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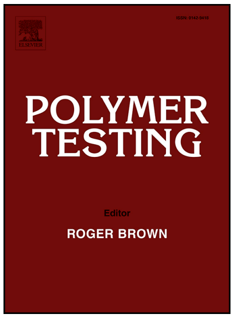

Superabsorbent polymers used for agricultural water retention

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Superabsorbent polymers used for agricultural water retention

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Abstract: Superabsorbent polymers (SAPs) have been widely used and are attracting increasing attention in agricultural field because they dramatically enhance water use efficiency. In this review, representative achievements in the design and modification of SAPs with specific functions are highlighted, as well as their applications in agriculture. Two key properties of SAPs, water absorption and retention behaviors, are discussed in detail. Moreover, the future developments of SAPs with remarkable comprehensive performances are also discussed.

Key Words: Superabsorbent polymers, Water retention, Agriculture.

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1. Introduction

Water plays a critical role in agricultural production. However, water shortages and droughts have caused soil desertification and salinization, which also challenge the sustainable development of agriculture as well as food security. Therefore, improving the utilization efficiency of water is of great importance in agriculture [1].

Due to super high water absorption and water retention capacity, superabsorbent polymers (SAPs) can be applied to effectively ameliorate utilization of water in agriculture, such as retaining moisture in the soil and reducing the irrigation water consumption [2, 3]. A great number of hydrophilic groups on the chain of SAPs help to absorb water hundreds to thousands of times their own masses. Moreover, three-dimensional networks either by chemical or physical crosslinks guarantee SAPs strong water-retention capacity even under certain pressures [4].

According to their source of origin, SAPs can be classified as natural and synthetic polymers. SAPs based on natural polymers, such as cellulose, starch and chitosan, have an obvious advantage of degradability. Nevertheless, they suffer from low water absorption rate thus have to be used in larger amount. On the other hand, although SAPs based on synthetic polymers, such as polyacrylicacid (PAA) and polyacrylamide (PAM), show the advantages of low cost, long service life and high water absorption rate, their non-degradation characters may exert adverse effects on the environment and plant growth [5, 6]. In order to enhance the performance of SAPs, various methods have been explored, including increasing their hydrophilicity and constructing specific network structures, such as interpenetrating polymer network (IPN), semi-interpenetrating polymer network (semi-IPN) and copolymer network.

Besides improving water use efficiency of soil, SAPs are also used for controlled release of fertilizers [7-9]. It is reported that about 40-70% of nitrogen (N) and about 80-90% of phosphorus (P) in conventional fertilizers cannot be absorbed by crops due to their high solubility in water and high diffusivity to the surrounding environment [10]. Loading fertilizers to SAPs not only improves fertilizers use efficiency but also

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avoids unnecessary environmental pollution [11]. Thus, SAPs are significant to the development of agriculture.

This review article is focusing on the progress of SAPs and their applications in agriculture, followed by their perspectives of future trends and rational design for desired properties.

2. Fundamental parameters for evaluating performance

In general, water absorbency and water retention rate are two basic parameters used to evaluate the properties of SAPs. They are both measured by the gravimetric method in distilled water or saline solution.

2.1. Water absorbency (WA)

The usual testing method for water absorbency of SAPs is as the following. The dry samples are firstly weighted as M_0 and then immersed into excessive water at a given physicochemical condition till equilibrium swelling. Then the swollen samples are filtered through a mesh to remove excess liquid and weighed as M. The water absorbency (Q_{eq}) is calculated by the following equation:

$$Q_{eq} = (M - M_0)/M_0 \qquad (1)$$

2.2. Water retention (WR)

The water retention properties of SAPs are measured by the following method. Firstly, the dry samples are weighted as W_d and soaked into excessive water till equilibrium swelling. Then the initial swollen samples filtered through a mesh are weighed as W_i and dried out at a given physicochemical condition. After a predetermined time, the samples are recorded as W_t, and this process is continued until no change in weight. The water retention properties were calculated by the following equation:

$$\text{Water retention (\%)} = (W_t - W_d)/(W_i - W_d) * 100\% \qquad (2)$$

3. Natural SAPs

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Natural SAPs, such as cellulose, starch and chitosan, are advantageous in terms of inherent degradability, biocompatibility, environmental friendliness and renewability [12]. However, their extraction process is complex, which consequently makes them more costly than some synthetic polymers. More seriously, the properties of natural polymers vary greatly depending on object of extraction, place of origin, or year of production. Therefore, many researches have tried to modify natural polymer with synthetic polymer for a better market prospect.

3.1. Cellulose

Cellulose is the most abundant natural organic substance in the world. It comes from a wide range of sources, including cotton, wood, plant straw and so on. Due to a large number of hydrophilic groups (hydroxyl groups) on the chain [13], cellulose can be readily exploited to prepare water-retention agents for agricultural applications [14, 15]. Nevertheless, the absorbency of neat cellulose is very low (below 30 g/g in distilled water) owing to highly dense crystalline structure.

