

SUPERABSORBENT MATERIALS

1. Introduction

Water-absorption materials are among the most useful products in the daily life of human beings. For a long period of time, humans have used a lot of water-absorbent materials, such as towels, dinner cloths, dishcloths, sponges, colloidal silica, and paper. However, these naturally occurring absorbents cannot meet human requirements because their capability of absorbing and preserving water is extremely limited (1,2). So, the study and development of novel water-absorption materials has long been the subject of great interest.

Superabsorbent materials (SAMs) are three-dimensionally cross-linked hydrophilic polymer networks that can absorb large volumes of aqueous fluids in a short time and can retain the absorbed water even under heating or some pressure (1–4). Compared with the conventional absorbents, SAMs have higher water-absorbing and water-retention capabilities as well as a faster water-absorption rate. By virtue of their unique advantages, SAMs have received considerable attention, and the design and application development of such materials have also made encouraging progress since the first SAM was reported by the U.S. Department of Agriculture (5). Currently, SAMs have been applied in many fields, including agriculture and horticulture (6–16), hygiene products (17–21), sealing materials (22,23), artificial snow (24,25), drilling fluid additive (26), fine coal dewatering (27,28), wastewater treatment (29–39), medicine for drug-delivery systems (40–44), construction engineering (45), and communication cables (46). Among them, the applications of SAMs in agriculture, horticulture, and hygiene products are still the dominant application fields. With the subsequent research and development of SAMs and their commercial production, more SAMs with special structure, composition, and performance will be developed and their application will also be expanded.

1.1. Development History of SAMs. The investigation and development of SAMs has a short history. In the 1950s, the Goodrich Corporation developed cross-linked poly(acrylic acid) polymer and used it as a thickening agent. Meanwhile, the Nobel Prize winner for chemistry Flory Paul John established the water-absorbing and swelling theory of polymer hydrogel (47), which has established a solid theoretical foundation for the development of SAMs. In 1959, the North Institute of the U.S. Department of Agriculture (48,49) developed an investigation on the acrylonitrile grafted starch and invented the HSPAN hydrolysis product of starch-*graft*-poly(acrylonitrile). This product was applied in agriculture and horticulture as a water-retention hydrogel. Subsequently, G. F. Fanta et al. (50,51) developed P-PAN SAMs through the graft copolymerization of wheat starch with acrylonitrile. The P-PAN products exhibited a high water absorbency of 300–1000 g/g and excellent water-retention properties. In the mid-1970s, the SAMs derived from cellulose were developed in Japan. In 1976, the cellulose-*graft*-poly(acrylonitrile) products in the forms of sheet, powder, and filaceous were prepared by Hercules Personal Products Corporation (52). In 1979, the starch-*graft*-poly(acrylic acid) production line with the output of 1,000 tons/year was successfully put into operation in Nagoya, Japan, and the products were used for feminine sanitary napkins and infant

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diapers. In 1978, the National Starch Corporation (Enoree, SC) prepared insoluble cross-linked poly(sodium acrylate) SAMs by using water-soluble acrylic acid as a raw material (53). By virtue of the simple production procedure, moderate cost, mildew resistance, and high water-absorption capability, poly(sodium acrylate) became one of the most frequently used SAMs. In 1980s, the other natural macromolecules and their derivatives, such as alginate, protein, chitosan, and pectin, have been used for the preparation of SAMs (54–56). In the 1990s, the inorganic materials, such as inorganic nanoparticles and natural clay minerals, were incorporated into pristine organic SAM networks to form superabsorbent composites (57). Compared with the conventional organic SAMs, the developed composites exhibited improved water-absorption rate, salt resistance, and gel strength. In addition, the use of cheap inorganic materials could greatly reduce the production cost. So, the investigation on this kind of SAMs has made great progress in recent years. Up until now, the research related to superabsorbent composite is still the most potential and promising subject in both academic and industrial fields.

1.2. Commercialization of SAMs. The commercial production of SAMs began in Japan in 1978 to produce feminine napkins (58). This early SAM is a cross-linked starch-*graft*-poly(acrylate). Because of the drawbacks of starch-based SAMs, cross-linked poly(acrylic acid) products eventually replaced the earlier starch-based SAMs and became the primary polymer applied for SAMs today (53). European countries subsequently developed the SAMs for use in baby diapers. This first diapers prepared using this technology only added a small amount of polymer (about 1–2 g). In 1983, a thinner diaper added 4–5 g of SAM and less fluff was marketed in Japan. Figure 1 depicted the increasing trends of the global yield of SAMs; it can be observed that the global yield of SAMs rapidly increased from 0.5 million tons/year in 1980 to 140 million tons/year in 2005 (59, 60). It was also predicted that the global total yield of SAMs will reach 160 million tons/year. Currently, the manufacture of SAMs is mainly centered in United States, Western Europe, and Japan, and dozens of companies produce these SAMs (61). In June 2000, the Chemdal Company of the United States was accompanied with BASF, and it became the biggest manufacturer of SAMs in the world (62). The demands for such materials will increase as the economy grows and society demands more. Table 1 gives the production capacity of the leading seven manufacturers of SAM in 2005. It can be noticed that the production of commercial SAMs was mainly centered in United States, Germany, and Japan, and the total outputs of these three countries accounts for about 94% of the global total yield (60). Meanwhile, the consumption of SAMs also rapidly increased in the past decades. In 1999, the consumption of SAMs in the world was estimated to be 800,000 tons. In 2004, the global demand for SAMs reached 1,000,000 tons. SAMs have become one of the most important polymer materials.

2. Characteristics of SAMs

In comparison with the traditional water absorbents, such as cotton, wool, sponge, colloidal silica, and calcium chloride, SAMs have remarkable advantages and unique characteristics, such as follows.

2.1. High Water Absorbency. The traditional water-absorbent materials can only absorb water about 20 times their own weight, whereas SAMs usually exhibit a stronger affinity to water and can absorb hundreds and even thousands of times their weight in water (Fig. 2) (63). The higher water absorbency of SAM is closely related to its composition and structure. Typically, large amounts of strong hydrophilic groups (such as $-\text{COO}^-$, $-\text{OH}$, $-\text{C}=\text{O}(\text{NH}_2)$ and $-\text{SO}_3\text{H}^-$) are found in the network structure of SAMs. When in contact with water, these hydrophilic groups can be ionized or can form hydrogen bonds with water molecules. On the one hand, the ionization of ionic groups makes the polymer chains charged, and the polymer network is expanded because of the electrostatic repulsion interaction. Also, the dissociation of ionic groups generated the osmotic pressure difference between internal network and external solution, which acts as a driving force for the penetration of water molecules. On the other hand, the hydrogen bonding interaction among hydrophilic polar groups and water molecules enhanced the affinity of polymer network with water. Compared with traditional absorbents, the particular molecular structure and three-dimensional network of SAMs cause it to have a higher water absorbency.

2.2. Strong Water-Retention Capability. Besides the high water absorbency, the strong water retention capability of SAM is also an advantage over general absorbents. The particle shape of SAMs (granule, fiber, and film) can be preserved well after swelling (ie, the swollen gel strength should be high enough to prevent loosening or a mushy or slimy state) (Fig. 2b). Therefore, SAMs hardly lost the absorbed water even under certain temperature or pressure, whereas the general absorbents can immediately lose the absorbed water when slightly heated or pressed. The excellent water-retention capability of SAMs is ascribed to the existence of special hydrophilic groups. Because of the reticular formation of three-dimensional hydrophilic networks, the absorbed water was fixed in the network space through various physical and chemical interactions. Thus, the absorbed water is hardly removable in contrast to the general absorbents.

2.3. Effectiveness and Persistence. Different from the conventional absorbents, SAMs have the reswelling capability and can be reused or recycled in practical application. After several swelling-deswelling-swelling cycles, SAMs can usually retain about 50% of its initial swelling capability. The reswelling capability of SAMs is beneficial to its practical application in many fields such as agriculture, wastewater treatment, and petroleum industry. In general, the persistence of SAMs is affected by its intrinsic characteristics, the external environment, and the dosage.

2.4. Safety. The lixivium solution of SAMs showed weak acidity or alkalence, and it has no obvious stimulation to the creatures. Many animal and agricultural experiments indicate that the SAMs used in food, medicine, and

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hygiene are safe and nontoxic, and the SAMs used in agriculture and forestry will not change the acidity and alkalinity of soil.

3. Water-Absorption Mechanism of SAMs

The traditional absorbents (such as cotton, sponge, paper, wood pulp, etc) can only absorb 10 to 20 times more water than their own weight, but SAMs can absorb hundreds and even thousands of times more water than its dry weight. In fact, the higher swelling capability is directly related to the molecular state of the polar groups in its network structure. Generally, the water absorption style of absorbents can be classified as two models: physical absorption and chemical absorption (64). The absorption of traditional absorbents into water is mainly physical absorption, and the water molecules penetrate into the internal network through capillarity. So, the absorbents can easily reach saturation, and the absorbed water can be squeezed out easily even under low pressure. SAMs are hydrophilic three-dimensional polymer networks constructed by chemical cross-linking and the physical tangle among polymer chains (65). Its water-absorption mechanism involves both physical and chemical absorption. After being absorbed, the water molecules are confined in the fixed polymer network space with the side length of 1–10 nm formed by the chemical or physical cross-linking. It is noticeable that the physical absorption not only included capillarity but also involved physical absorption of the three-dimensional macromolecular network. Although this kind of absorption is not as fast as the chemical absorption, the absorbed water still keeps the physical and chemical properties of general water except that the motion of the water molecules were limited.

