducted by Mousavinia et al. [124] encouraging results

were obtained. Briefly, as exhibited in Figure 11, based on the NTEP standard (The National Turfgrass Evaluation Program), the turf density, colour intensity and coverage percentage is increased, while its wilting level is substantially decreased when SAP is used [8].

The effect of levels of SAP and different drought stress levels on growth and yield of olive plants [125, 126] and forage corn [126] have been investigated. Effect of SAP on the efficiency of clay mulch and biological fixation of sand dunes has been also studied [127]. Asadzadeh et al. have investigated the food element-enriched SAP in low-water treated hydroponic substrates [128]. SAP materials have shown excellent influence on decreasing damages (up to 30%) in the productive process of the olive sapling [129].

Meanwhile, non-cross-linked anionic polyacrylamides (PAM, containing <0.05% AM) having very high molecular weight ($12–15×10^6$ g.mol^{-1}), have also been used to reduce irrigation-induced erosion and enhance infiltration. Its soil stabilizing and flocculating properties improve runoff water quality by reducing sediments, N-dissolved reactive phosphorus (DRP) and total P, chemical oxygen demand (COD), pesticides, weed seeds, and microorganisms in runoff. In a series of field studies, PAM eliminated 80-99% (94% avg.) of sediment in runoff from furrow irrigation, with a 15-50% infiltration increase compared to controls on medium to fine-textured soils [130].

Other Areas
Various applications and active fields of applied research works on SAPs are well-reviewed by Po [5]. In addition to the hygienic and agricultural areas, SAP materials are (or can potentially be) used in many other fields, e.g, artificial snow, ornamental (coloured) products, entertaining/educational toys and tools, building internal decoration, fire extinguishing/retarding gels, cryogenic gels, food/meat packaging, etc. [5]. Concrete strengthening [131], reduction of the ground-resistance in the electrical industry [132] and controlled release of pesticides and agrochemicals [119-121, 133-141], are other instances for the SAP applied research. In the field of food processing, for instance, yogurt dewatering was recently investigated using permeable membrane and acrylic SAP [142].

Most recently, photochromic SAPs with excellent water absorption (2800 g/g) were synthesized using an azobenzene surface cross-linker [143]. Under irradiation at 350 nm, water expulsion from the SAP is observed. The SAP preparation and characterization has been investigated in details [143,144]. These photo-active hydrogels may be candidates to design new photochemically controlled systems for pharmaceutical, biomedical or optical switching applications.

A surprising application of SAP materials was examined by Peter Cordani for modifying the weather condition [145]. Thus, a hurricane was seeded with almost 30,000 lbs of a SAP by means of a transport plane flying through the leading edge of the storm. Within 20 seconds, the SAP obtained over 70% of its absorption capacity or nearly 300 times its weight. 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 seeded close to land, the storm did not have sufficient time to reform to its previous destructive strength.

SAFETY AND ENVIRONMENTAL ISSUES

Alike each man-made material, some common matters are also primarily questioned about the SAP materials: (a) the toxicity and safety, and (b) the environmental fate.

SAP materials cannot return to their starting monomers, i.e., they are scientifically irreversible to toxic initiating materials. Here, like so many polymers, the starting toxic monomers are converted chemically to totally non-toxic product via polymerization reaction [2-6]. SAPs are organic materials with well-known general structure. For instance, the agricultural SAP with the name of "cross-linked acrylamide/potassium acrylate copolymer" has been recorded in the most valid data centre of chemicals, i.e. the Chemical Abstracts, with CAS No. 31212-13-2. In the material safety data sheet (MSDS) of the superabsorbent manufacturers, they are called as "Safe and Non-toxic Material" [146-149].

The conventional SAP materials are neutral and inert. They are moderately bio-degraded in the soil by the ionic and microbial media to convert finally to water, carbon dioxide and organic matter [146-151].

Therefore, SAPs do not contaminate the soil and environment. They do not exhibit systemic toxicity (oral LD50 for rate ~5000 mg/kg). In addition, their safety in the soil has been approved by the Agriculture Ministry of France (APV No 8410030) [146].

Research has shown little or no consistent adverse effect on soil microbial populations [152]. The environmental fate of SAPs and their microbial degradation was investigated by many researchers [152-157]. The researchers at the University of California, Los Angles (UCLA) found that no toxic species were remained in soil after several-year SAP consuming [158].

CONCLUSION AND OUTLOOK

During more than one decade research on SAP materials, we have realized that everybody is impressed by observing the surprising behaviour of swelling of SAP particles poured in a glass of water. It is really fantastic, however, beyond the "glass-of-water presentation", SAPs have been applicable increasingly in many uses ranged from personal care products to agriculture.

SAPs are commonly made from petrochemical starting materials, i.e., acrylic monomers. However, bio-modified or natural-based SAPs are being interested due to the world steadfast decision towards the environmental protection. The biopolymer-contained SAPs, however, possess typically higher cost and less performance than their fully synthetic counterparts. Besides various applications, the most volume of SAP world production (10^6 tons/year) is yet consumed in hygienic uses, i.e., disposable diapers (as baby or adult diapers, feminine napkins, etc.).

SAPs have created a very attractive area in the viewpoint of super-swelling behaviour, chemistry, and designing the variety of final applications. When working in this field, we always deal with water, aqueous media and bio-related systems. Thus, we increasingly walk in a green area becoming greener via replacing the synthetics with the bio-based materials, e.g., polysaccharides and polypeptides. This, however, is a long-term perspective. More or less, the acrylic kingdom will extend its domination in the future markets.

In spite of the SAP attractiveness, there are some drawbacks seeming to be worth noting. First of all, the researchers do not use a unified standard for swelling measurement in their works, a problem that makes the comparison of hydrogels more or less impossible.

Another drawback in this field in general is an absence of sol fraction data in nearly all reports involving the SAP synthesis. Considering this fact that hygiene occupies the largest market for SAP and diapers making up 83% of the worldwide market applications for superabsorbing hydrogels, the necessity of producing new kind of SAPs with high gel content (minimum extractable or soluble fraction) seems more tenable. Thus, there is now a need to develop new hydrogels with minimized sol fraction and residual monomer; characteristics that usually are neglected by the academic researchers. Another point to note is that, unlike the SAPs manufacturers, the academic researchers do not usually report saline-absorbency under load (AUL) values in the case of newly synthesized hydrogels. It should be emphasized that load-free absorbency (free-swelling) that are usually reported in research articles, is not an important factor from the practical or industrial point of view. Thus, measurement and reporting the mentioned practical data will be extremely beneficial.

Finally, considering high-cost and increasing prices of crude oil, the necessity of preparing natural-based SAPs seems more obvious. This paves the way to further developments in this area in the mid and far future ahead.

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