Destroying the dense crystalline structure via modification of cellulose is a common method to enhance water absorbency, such as etherification, esterification and sulfonation of hydroxyl groups. For example, etherification reaction was carried out with 2-chloroethanol and cellulose. The resulting hydroxyethyl cellulose was then grafted on the copolymer of acrylate and acrylamide (P(AA-co-AM)) and the maximum water absorbency of the product reached 240 g/g in comparation with 200 g/g of wheat straw-g-P(AA-co-AM), which confirmed the effect of etherification [16]. Chloroacetic acid was used to etherify cellulose to produce carboxymethyl cellulose. In situ grafting acrylic acid (AA) on carboxymethyl cellulose (CMC) backbone in the presence of graphene oxide (GO) as filler, the optimized water absorbency of the product (CMC-g-PAA/GO) was 750 g/g in distilled water and 85 g/g in 0.9 wt% NaCl solution, respectively [17]. Esterification crosslinking of cellulose with 1,2,3,4-butanetetracarboxylic dianhydride (BTCA) was carried out, and the maximum water absorbency of the hydrogel produced in the tetrabutylammonium fluoride/dimethyl sulfoxide (TBAF/DMSO) system was 987 g/g [18]. Besides,

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increasing charge density of cellulose also has been reported to be able to enhance swelling rate when the network is in the linear elastic state [19]. Moreover, combining the modified cellulose with synthetic SAPs or water-absorbing fillers (e.g., clay) can further improve water absorbency.

Apart from high water absorption ability, favorable salt resistance and mechanical property are also important for expanding applications of cellulose-based water retaining agents. For example, cellulose mixed with linseed gum solutions and cross-linked by epichlorohydrin demonstrated exceptional salt tolerance, showing considerable water absorbency of about 210 g/g in 0.1 M NaCl [20]. Implementing distinctive network structures can potently increase mechanical performances. IPN composed of cross-linked cellulose nanofibril and linear polyacrylamide structural rendered robust mechanical strength and good water retention ability even in solutions with high salt concentration [21].

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3.2. Starch

Starch is a biomacromolecule polymerized of glucose and widely used as water retaining agents, which is strong in hydrophilicity, degradability and environmental friendliness but weak in water absorbency (below 10 g/g in distilled water), mechanical stability and salt tolerance.

Grafting AA to starch is a common method to improve the water absorbency of starch-based water retention agents. For example, AA was used to polymerize with sulfamic acid-modified starch by solution polymerization. The water absorbency of the resulting product was 1026 g/g in deionized water and 145 g/g in 0.9 wt% NaCl solution as a result of the adsorption and transfer of water molecules by the sulfonic acid groups, which increased by 100 and 13% compared with starch-grafted acrylic polymer, respectively [22]. And 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was added into the mixture of AA and cassava starch (St) to improve the storage modulus and crosslinking density of St-g-AA-AMPS SAP. Results confirmed that the introduction of AMPS was beneficial to form perfect network structure. The maximum swelling ratio reached 1200 g/g and 90 g/g in distilled water and 0.9 wt%

NaCl solution respectively. The re-swelling capability, water retention and salt tolerance were also improved due to the high ionization constant and hydrophilic ability of AMPS [23].

Hybriding starch and inorganic fillers is another method to improve water absorbency even in salt solution and under load. For example, the water absorbency in distilled water of nanocomposite hydrogel comprising starch-graft-poly(acrylicacid-co-acrylamide)/polyvinyl alcohol and nano-clinoptilolite was improved to 365 g/g compared to 286 g/g of neat hydrogel. Moreover, the water absorbency in 0.9 wt% NaCl solution increased from 46 g/g of pure hydrogel to 54 g/g of nanocomposite hydrogel, and the water absorbency at pressure of 0.9 psi also increased from 30 g/g of neat hydrogel to 37 g/g of nanocomposite hydrogel, which made it potentially useful for agricultural application [24]. Besides, the addition of chemically modified natural char nanoparticles (NCNPs) into starch-g-poly(AA-co-AM) superabsorbent also showed a substantially enhanced water absorbency (390 g/g in distilled water) in comparison with the neat hydrogel (202 g/g in distilled water), which can be attributed to the coexistence of the physical and covalent cross-linkage in the NCNPs/Hydrogel nanocomposite. The water-retention (%) capability after 14 days increased from 7% of neat hydrogel to 23% of nanocomposite hydrogel. And the absorbency of NCNPs/Hydrogel under load also showed an improvement [25].