The main chain of SAMs may be starch, cellulose, or synthetic resin containing numerous hydrophilic groups (hydroxyl, carboxyl, amide, and sulfonic groups). These chains containing hydrophilic groups were cross-linked in the presence of a cross-linker and formed a three-dimensional hydrophilic network. The particular network structure is the key factor for the high water-absorbing capability of SAMs. Before absorbing water, the polymer network is a solid network bunch (Fig. 2a). After contact with water, the ionic hydrophilic groups of SAMs were dissociated and the anions were fixed on macromolecule chain with portable cations around them. The typical mechanism for the swelling of SAMs was depicted in Fig. 3. It can be noticed that the electrostatic repulsion among the anions makes the polymer network expanded, and the osmotic pressure difference between internal network and external solution was generated at the same time. The osmotic pressure difference acts as a driving force and promotes the penetration of water molecules into the polymer network. With the increase in the amount of absorbed water, the osmotic pressure difference tends to zero and the elastic contractile force of polymer chains also gradually increased with the expanding of polymer network. When the elastic contractile force counteracted the electrostatic repulsion, the swelling equilibrium was achieved. As a whole, the water-absorption mechanism of SAMs is mainly dependent on the affinity of hydrophilic groups with water as well as the interior three-dimensional network structure. The larger the pore size of the three-dimensional network,

the higher the water absorbency. Obviously, the three-dimensional reticular formation is a structural factor of absorbing water for SAMs.

4. Factors Affecting the Properties for SAMs

4.1. Intrinsic Structure of SAMs. The absorbency and swelling capacity of SAMs are controlled by the type and cross-linking degree of the polymer. The SAMs with low cross-linking density generally have a higher absorbent capacity and can swell to a greater degree. In reverse, the water absorbency of SAMs decreases with the increase in cross-linking density (47). However, SAMs must have a proper cross-linking degree and must swell but not dissolve. Ion-type SAMs usually have better water absorbency than nonionic ones, and the affinity of hydrophilic groups with water follows the order of $-\text{SO}_3\text{H} > -\text{COOH} > -\text{CONH}_2 > -\text{OH}$. In addition, the water absorbency of SAMs was also affected by the particle size. A small particle size usually corresponds to a high water absorbency (66). However, the particle size can not be too small and the moderate particle size is 20–145 mesh.

4.2. pH of External Solution. As described previously (67–69), the water absorbency of anion-type SAMs almost keep constant over the wide pH range from 4 to 11. This behavior is favorable to the application of SAMs in various fields such as agriculture and hygiene products, and it can be ascribed to the change of hydrophilic groups in various pH solutions. According to the literature (70), the pKa of poly (acrylic acid) is about 4.7, and thus the $-\text{COOH}$ groups can be easily ionized above the pH value of 4.7, and the $-\text{COO}^-$ groups can also be deionized when pH is less than 4.7. The external pH value is considered to be the governed factor influencing the ionization degree of $-\text{COOH}$ groups. When pH is less than 4, numerous $-\text{COO}^-$ groups transformed into $-\text{COOH}$ groups, which increased the hydrogen bonding interaction among hydrophilic groups and generated additional physical cross-linking. As a result, the water absorbency of SAMs rapidly decreased. In the pH range from 4 to 11, the $-\text{COO}^-$ groups coexisted with the $-\text{COOH}$ groups and formed a buffer system, and the external pH after swelling of the SAM almost remain constant (71, 72). Thus, the water absorbency also keeps constant in the pH range of 4–11. However, in basic media, the number of cations in polymeric network was increased, which can screen the negative charge on polymeric chains and restrict the expansion of polymer voids. As a result, the water absorbency was also decreased.

4.3. Ionic Strength of External Solution. The greater the ionic strength of external solution is, the lower the absorption capacity of SAMs. The water absorption capability of SAMs in saline solution is much lower than that in distilled water (73–75). Generally, the saline-resistant property of nonionic SAMs is better than ionic ones. Buchanan et al. (76) proposed that SAMs usually exhibited water absorption capability in univalent cationic saline solution with equal concentration, and the water absorbency in multivalent cationic saline solution was decreased as a result of the complexation of the metal ions with hydrophilic groups.

5. Classification of SAMS

5.1. Starch-Based SAMS. Starch is an easily available, low-cost, and biodegradable natural biopolymer with large amounts of reactive hydroxyl groups. It can be easily modified through the ring-opening reaction or graft polymerization reaction that occurs on $-OH$ groups to form various derivatives and graft copolymers (77, 78). A starch-based SAM was firstly prepared by the U.S. Department of Agriculture (5). The detailed procedure was as follows. Starch was first gelatinized at a certain temperature, and then the gelatinization was initiated by an initiator (ceric ammonium nitrate). Subsequently, the monomer acrylonitrile was added into the reactor and the graft copolymerization reaction was carried out at $30-35^{\circ}C$. The graft polymerization products were hydrolyzed in strong alkali solution, and the nitrile groups ($-CN$) are converted to hydrophilic amide groups ($-CONH_2$), carboxyl groups ($-COOH$), or carboxylate groups ($-COO^-$). Currently, the starch-based SAMS mainly include the graft copolymers of starch with acrylonitrile, acrylamide, acrylic acid, and vinylsulphonate, as well as the directly cross-linked product of modified starch, such as carboxyl-methyl starch and hydroxyethyl starch (79). Figure 4 gives the production flowcharts of the representative graft copolymers of starch with acrylic acid, acrylonitrile, and acrylamide, and it depicts the typical production procedure of starch-based SAMS. In this process, the most frequently used synthesis method is free-radical polymerization in aqueous solution, and it used initiator systems including a thermal initiator such as persulfate, the redox initiation pairs such as $H_2O_2-Fe^{2+}$ pairs, and the ionic initiator such as ceric ammonium nitrate.

Because of the difference of initiator system, the graft polymerization of starch may occur through two distinct mechanisms: One is the ring opening of starch (Fig. 5a), and the other is the direct reaction starch main chains (Fig. 5b). The ring-opening reaction usually occurs when the ionic initiator was used, and the direct reaction occurs under the condition of other thermal or redox initiation systems. Ceric ammonium nitrate is a typical ionic initiator; it can complex with the functional groups of starch such as $-OH$ because of the presence of molecular oxygen and then dissociate to generate macromolecular radical (48). The amylose rings may be opened in this process, and the formed active radical sites may initiate the vinyl groups of monomer to promote the propagation of polymer chains (Fig. 5a) (80–83). When using thermal initiator, such as ammonium persulfate, or redox initiator pairs, such as potassium permanganate, the active grafting sites may also occur on the main chains (Fig. 5b). At the stage of initiation, the hydroxyl group of starch was first oxidized as aldehyde group, and the aldehyde group may rearrange as enol structure. Enol can react with $Mn(IV)$ or $Mn(III)$ ions to generate macroradicals (84). These radicals can act as the active centers during reaction and can initiate vinyl monomers to process the chain propagation that is essential to the continuous grafting polymerization. In the course of the chain propagation, the cross-linker containing vinyl groups also participates in the grafting copolymerization reaction, which makes the copolymer forming a cross-linked structure.

5.2. Cellulose Based SAMs. As is well known, cellulose is the most abundant natural renewable resource in the world. It is derived from wood pulp and is composed of linear chains of covalently linked glucose residues (85). Because cellulose is a low-cost, renewable, biodegradable, and nontoxic substance, it has been used as matrix polymer for the design and synthesis of SAMs with better water absorption capabilities and environmentally friendly characteristics. The commonly used method to prepare cellulose-based SAMs is the graft polymerization of vinyl monomers onto the macromolecular chains of cellulose in the presence of cross-linker, and the representative production flowchart of cellulose-*g*-poly(acrylamide) superabsorbent is shown in Fig. 6. After this procedure, large amounts of hydrophilic groups such as carboxyl or sulfonic groups have been introduced, and the three-dimensional network used for holding water is formed. The cellulose-based SAMs mainly involve the graft copolymer of cellulose or their derivatives with acrylonitrile, acrylic acid, acrylamide, and vinylsulphonate. In addition, the cross-linked etherification products, esterification products, and carboxyl methylation products of cellulose are also important members in the family of cellulose-based SAMs.

The graft mechanism of vinyl monomers onto cellulose is similar to that of starch. The C₂–C₃ bonds of cellulose can be opened in the action of ionic initiator to form –C=O groups, which can dissociate to generate macroradicals as shown in Fig. 7a. The macroradicals may open the C=C bonds of vinyl monomers and process the chain propagation (86–88). After cellulose is saponified, its active main chains can also be initiated by other radical initiators to form macroradicals and initiate vinyl monomers to form graft copolymers (89). In the presence of a cross-linker, the graft copolymer chains can be cross-linked to form a three-dimensional hydrophilic network structure (Fig. 7b).

5.3. Synthetic SAMs. Synthetic SAMs [including poly(acrylate), poly(acrylamide), poly(acrylonitrile), and poly(vinylsulphonate) and their copolymer with other hydrophilic monomers] and the grafting copolymer of poly(vinyl alcohol) with other vinyl monomers are the most frequently studied among the superabsorbent families (90). The representative production flowchart of poly(sodium acrylate) SAM was shown in Fig. 8. It can be noticed that the production procedure is remarkably simpler than that of starch and cellulose. Among numerous synthetic SAMs, ion-type SAMs usually have higher water absorbency; however, their salt-resistant properties are poor and their water-absorbing rate is slow. In contrast, the nonionic SAMs frequently exhibit better salt-resistant properties and a higher water-absorbing rate. Thus, the copolymerization of ionic and nonionic monomers has attracted great interests, and such materials become the part and parcel in the family of synthetic SAMs. For example, the introduction of nonionic monomers (acrylamide or 2-hydroxyethyl acrylate) into the poly(acrylic acid) system may greatly enhance the salt-resistant properties (91). Using 2-hydroxyethyl acrylate-containing hydroxyl groups and acrylamide-containing amide groups as nonionic monomers to copolymerize with sodium acrylate, the water absorption capability of the SAMs can be greatly improved as a result of the synergistic effect of different hydrophilic groups (92). The spherical poly(acrylate) SAMs with the particle size of 20–50 nm can be obtained through suspension polymerization and azeotropic dehydration techniques, which exhibit an improved surface area and

water absorption rate. The linear poly(vinyl alcohol) can be cross-linked using phosphoric acid to form three-dimensional network SAMs with the best absorbency of 480 g/g in distilled water (93).