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3.3. Chitosan

Chitosan is a linear chain polysaccharide derived by deacetylation of chitin, which is abundant in the outer skeleton of crustaceans and the cell walls of fungi [26]. A range of inherent properties, such as excellent biocompatibility, biodegradability and repeatability, make chitosan a very attractive material for water retention agents. However, chitosan has horribly low water absorbency (below 10 g/g). Benefited from a large number of amino and hydroxyl groups on chitosan, it provides an opportunity to improve the water absorption of chitosan through chemical modification [27].

In order to enhance chitosan's water absorbency, many approaches have been proposed. For example, (2-pyridyl) acetyl chitosan chloride (PACS) was chose to polymerize with AA and AM in aqueous solution. The resulting superabsorbent polymer exhibited excellent water absorbency, which can absorb 615 times its dry weight of distilled water and 44 times its dry weight of 0.9 wt% NaCl solution. This product also showed good antibacterial properties against Escherichiacoli and Staphylococcus aureus [28], which has a broad application prospect.

In addition, considering the main grafting site in the reaction of AA grafted chitosan is the amino group, increasing the number of amino groups on chitosan backbone was inferred to further improve the water absorbency and salt tolerance of chitosan-g-AA. Thus 2-chloroethylamine hydrochloride modified chitosan was chose to graft acrylic acid. The results confirmed this hypothesis that the water absorbency of the product was 644 g/g in water and 99 g/g in 0.9 wt% NaCl solution under the optimized conditions [29].

3.4. Others

As is known to all, alginate is a natural SAP containing abundant hydrophilic carboxyl groups, which make it potential as water retention agent. Compared with 390 g/g of the pristine PAM, the water absorbency of PAM/Na-alginate (Alg) increased to 578 g/g, implying that the introducing of Alg can promote water absorption. Furthermore, maize plants treated by PAM/Alg hydrogels showed 50% increase in the grain yield, suggesting their possible use as soil conditioners and a water reservoirs for plant-soil system [30].

Konjac glucomannan (KGM) has attracted researchers' attention in recent years due to its superior water absorption and film formation ability compared with starch. KGM-g-poly(AA-co-AM) achieved maximum water absorption rate of 650 g/g in distilled water and 70 g/g in 0.9 wt% NaCl solution [31]. Moreover, the water absorption rate in distilled water of KGM-AA polymers can reach to 1941 g/g by adding kaolin as fillers, which indicates kaolin is a potential material to enhance water absorbency [32].

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Lignin has also been reported to have the ability to improve the water absorption of materials. Organosolv lignin that extracted from hybrid poplar was grafted on 2-hydroxyethyl methacrylate (HEMA) to fabricate lignin-methacrylate composite hydrogels. The water retention rate and thermal stability of resultant composite hydrogels were increased by 39% and 20%, attributed to the denser cross-linked networks [33].

Polyaspartic acid (PASP) can be commonly found in many kinds of mollusc. Owning to a large amount of carboxyl groups and distinctive space structure, PASP exhibited outstanding water adsorption capacity (300-350 g/g), which can increase the survival rate and relative water content of leaf by 8-12% and 4-16%, respectively [5].

In addition, natural proteins have also been reported to enhance the properties of water retention agents. For instance, chicken feather protein was grafted onto poly(potassium acrylate) and then formed a semi-IPN with polyvinyl alcohol and combined with nitrogen (N) and phosphorus (P) (CFP-g-PKA/PVA/NP), which demonstrated high water absorbency of 609 g/g and reduced the water evaporation of soil from 40% to 18% during 60 days. The resulting product also exhibited a good degradability and controlled release of N and P [34]. In addition, leather waste (LW) as macromonomers and AA and dimethyldiallylammonium chloride (DMDAAC) as monomers were used to synthesized LW-g-p(AA-co-DMDAAC), which showed great equilibrium swelling capacity of 3203 g/g in distilled water and 181 g/g in 0.9 wt% NaCl solution [35]. Water absorbency and retention capacity of various natural SAPs based agricultural water retention agents are summarized in Table 1.

Table 1. Water absorbency and retention of various natural SAPs based water retention agents.

Water retention agents	**WA^a (g/g)**	**WA^b (g/g)**	**WR**	**Reference**
hydroxyethyl cellulose-g-P(AA-co-AM)	240	-	25%, 14 d at RM, soil with 1 wt% materials	[16]
CMC-g-PAA/ GO	750	85	70%, 80 min at 100^{o}C	[17]
Cellulose-g-BTCA	987	-	-	[18]
Linseed gum/cellulose	320	210 (0.1 M NaCl)	30%, 7 d at 40^{o}C	[20]
Sulfamic acid-modified starch g-AA	1026	145	-	[22]
St-g-AA-AMPS	1200	90	60%, 10 h at 60^{o}C	[23]