5.4. Biodegradable SAMs. Because of the increasing attention to environmental protection issues, the environmentally friendly characteristics of materials have become an essential index to evaluate their applicability in practice. Therefore, the biodegradable SAMs have been extensively concerned along with their water absorption and water-retention capabilities. Currently, the biodegradable SAMs are mainly focused on the natural polysaccharide family (94, 95). Besides the above described starch (96–98) and cellulose (99), other natural polymers, including chitosan (100–102), guar gum (103), gelatin (66), protein (104), carrageen gum (44), sodium alginate (105), cashew gum (106), and dextrin (107), as well as the synthetic polymer family, including poly(lactic acid) (108), poly(vinyl alcohol) (109), and poly(amino acid) (110), are important biodegradable raw materials. Poly(lactic acid) SAM is actually composed of poly(lactic acid) and components with superabsorbent properties, in which poly(lactic acid) is biodegradable and the water-absorption components may be provided by the familiar SAM. The combination of sodium alginate with poly(acrylic acid) formed a SAM with semi-interpenetrating network structure, in which sodium alginate may decompose by the natural erosion force and poly(acrylic acid) may enhance the swelling capability of SAM. Poly(amino acid) contains hydrophilic amino groups and hydroxyl groups, and it is a biodegradable polymer material (111). The Nippon Shokubai Chemical Corporation and Mitsubishi Chemical Corporation developed poly(succinimide) using aspartic acid as a raw material and prepared poly(aspartic acid) SAMs through the hydrolysis of poly(succinimide). Chitosan is the world's second most abundant natural biopolymer with highly reactive hydroxyl and amino groups, which can be easily modified through various chemical and physical means to prepare SAMs. Different from the other polysaccharides, the granular chitosan-based SAMs can be formed directly in aqueous solution by controlling the reaction condition (101). Currently, the biodegradable SAMs have mainly been used in diapers, sanitary napkins, medicine, and agriculture. Among them, the applications in medicine and hygiene products are the fields with the most earning and growth potential.

5.5. Superabsorbent Composites. In the 1980s, Panduranga et al. (112) compounded organic SAMs with other materials. The incorporation of fillers can effectively improve the salt-resistant properties, gel strength, thermal stability, and water-retention capabilities of the SAMs. Hence, the superabsorbent composites have been researched extensively. Typically, an organic superabsorbent polymer can compound with inorganic matters or other organic matters to prepare superabsorbent composites with excellent performance and low cost.

Organic-Inorganic Superabsorbent Composite. Currently, the introduction of inorganic materials into an organic superabsorbent network to form an organic-inorganic superabsorbent composite has become an ideal strategy and preferred method because such materials exhibited better water-absorbing capability and rate, salt-resistance, and gel strength than the pristine organic SAM (57). Meanwhile, the production cost can also be reduced by virtue of the addition of cheap inorganic materials, which is favorable to the industrialization of SAMs. The inorganic matters that can compound with organic superabsorbent can be

divided into two classes: (1) inorganic hydrogels, such as aluminum, iron, tin, titanium, silicon, and chromium gel (113–117); and (2) inorganic clay minerals, such as kaolin (118), bentonite/montmorillonite (119–123), sericite (124), attapulgite (69, 73, 98, 125), rectorite (126), vermiculite (103, 127), and diatomite (74). Usually, the inorganic hydrogels or minerals have good salt-resistant properties, and so the introduction of inorganic matter can improve the salt-resistant property of the organic SAMs.

Because inorganic minerals are low cost, easily deep processed, and compounded with organic monomers or polymer, a superabsorbent composite based on inorganic minerals has been extensively studied throughout the world in recent years. The most commonly used method for preparing an organic-inorganic superabsorbent composite is solution polymerization. Figure 9 depicted the production process of the popular poly(sodium acrylate)/clays and starch-*g*-poly(acrylic acid)/clays superabsorbents as a representation of petroleum-based and natural polymer-based superabsorbent composites, respectively. By using the similar procedure, a lot of superabsorbent composites derived from various organic polymers and inorganic minerals have been prepared and evaluated [eg, poly(acrylic acid)/attapulgite (128), poly(acrylamide)/attapulgite (129), poly(sodium acrylate)/vermiculite (130), poly(acrylic acid)/diatomite (74), starch-*graft*-poly(acrylamide)/mica (97), chitosan-*graft*-poly(acrylic acid)/attapulgite (101), pectin-*graft*-poly(acrylic acid)/kaolin (66), and dextrin-*graft*-poly(acrylic acid)/montmorillonite (107)]. In these composites, the incorporation of clays can obviously improve the water absorbency and water-absorbing rate of the SAM. Clays have been proposed to participate in the polymerization reaction through the active silanol groups on their surface, and so the network structure was improved and the intertwisting of polymer chains was also prevented because of the incorporation of rigid clay minerals (57). As a result, the performance of SAMs can be improved greatly.

Organic-Organic Superabsorbent Composite. To prepare composite materials through the blending or compounding of superabsorbent with other polymers is an important method to improve the performance of SAMs. Currently, the method of preparing a superabsorbent composite through the blending process of the SAM and other polymer include melting photoresist, dispersion liquids, and solution methods. For example, the superabsorbent fiber is a copolymer fiber that contains carboxylate or carboxylic acid alkyl ester and can be made by the combination of organic superabsorbent with fibers. The semi-interpenetrating polymer network hydrogel based on poly(vinyl alcohol) and poly(acrylamide-*co*-sodium methacrylate) was prepared in aqueous solution through the composite of poly(acrylamide-*co*-sodium methacrylate) with poly(vinyl alcohol) (109). The carrageenan-*g*-poly(acrylamide)/poly(vinylsulfonic acid, sodium salt) polymer hydrogel was prepared through the grafting polymerization of carrageenan gum with acrylamide and followed by the semi-interpenetrating poly(vinylsulfonic acid, sodium salt) (131). The functional materials prepared by the combination of superabsorbent with plastic or rubber have been used in engineering, especially in building materials and water-proofing materials. For instance, the sealing materials can be obtained by compounding SAM with rubber and can be used as leak-stoppage materials in tunnel or subway engineering.

Among numerous organic-organic superabsorbent polymers, the SAM containing sodium humate (SH) is an important family. Figure 10 presented the molecular structure scheme of sodium humate (13). It can be observed that SH is composed of multifunctional aliphatic and aromatic components. Many functional hydrophilic groups exist, such as carboxylates and phenolic hydroxyls on its structure. As an organic fertilizer, SH can regulate plant growth, accelerate root development, improve soil cluster structures, and enhance the absorption of nutrient elements. SH can participate in the polymerization reaction and the construction of three-dimensional superabsorbent polymer network through its active $-OH$ or $-COOH$ groups (132). Figure 11 showed the preparation procedure of poly(acrylic acid)/sodium humate. It can be observed that the preparation procedure is simple and is similar with that of clays, and the sodium humate powder can be added directly into the reaction system without additional treatment. So far, much research conducted on the preparation of SAMs that contain sodium humate [eg, poly(acrylic acid)/humate (13), poly(acrylic acid-co-acrylamide)/sodium humate (132), sodium alginate-g-poly(acrylic acid)/sodium humate (105), guar gum-g-poly(sodium acrylate)/sodium humate (72), poly(acrylic acid-co-acrylamide)/organo-montmorillonite/sodium humate (133), starch-g-poly(acrylic acid)/sodium humate (134), chitosan-g-poly(acrylic acid)/sodium humate (135), poly(acrylic acid-co-acrylamide)/sodium humate/attapulgitite (136), and poly(acrylic acid-co-acrylamide)/sodium humate/organo-attapulgitite (137)]. With the increasing need for using naturally occurring resources as a substitute for petroleum-based polymers, the composite of superabsorbent networks with other fillers, including clay and sodium humate, are promising research fields.

5.6. SAMs with Slow Release Characteristics. SAMs are now commonly made from the polymerization of acrylic acid blended with sodium hydroxide in the presence of an initiator to form a sodium salt of poly(acrylic acid) (sometimes referred to as cross-linked sodium polyacrylate) (138). This polymer is used in the most common types of SAMs made in the world today. Other materials are also used to make SAMs, such as polyacrylamide copolymer, ethylene maleic anhydride copolymer, cross-linked carboxymethyl cellulose, polyvinyl alcohol copolymers, cross-linked polyethylene oxide, and starch-grafted copolymer of polyacrylonitrile. The latter is one of the oldest superabsorbent forms created. However, all these SAMs are derived from the expensive petroleum-based monomers, and their function is also simple. With the increasing demands for agricultural water-saving materials, the multifunctional SAMs with water-absorbing and retention functions, as well as fertilizer-release characteristics, have received considerable attention. The study and development of such materials has recently made great progress in both academic and industrial domains. Currently, the study and development of superabsorbent fertilizers is mainly focused on encapsulated fertilizer; superabsorbent and composite fertilizer is obtained by adding fertilizer directly into superabsorbent network. In recent years, the encapsulated phosphate fertilizer (93), nitrogen and phosphate fertilizer (139), and nitrogen, phosphate, potassium fertilizer (140) was prepared, and the superabsorbent copolymer containing humate fertilizer was also developed (13, 72, 132–137). The SAMs with fertilizer-release characteristics will be a prospective material in modern agriculture. However, the translation of research results to industrial use faces many challenges.

6. Preparation Methods of SAMs

Because of the differences within raw materials, dispersion medium, reaction conditions, and initiation style, various kinds of SAMs usually corresponded to distinct preparation methods. Today, SAMs are usually made using one of the primary methods as follows: bulk polymerization, suspension polymerization, solution polymerization, and polymerization by irradiation (141–146).

6.1. Bulk Polymerization. Bulk polymerization is carried out in the absence of any solvent or dispersant and is thus the simplest in terms of formulation. It is used for most step-growth polymers and many types of chain-growth polymers. In the case of chain-growth reactions, which are generally exothermic, the heat evolved may cause the reaction to become too vigorous and difficult to control unless it is cooled efficiently. Bulk polymerization has several advantages, such as follows: There is no need to remove solvent out of the product because no solvent is used; the purity of product is high and the manufacture procedure is simple; and the needed equipment is less and the production period is short. However, this process has several disadvantages, such as follows: The viscosity of reaction system is high and the reaction conditions are difficult to be controlled; and the generated heat is hardly removable and the product is difficult to be discharged.

6.2. Suspension Polymerization. Suspension polymerization (also known as pearl polymerization, bead polymerization, and granular polymerization) is a polymerization process that uses mechanical agitation to mix the monomer or mixture of monomers in a liquid phase such as water, which polymerizes the monomer droplets while they are dispersed by continuous agitation. This method has the following advantages: The viscosity of reaction system is low; the polymerization reaction is stable; the reaction heat can be easily dissipated; the product granules are uniform; and the posttreatment of products is simple. However, this method has also some disadvantages, such as follows: There are some dispersants in the product and so the organic solvents need to be recycled, which requires a lot of investment; and it may induce environmental pollution to some extent. The suspension process is practiced by only a few companies because it requires a higher degree of production control and product engineering during the polymerization step. In this process, aqueous solutions were usually used as the dispersion phase and water-insoluble hydrocarbon solvents were used as the continuous phase. The water-soluble monomers or other polymer matrices dissolved or suspended in the aqueous phase in the form of a liquid drop. After being initiated, the polymerization reaction is carried out in the aqueous liquid drop, and the polymer particle or polymer microsphere with the diameter of 0.01–10 mm can be directly formed during reaction periods. For example, the granular *N*-succinylchitosan-*graft*-polyacrylamide/attapulgate superabsorbent composite with improved properties can be formed by suspension polymerization using water as the dispersion phase and heptane as the continuous phase (142).

6.3. Solution Polymerization. Solution polymerization is a polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization

reaction. The liquid is usually also a solvent for the resulting polymer or copolymer. This method is characterized by low viscosity of reaction system, uniformly dispersed initiator, and high initiation efficiency. In addition, the reaction solvent is water, which can greatly reduce the production cost. A product with uniform molecular weight can be obtained and made into film, powder, or other forms. The requirement of production process to equipment is low, and so the investment can be obviously diminished. The reaction conditions can be easily controlled, and the production process does not induce pollution and is favorable to achieve the no-polluting production. However, there are some problems, such as a lower monomer concentration, slow polymerization rate, low molecular weight of polymers, complex post-processing procedures, and lower production capacity.

6.4. Polymerization by Irradiation. SAMs can also be prepared by the initiation of ionizing high-energy radiation, like gamma rays and electron beams. This new technique is different from the traditional synthetic methods. The irradiation of polymer solution may result in the formation of radicals on the polymer chains. In addition, radiolysis of water molecules generated hydroxyl radicals that can attack the polymer chains; this process induced the formation of macroradicals. The recombination of macroradicals located on different polymer chains formed covalent bonds and cross-linked structures. The substitution of irradiation to traditional chemical initiator prevented the residual of chemical initiators and constitutes a pure and initiator-free SAM (147).

7. Potential Application of SAMS

Because of the excellent properties compared with general absorbents, SAMs have shown unique advantages and wider application prospect. Similarly, the extensive and particular application fields as well as the great market potentials of SAMs act as a key impetus for the development and industrial research of novel SAMs with special structure and functionality. Currently, the investigation on SAMs is mainly focused on the following aspects.

7.1. Agriculture and Forestry. SAMs have significant effects on improving the physical properties of soil; enhancing the water-absorbing, water-retaining, and fertilizer-retention capabilities of soil; and accelerating the growth of plants. Therefore, SAMs have enormous potentiality and broad application prospect in modern agriculture as a water-saving material. Instead of a chemical fertilizer, pesticides, and plastic films, SAMs may become novel agricultural chemicals that can generate an important impact on the production of crops. By developing the application technology of SAMs in agriculture, the whole water-saving system centered on the application of SAMs can be established and used for relieving the shortage of water resources and for promoting the development of dry farming. In the 21st century, the shortage of water resources has not been alleviated, and water-saving agriculture is still a strategy related to national welfare. And so the application of SAMs in this field will exhibit unprecedented potential and significance. In this section, the application region and efficiency of SAMs in agriculture and forestry was summarized and introduced as follows.

Water Retention and Drought Resistance. SAMs may promote the development of plant roots, improve the emergence rate of seeds, promote the growth of plants, and delay the wilting of plants. Applying SAMs in soil may absorb large quantities of water during rainfall or irrigation conditions, and then release slowly the absorbed water during drought conditions. This effect can prolong the irrigation interval, enhance the ability of crops to resist drought, and improve the efficiency of the water resources. Experimental research confirmed that the concentration of protein in fruit plant leaves after SAMs were employed was decreased compared with the blank sample, which reflects the improvement water efficiency in soil.

Figure 12 (148) depicts the practical water-retention capability of polyacrylamide/attapulgite (30 wt%) superabsorbent composite for tap water and water from the Yellow River in sand soil at various amounts. It can be observed that the water-retention time was obviously prolonged after adding superabsorbent composite, and the water retention capability of sand soil was enhanced.

Fertilizer Retention. Besides water, fertilizer is an essential factor that affects the growth and quality of plants or crops. The fertilizer available in soil usually exists in the form of soluble saline, such as ammonium sulfate, potassium sulfate, magnesium sulfate, ammonium nitrate, urea, or ammonium dihydrogen phosphate. In rainfall or irrigation situations, the water content in soil is increased, but the water-retention capability of soil is poor, and so numerous fertilizer nutrients were lost before they could be absorbed by the plant. This results in a great waste of fertilizer resource. If a certain amount of SAMs are added in the soil, the water-absorbing and water-retention ability of soil is greatly improved. As a result, the soil containing SAMs may absorb more fertilizer dissolved in water, reduce the loss of fertilizer, increase the absorbability of soil to fertilizer, and enhance the fertilizer conservation capability of soil.

To Improve the Physical Properties of Soil. After SAMs are applied in soil, they swell when the external water is sufficient and deswell when the content of soil water is low. This swelling-deswelling behavior of SAMs in soil induces an alternant change in the volume of SAMs between expansion and contraction. As a result, the regular change can make the soil around SAMs become loose and can increase the hole of the soil. This strategy greatly improves the permeability of soil to a certain extent. Experimental tests indicate that the use of SAMs facilitates the formation of the granule structure in soil, especially for those sizing the range of 0.5–5 mm. Meanwhile, with the increase of SAMs in soil, the number of macroaggregates (>1 mm) increased. This may play a key role in stabilizing the soil structure, improving the penetrability of soil, preventing the soil crust, and reducing the evaporation of water in the soil.

Prevention of Desertification and Ecological Recovery. The desertification of land has become a worldwide problem affecting regular crop production and the sustenance of human life. Especially in recent years, the process of desertification was accelerated and the area of desertification land was increased as a result of the aggravation of global warming and vegetation destruction. This certainly increased the difficulty of recovering the ecological environment. As is known, the desert region experiences drought and water shortages throughout the year. Even if a rainfall occurs, the rainwater was lost rapidly through the natural drains in the ground surface and the evaporation within air because of

the poor water-retention capability of the sandy soil. Thus, most plants cannot survive in the desert because of the shortage of water, and so enhancing the water-retention capability of sandy soil became a key to recovering the desertification lands. SAMs possess excellent water-absorbing and water-retention properties; they can act as a "microreservoir" to provide water continuously for the growth of plants and to prevent the leakage of water in sandy soil. For example, the commercial SAMs ranging in size from 1 to 3 mm were mixed with sands on the surface of the desert soil; these SAMs can absorb the rainfall and the dews, and then swell to become a block gel. These gels not only supply the evaporated water during the day, but also they can form a dense layer to prevent the evaporation of the water in the sandy soil. Thus, the water storage of the sandy soil increased and had better retention rates, which provides the possibility of expanding crop production within the desert.

Another significant function of SAMs in desert recovery is that they can improve the thermal conductivity of the sand. After the SAMs are applied, the temperature difference between day and night was decreased, the rising rate of temperature during day was slowed, and the decreasing rate of temperature on night was slowed. This effect is more obvious in sand than in soil. The decrease of the temperature difference between day and night is favorable to the growth of plants in sandy soil.

Slow-Release Carrier of Other Agrichemicals. The combination of chemical fertilizers, pesticide, and medicine, catalyst with SAMs to form the slow- or controlled-release system of the key materials, which can improve the release rate of the agrichemicals and can also enhance their efficiency. For example, the urea fertilizer can be coated in SAMs through a chemical method to form a granular slow-release nitrogen fertilizer (149). The urea fertilizer can be released slowly when the SAMs are swollen in water or soil, and thus the efficiency of the fertilizer is improved greatly.

7.2. Hygiene Products. The use of SAMs to manufacture hygiene products is a mature application field and currently accounts for about 70% of the total production output of SAMs. For example, the popularization rate of disposable diapers in Japan was only 5% to 6% in 1973, but this value increased to 30% in 1987. In the same year, the corresponding production rate of disposable diapers reached 100%, 98%, and 80% in Sweden, France, and the United States, respectively. Currently, the SAMs used for hygiene products are mainly consumed by developed countries and are used for fabricating baby diapers, adult incontinence products, and sanitary napkins.

7.3. Baby Diapers. In the past 30 years, baby diapers have been greatly improved and have experienced large changes. The general baby diaper is composed of three parts: The bottom layer is the impenetrable layer, the middle layer is the core layer for absorption, and the top layer is the porous thin layer. The top layer is contact with the baby's skin and helps the core layer to absorb liquids, which causes the urine to absorb easily through this layer, and it does not remain on the surface of baby skin. This layer is generally made using porous hydrophobic materials, such as polyester or polypropylene nonwoven fabric. The bottom layer should also be made using hydrophobic material for keeping the baby's clothes dry, but it cannot be porous, such as polypropylene film. The core layer contains the urine and can sustain pressure from the baby. The earlier core

layers were mainly composed of crepe paper; the urine only remained in the gaps of the paper fibers. To reach a large absorption rate, the paper layers must be thick. However, the substitute of SAMs for paper is a great improvement. Diaper manufacturers began to design diapers to take advantage of the amazing liquid retention ability of the polymer. SAMs can absorb and retain under a slight mechanical pressure about 30 times their weight in urine. The swollen gel holds the liquid in a solid, rubbery state and prevents the liquid from leaking onto the baby's skin and clothing. Currently, baby diapers with a rapid absorption rate and without side leakage have been designed and are used extensively throughout the world. In the last century, the emergence of ultrathin diapers reduced the dosage of wood pulp about 50% as a result of the use of SAMs.

Adult Incontinence Materials. Adult incontinence materials were used during the Second World War. The design and production of these products was derived from the concept of baby diapers. To reduce the size of SAMs and increase the absorbency, SAMs were added into adult incontinence materials. However, the volume and flow rate of urine for adults is much greater than that for babies, and these problems can be solved by using SAMs. Products with a multilayer urine absorption pad were developed by numerous manufacturers.

Sanitary Napkins. Women's sanitary napkins containing SAMs were produced initially in Japan. Like with baby diapers, sanitary napkins should be comfortable, should be thin in size, and should prevent side leakage of liquids. Using SAMs in such products can easily meet these requirements. However, the composition and viscosity of liquids absorbed is distinct from that of the baby diaper. In recent years, the demand for SAMs for hygiene products has increased rapidly in both developed and developing countries.

7.4. Medicine. SAMs can form soft hydrogel after swelling, and so it has better adaptability, as well as no stimulation or side effects to the human body. This is favorable for its application in medicine. In recent years, SAMs have been applied extensively in various fields of medicine (eg, medical test tablets to retain the examined liquids; exterior drug paste with high water content; bandages that can absorb blood and secretion from surgery or trauma; and artificial antibacterial skin in which the water and drug can penetrate but the animalcule can not permeate. In addition, SAMs have also exhibited potential applications in drug-release carriers and contact lenses. Using SAMs as drug carrier, the drug-release rate can be controlled through altering the structure and swelling ratio of SAMs in various mediums. The soft contact lens fabricated using SAMs has better oxygen-permeating properties than the others, it is comfortable to its wearer, and it can be used for a long time compared with the hard lens (144). In addition, SAMs also exhibited potential use in medical dressings and plasters. In wound care, SAMs may absorb wound secretions and help to maintain a moist wound environment, which supports and improves the healing process.

7.5. Wastewater Treatment. The polymer chains of starch and cellulose is semi-rigid and can expand after absorbing water. After grafting flexible polyacrylamide chains, the resultant network polymer have strong flocculation capability to the suspension particles especially to the ultrafine particles. So such materials can be used as effective flocculation agents. Because SAMs usually contain a large amount of hydrophilic groups with strong chelating

ability, they are used widely to remove heavy metal ions from aqueous solution. Compared with the traditional adsorbents, such as activated carbon, ion-exchange resin and clays, SAMs have higher adsorption capacity for heavy metal ions. SAMs may enrich heavy metal ions through the complexation action among hydrophilic groups, metal ions, and three-dimensional network adsorption. SAMs can enrich various kinds of heavy metal ions, including Cr^{3+} , Co^{2+} , Pb^{2+} , Hg^{2+} , Ni^{2+} , Zn^{2+} , and Cu^{2+} , and they can be easily desorbed and recycled. Moreover, SAMs also exhibited higher adsorption capacity for some dyes, such as methylene blue, methyl violet, congo red, and magenta. Because of the excellent performance and low cost, the application of SAMs in wastewater treatment is the field with the most potential.

7.6. Cable and Electronics. Cable wraps can protect subterranean cables from mechanical and weather-related damage. Cable insulation consists of several layers of materials to protect against damage from infiltrating water or moisture. When the outer plastic cover is damaged and the external liquid is penetrated, it can cause damage over some distance from the point of a breach because of the capillary effects in the cable. According to the sealing principle related to the swelling characteristics of SAMs, it can be used in the communication cable to avoid corrosion and damage from the external moisture. For instance, SAMs can be used as a raw material and are further combined with nonwoven fabric to prepare a sealing belt, which can prevent moisture from entering the communication cable. SAMs swell instantly when they come into contact with moisture. They absorb the moisture and seal the damaged location. This kind of sealing belt can be made by painting a mixture of SAM with butyl rubber onto the polyester belt.

7.7. Packaging Materials. High-performance superabsorbent granules can be incorporated as filler in the fabrication of soaker pads used in food packaging. Because SAMs can absorb huge volumes of liquids, the use of small amounts of SAMs may achieve better effects in contrast to the traditional colloidal silica. This is favorable to reduce the cost of the packaging materials. Furthermore, the food, some of which is delicate, stays fresh longer and looks more attractive. Luquasorb FP 800 (BASF, Florham Park, NJ) has received the approval by the U.S. Food and Drug Administration for indirect food contact. This approval governs the packaging of meat, poultry, fruit, fish, and vegetables. By virtue of the excellent hydrophilicity, as well as the special anti-fog and dew-proofing properties, SAMs may be used as novel packing film materials. It has been proved that the packing thin film prepared by SAMs with particular properties may retain the freshness of foods effectively.

7.8. Construction Engineering. By using the swelling characteristics of SAMs in water, SAMs can be used to prepare water-dilated sealant, pipeline construction lubricant, and dew-resistant wall paper and water bar. Adding SAMs into concrete can absorb basic precipitation to prevent cement from cracks, pockmarks, and whitening. In tunnel projects, adding SAMs into the mud with large amounts of water may allow it to gelate and can cause the mud to discharge more easily. The use of SAMs in tunnels may prevent groundwater from flowing into the tunnel.

7.9. Daily Chemical Industry. In the process of producing cosmetics such as vanishing cream, face powder, and floral water, the addition of SAMs

(about 0.5% to 1%) to substitute alkali may relieve skin stimulation and restrain the evaporation of scents and alcohol. Also, the application of SAMs can make the fragrance of cosmetics more permanent, can retain water, and can thicken and prevent cosmetics from drying. SAMs can moisten skin, avoid chapping, and make the skin brighter. Adding polyacrylate SAMs into hair dye can improve the dyeing effects. Adding SAMs into shampoo can appropriately improve its viscosity and can play a protective role for the hair and scalp to avoid dryness.

After adding SAMs, performance of hairspray can be greatly improved. The hair treated with hairspray can be easily washed and combed. By adding fragrances into SAMs, the aromas may be retained for a long period of time. In recent years, fragrance-depositing material improved greatly. It has been used extensively in air-refreshing agents, fragrance paper, and other aroma packaging films.

7.10. Industry. SAMs can absorb moisture in conditions of high humidity but can release the absorbed moisture in conditions of low humidity. Balancing SAMs with moisture, the nonwoven fabric containing SAMs can be constructed. Because SAMs were added, the fabric can prevent dew condensation and can be used to decorate the interior wall. Currently, the dew-resistant lacquer that was widely used in the computer room of hydraulic power plant has been developed and industrialized successfully. The cable may be damaged in the course of construction. To prevent water from permeating through the cable, the expansion powder containing SAMs can be used to protect the cable and to form a shield with a long-lasting water seal. Thus, the damaged place of the wire can be mended by oneself and form the new insulating barrier, which greatly improved the safety and service life of cable. In the field of chemical industry, SAMs can be used as oil-water separation agent. By using the large water-absorbing and small organic solvent-absorbing characteristics, SAMs were applied to remove and separate water mixed in oil. In addition, SAMs are used extensively in the paper-making industry. The bacteria-detected paper pad with superabsorbent capacity was obtained by mixing cotton pulp with SAMs, constructing it into a paper pad, and then compounding the paper pad with an inter-layer containing SAMs. Also, moisture-retaining tissues and wrapping paper can be made by adding SAMs.

7.11. Fire-Proof and Fire-Extinguishing Agents. Because SAMs can absorb water but cannot absorb oil, these materials can be used as oil-water separation agent and a fire extinguishing agent. The Degussa Company of Germany has developed a novel "firesorb" fire extinguishing agent containing SAMs, which has superb fire-proofing and fire-extinguishing performance because of its strong heat absorption capability, which is five times higher than water. Also, using such a fire-extinguishing agent may reduce the water consumption by 50% and may greatly shorten the duration of fire extinguishing processes. According to the local regulation of Germany, "firesorb" gel may be discharged safely into the municipal water system.

7.12. Smart Materials. The so-called smart materials refer to the materials that may perceive and respond to environmental conditions. Because the volume of SAMs changes greatly with a tiny change in the external environment (such as solvents, pH, temperature and electric field strength, etc), various smart materials could be developed, such as shape memorizing materials, artificial

tactile system, chemical valves, and drug-delivery systems. In addition, SAMs can be used as a humidity sensor for various applications.

7.13. Dust Depressor. The dust depressor made using SAMs has improved water absorption, evaporation resistance, and periodic moisture-absorbing and moisture-release characteristics. After the gel of SAMs was sprayed on the dusty surface, the gel may evaporate and lose viscosity. After the gel absorbs water again, the dust surface becomes more viscous. Because of the viscosity, the dust deposited on the dust surface cannot fly again because of adhesion. Like this, the dust on the mobile tire was adhered, and the dust blowing on the ground caused by the mobile tire may be controlled as well. SAMs were used as a dust depressor in blasting operations and mining.

7.14. Artificial Snow. SAMs can be used to make artificial snow for skiing. Because SAM polymers absorb hundreds of times more water than their weight, the result is a frozen gel just like "powder snow." Using this kind of snow, the environmental temperature can be 10°C higher than for natural snow. This artificial snow can make skiing more comfortable.

8. Developing Direction and Prospect of SAMs

Based on the wide ranging and potential applications, the design and development of novel SAMs and their industrialization becomes a key marketing factor. According to the current research on SAMs, the subsequent development of SAMs will occur in the following fields.

8.1. To Strengthen the Study on Water-Absorbing Theory and Mechanism. The current research is focused mainly on the synthesis, properties, and characterization of superabsorbents; however, little work is related to the water-absorbing essence, especially to the relationship between water-absorbing properties and the structure of SAMs. In the subsequent research, researchers should explore water-absorbing mechanisms using many experiments to improve the use of SAMs. The relationships between the cross-linking structure and the water-absorption performance, as well as between the structure and aggregation of molecular chains and performance must be clearly interpreted. This will optimize the preparation processes and enhance the comprehensive performance of SAMs.

8.2. To Improve the Performance. Currently, researchers should ensure that SAMs have excellent water-absorption capability, water absorption rate, gel strength, and salt-resistance performance. However, almost all the SAMs used in practice cannot meet these requirements and still have some drawbacks. For example, the water absorbency is high in pure water but is low in salt solution; the water absorbency is high but the gel strength is extremely poor; the water absorbency is high but the water absorption rate is slow; and the function is simplex. Generally, the SAMs used for hygiene products are required to have a fast fluid-absorbing rate, high gel strength, and better salt-resistant properties. The SAMs used for agriculture are required to have excellent salt-resistant properties, pH stability, reusability, and fertilizer-release performance. Among these properties, the salt-resistant performance, gel strength, water-absorbing rate, and multifunctionality of SAMs limit the development and application of

SAMs, and are a challenge for the material designers. So far, many kinds of raw materials or synthetic methods were adopted to improve these performances of SAMs; however, no breakthrough progress was obtained. Therefore, the SAMs with special structure and composition should be designed and a novel preparation process should also be developed in the future.

8.3. To Improve the Biodegradability of SAM. With the increasing public concerns for environmental protection, the environmentally friendly characterization of materials attracts great attention. As a unique water-manageable material, the consumption of SAMs has increased, and so the biodegradability of SAMs is required and becomes an important factor affecting its mass use in various fields. The design and synthesis of biodegradable SAMs with excellent performance is the future direction of development. Among numerous means, the use of raw materials available in nature for the fabrication of biodegradable SAMs still has the most potential.

Cellulose is the most abundant biodegradable polymer in the world; it contains a large number of hydrophilic hydroxyl groups and has strong water-absorption capability. It can be modified through chemical cross-linking, grafting, or other means to produce SAMs with high water absorbency and other functionalities.

Starch is an easily available polysaccharide compound, which is found widely in plants such as corn, potatoes, and sweet potatoes. Similar to cellulose, starch is also a good biodegradable natural polymer. Many SAMs have been fabricated through the modification of starch and applied in various fields. Although starch-based SAMs have some drawbacks, their unique environmental advantages make them the most prospective SAMs.

Amino acids contain numerous hydrophilic carboxyl and amino groups. Because poly(amino acid) can decompose under certain conditions, it can be used as a raw material for designing biodegradable materials. For example, cross-linked polyaspartic acid can absorb 500 times its weight of pure water and 50 times its weight of physiological saline. By comparison with cellulose and starch, the research and development on amino acid-based SAMs receive little attention.

8.4. To Reinforce the Compounding of Functions. Currently, the SAMs used in practice still have some drawbacks, including poor salt resistance, low gel strength, and slow water-absorption rate despite their properties have been improved to some extent. The combination of superabsorbent polymers with other fillers for deriving new SAMs is the most often-used method for improving the gel strength, water-absorption properties, salt-resistant performance, and thermal stability, as well as for reducing the production cost. The superabsorbent polymer may compound with other inorganic, organic, or polymer substance, and the resultant composite exhibits improved properties. For example, introducing inorganic clays into a superabsorbent network can enhance the water absorbency and gel strength (150); introducing sodium humate into a superabsorbent network may improve the water absorbency and endow SAMs with fertilizer-release characteristics (151). However, the preparation and application technologies are still not fully developed. By analyzing the current technologies, the following areas must be examined in the future.

- (1) The research and exploration of the compounding mechanisms of the superabsorbent network with other fillers should be strengthened. Currently, the research on superabsorbent composites is focused mainly on the development and property evaluations. Little efforts were engaged to explore the compounding mechanisms. Hence, defining the compounding mechanism and the corresponding improvement direction contribute to develop the new type of superabsorbent composites with improved overall performance.
- (2) To improve the quality and performance of SAMs, new functional fillers should be introduced and new synthesis methods should be developed. Although the performance of some current SAMs has been greatly improved, the improvement of its overall performance is still one of the development trends in the future.
- (3) The research and development on the modification of inorganic minerals as well as their superabsorbent composites should be strengthened. Inorganic minerals, such as kaolin, mica, bentonite, rectorite, and vermiculite, have a typical layered structure and can be exfoliated or intercalated by polymers to form nanocomposite materials. Considerable efforts have been made to modify inorganic clay minerals by organic molecules or metal ions through ion-exchange or intercalation processes (152–156). Especially, Frost and colleagues (120, 122, 157–169) have conducted numerous systematic experiments on the modification of clays by some novel modifier, evaluated their physical and chemical properties, and explored their possible applications. According to the research results, the modified clays exhibited more excellent properties than raw clays. Thus, it is significant and promising to develop new types of modified clays and use them as fillers for the fabrication of superabsorbent nanocomposites.

8.5. To Develop New Monomers and Initiators. For an individual SAM, the type of monomers usually determined the composition of hydrophilic groups in a polymer network (96), and the initiator system may affect the polymerization or graft efficiency as well as the amount of residual monomers (170). The traditional monomers included anionic monomers (ie, acrylic acid, 2-acrylamido-2-methyl propane sulfonic acid, maleic acid, and methyl acrylic acid), non-ionic monomers (ie, acrylamide and acrylonitrile, etc) and cationic monomers (ie, diallyl dimethyl ammonium chloride). Although these monomers have frequently been used for the preparation of SAMs and the resultant products also exhibited excellent properties, it is still essential to develop or use new monomers and initiators in superabsorbent fields for improving the properties and extending the application of SAMs. Thus far, only little new monomers including itaconic acid (96), 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (171), *N*-acryloylmorpholine (172), crotonic acid (173), sodium 1-(acryloyloxy) propan-2-yl phosphate (174), tri-*n*-alkyl-4-vinylbenzyl phosphonium chloride (175), and *N*-vinyl-2-pyrrolidone (176), as well as initiation system such as hydrogen peroxide and L-ascorbic acid redox pair (74), have been reported. In recent years, some initiator-free SAMs created by irradiation or microwave techniques have been developed. As a whole, the use of new monomers and initiators and the

development of new initiation techniques will be examined for improving the comprehensive performance of SAMs.

9. Summary

The particular performance and the extensive application have made SAMs one of the most rapidly developed polymer materials. The application domain of SAMs has been extended from the traditional agriculture and hygiene products to medicine, wastewater treatment, and construction engineering. The extended application has increased the demand for SAM products, and the long-term sustained sales and sales growth in the superabsorbent industry was expected. For this, more and more manufacturers improved the properties and reduced the production costs. Various raw materials and methods were used and developed to prepare novel SAMs, and the investigation goal was directed to translate the research results into the industrial production of new SAMs. Because the multifunctionality of materials is a main goal of material researchers, the multifunctionality of SAMs has also been examined, and many materials with excellent water-absorption and water-retention properties, as well as fertilizer-release and drug-release functions, have been developed. Research related to such materials and their industrial use will be a challenging topic in the future. Although SAMs have found wide application in various fields, their popularity is limited because of the high cost. Researchers and manufacturers have focused on reducing the production cost of SAMs. They incorporated cheap inorganic clays into superabsorbent networks for improving performance and reducing production cost, and some encouraging results were achieved.

On the whole, the rising demand for SAMs and increased study and development of novel SAMs contributed to the growth of commercial superabsorbent products. Simply, the future of SAMs may be intertwined with continued technology development and production of superabsorbent products with the goal to lower the overall manufacturing cost and improve the performance. It becomes evident from this article that a variety of technologies is involved with SAMs; these technologies include bulk polymerization, suspension polymerization, solution polymerization and polymerization by irradiation. Among them, the solution polymerization is the most simple and suitable method to be used in industrialization. Advances in production technologies of SAMs will most likely be achieved through advances in these related fundamental polymerization technologies. Thus, achieving higher production efficiencies and correspondingly lower production costs through technology development should advance the superabsorbent industry.

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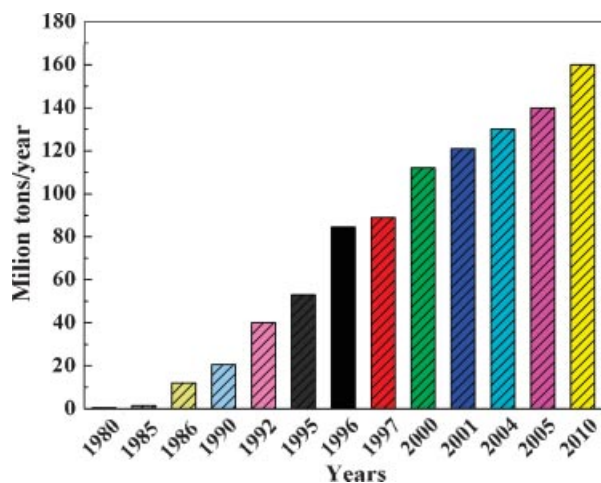


Fig. 1. Global production capacity of SAM and tendency.

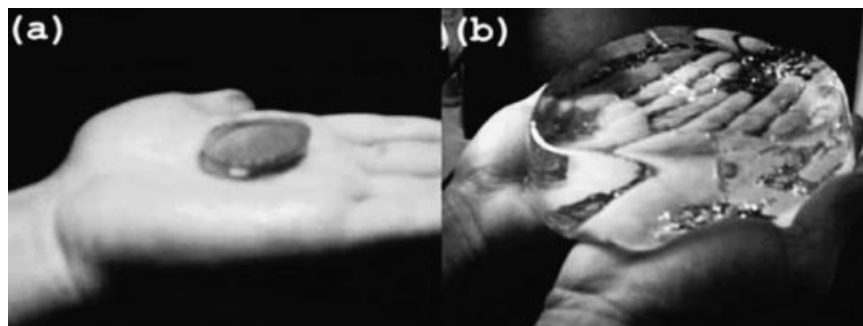


Fig. 2. The digital photos of SAM before swelling (a) and after swelling (b) in water (63). Reproduced with permission of the Wiley Periodicals, Inc.

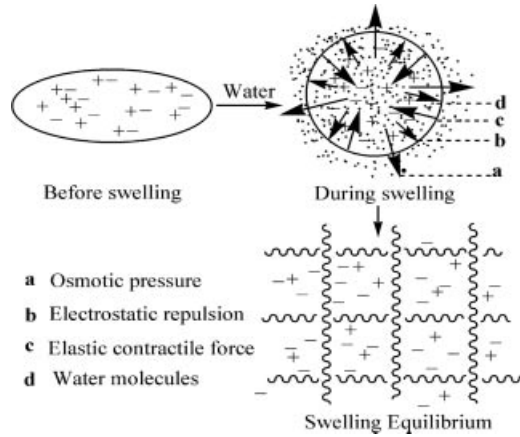


Fig. 3. The swelling process of SAMs in water under the action of three forces.

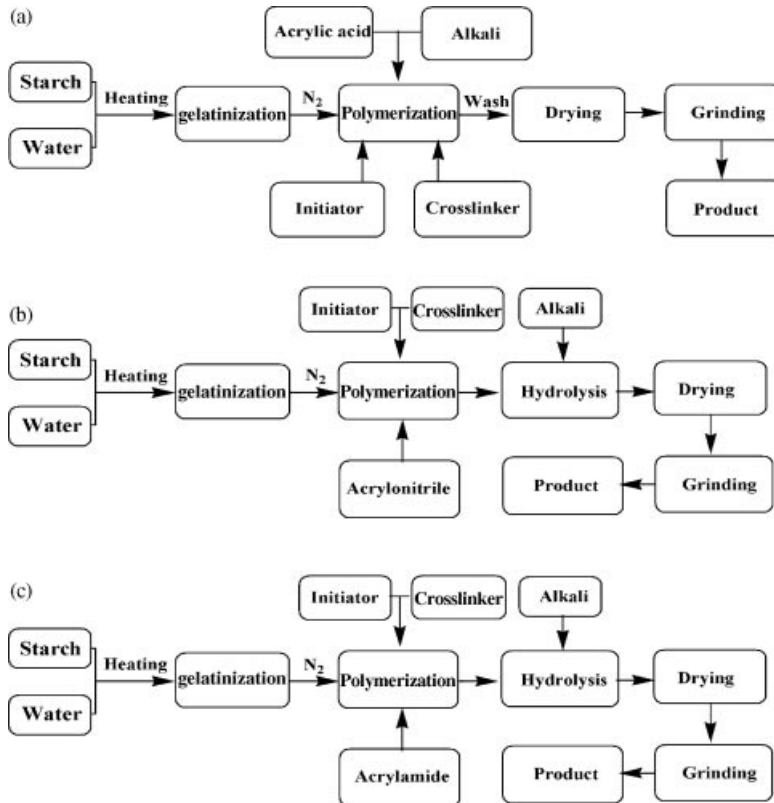


Fig. 4. The preparation flowchart of (a) starch-g-poly(acrylic acid), (b) starch-g-poly(acrylonitrile), and (c) starch-g-poly(acrylamide) SAMs.

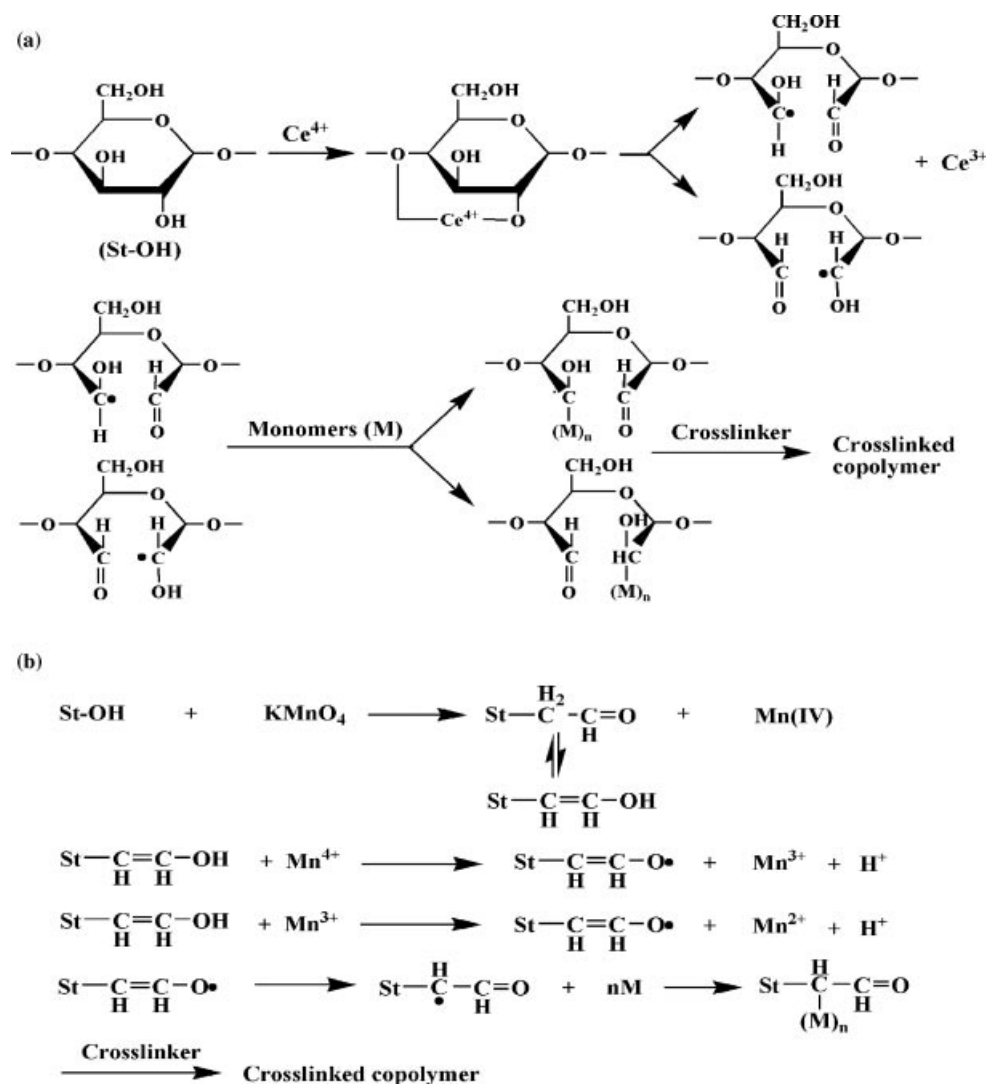


Fig. 5. Proposed graft polymerization mechanism of starch: (a) initiated by cetic ammonium nitrate and (b) initiated by potassium permanganate.

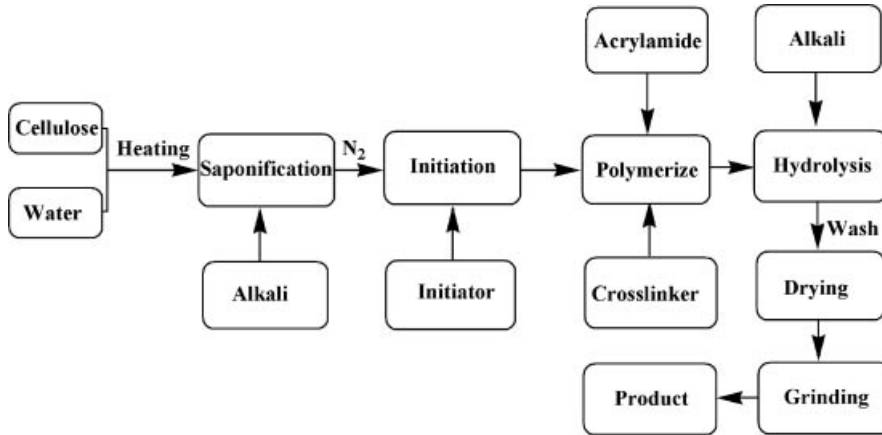


Fig. 6. Preparation flowchart of the cellulose-g-poly(acrylamide) SAM.

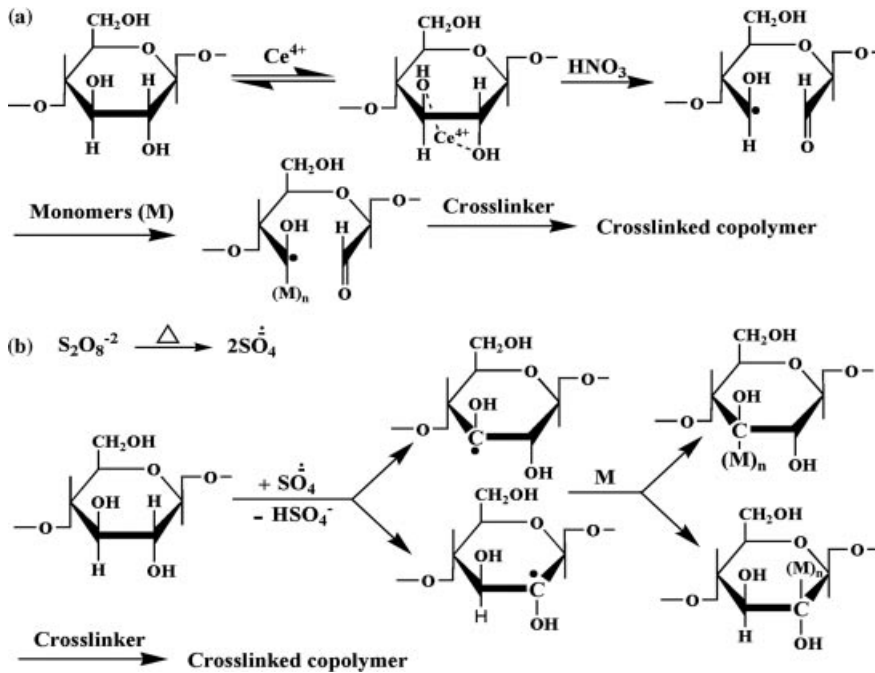


Fig. 7. Proposed graft polymerization mechanism of cellulose: (a) initiated by cetic ammonium nitrate and (b) initiated by ammonium persulfate.

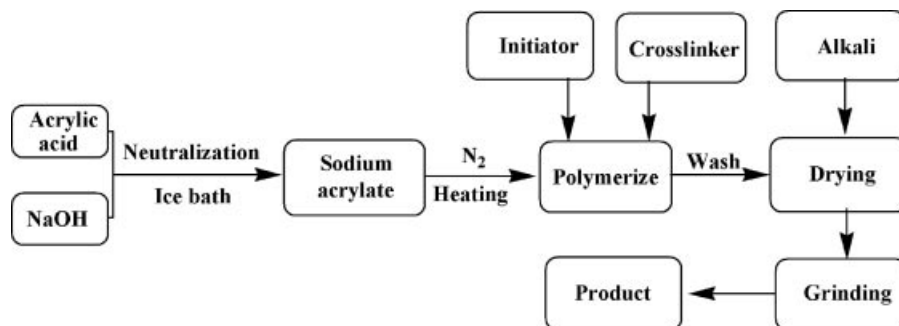


Fig. 8. Preparation flowchart of the poly(sodium acrylate) SAM.

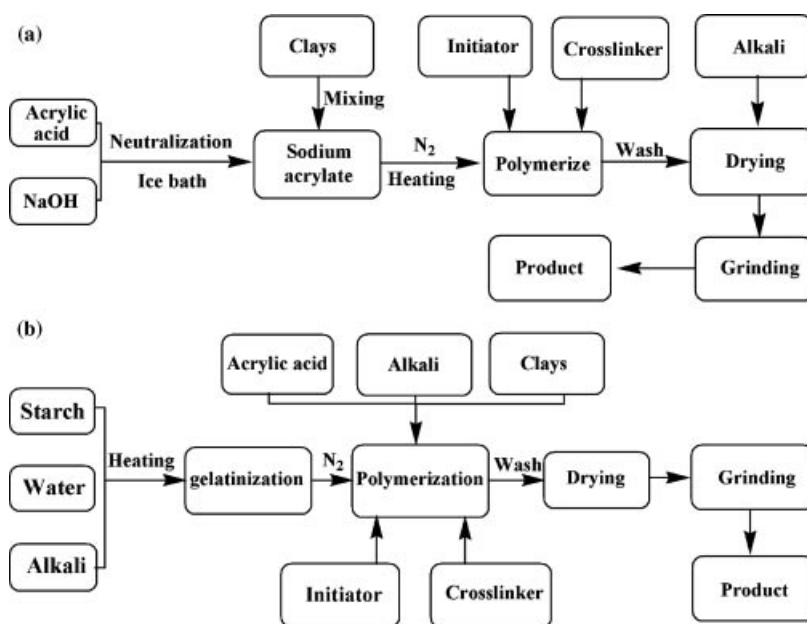


Fig. 9. The preparation flowcharts of (a) poly(sodium acrylate)/clay and (b) starch-g-poly(acrylic acid)/clays superabsorbent composites.

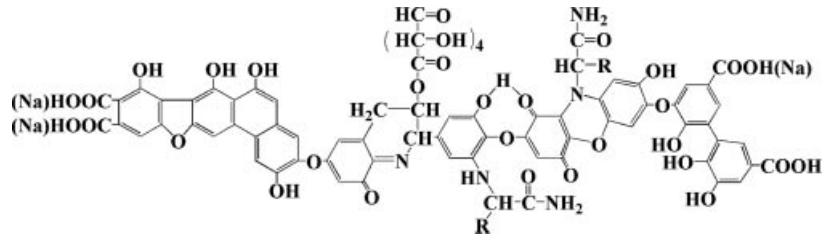


Fig. 10. The molecular structure of sodium humate.

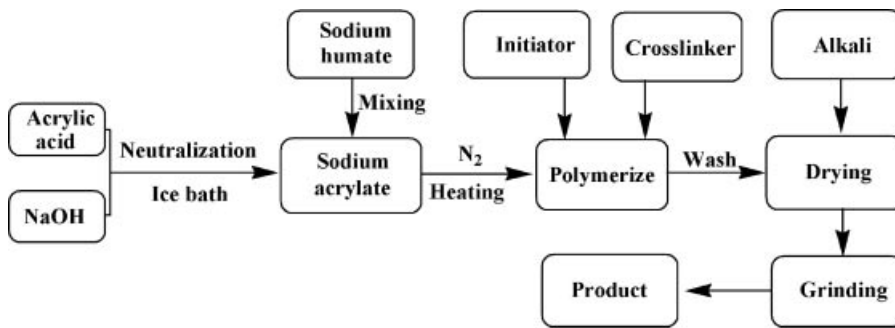


Fig. 11. The preparation flowchart of poly(sodium acrylate)/sodium humate superabsorbents.

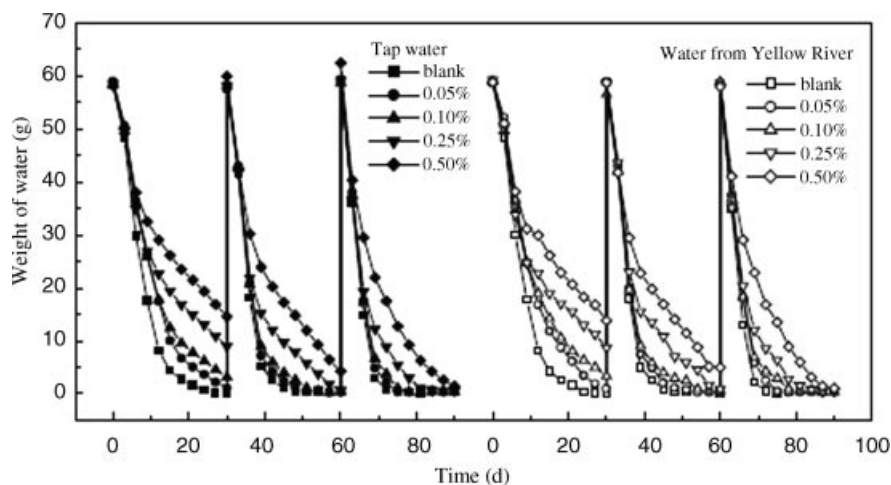


Fig. 12. Practical water retention capability of polyacrylamide/attapulgate (30 wt%) superabsorbent composite in sand soil (148). Reproduced with permission of the Wiley Periodicals, Inc.

Table 1. Production capacity of the leading seven manufacturers of SAMs in 2005 (60)

Code	Manufacturer	Country	Production capacity (million tons/year)
1	BASF	Germany	30.5
2	Stockhausen	United States	29.5
3	Nippon Shokubai	Japan	29
4	Dow Chemical	United States	15
5	San-Dia Polymers	Japan	14.5
6	Sumitomo Seika Chemicals	Japan	9.2
7	Kolon	Korea	4