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Starch-g-poly(AA-co-AM)/PVA /clinoptilolite	365	55	34%, 6 h at 40^{o}C	[24]
Starch-g-poly(AA-co-AM)/NC NPs	390	202	66%, 6 d, soil with 1 wt% materials	[25]
Poly(AA-co-AM)/PACS	615	44	> 60%, 72 h at 25^{o}C	[28]
Amino ethyl chitosan-g-AA	644	99	71%, 24 h	[29]
PAM/Alg	578	-	63%, 4 d	[30]
KGM-g-poly(AA-co-AM)	650	70	20%, 7 d, soil with 0.3 wt% materials	[31]
KGM-AA-AM/KGM-AA-AM	1941	93	-	[32]
PASP	300-350	-	-	[5]
CFP-g-PKA/PVA/NP	609	-	-	[34]
LW-g-p(AA-co-DMDAAC)	3203	181	90%, 13 h at 30^{o}C	[35]

(^{a}: water absorbency in distilled water under optimal conditions; ^{b}: water absorbency in 0.9 wt% NaCl solution under optimal conditions; WA: water absorbency; WR: water retention.)

4. Synthetic SAPs

SAPs that made from synthetic polymers (also referred to as superabsorbent resin (SAR)), such as PAA, PAM and PVA, generally have superior water-absorption and water-retention properties than natural polymers. However, synthetic polymers cannot be degraded in soil after many years and may cause serious soil pollution. Therefore, combining synthetic SAPs with natural polymers can balance the contradictory relation of absorbency and retention of water and biodegradability.

4.1. Polyacrylicacid (PAA)

Polyacrylicacid (PAA) and sodium polyacrylate (PNaA) SAPs are the most widely used water retention agents as a result of superior water absorbency (300-500 g/g in water) and water retention capacity. Nevertheless, the effectiveness of them is hampered by low salt resistance, weak mechanical strength and non-degradability. Therefore, effective approaches to improve their salt-tolerance, mechanical properties and degradability are urgently needed.

The addition of clay, such as kaolin, montmorillonite and bentonite, has been recently reported to have effects of increasing water absorbency and enhancing mechanical performances of SAPs. For example, a slow-release fertilizer with a

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semi-IPN structure based on kaolin-g-P(AA-co-AM) and linear urea-formaldehyde oligomers (UF) showed excellent water absorbency of 68 g/g in tap water and controllable release of fertilizer [36]. Hybrid linear low density polyethylene (LLDPE)-g-PAA/montmorillonite showed optimum water absorbency of 800 g/g in distilled water [37]. A semi-IPN structure composed of cotton stalk (CS)-g-PAA/bentonite (bent) network and linear polyvinylpyrrolidone (PVP) and urea displayed optimized water absorbency of 1018 g/g in distilled water and 71 g/g in 0.9 wt% NaCl solution, together with reinforced mechanical stability [38].

The introduction of natural polymers into the cross-linked copolymer systems of AA and 2-acrylamido-2-methyl propyl sulfonic acid (AMPS) has been extensively studied to achieve both excellent absorbency and superior degradability. For example, sodium humate (SH), a natural organic material containing huge amounts of carboxylates and phenolic hydroxyls, was grafted on poly(AA-co-AMPS). The producing poly(AA-co-AMPS)/SH showed obviously higher water absorbency of 1380 g/g in distilled water and 117 g/g in 0.9 wt% NaCl solution, in comparation with neat poly(AA-co-AMPS) of 600 g/g in distilled water and 60 g/g in 0.9 wt% NaCl solution [39]. Moreover, adding SH to the surface of poly(AA-co-AMPS) also showed the ability to increase water absorbency (1000 g/g in distilled water and 80 g/g in 0.9 wt% NaCl solution) [39]. When chitosan was introduced to poly(AA-co-AMPS)/SH, the optimum water absorbency of poly(AA-co-AMPS)/chitosan/SH reached 1097 g/g and 103 g/g in deionized water and 0.9 wt% NaCl solution, respectively [40], which resulted from the small contribution of chitosan to water absorption capacity. The degradation performance test showed that degradation rate of this product in soil could reach 31.9% after 100 days. When added hydroxymethyl cellulose sodium (NaHMC) and laterite into poly(AA-co-AMPS), the optimum water absorption of the hybrid product was 1329 g/g, 269 g/g and 140 g/g in distilled water, tap water and 0.9 wt% NaCl solution, respectively [41]. Replacing NaHMC with hydroxypropyl cellulose (HPC), the obtained HPC-g-P(AA-co-AMPS)/laterite showed water absorption of 1427 g/g, 272 g/g and 143 g/g in distilled water, tap water and 0.9 wt% NaCl solution, respectively.

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And after repeated water absorption for 5 times, the water absorption was 946 g/g, indicating good application prospects [42].

Amazingly, a composite hydrogel of AA and maize bran prepared by UV-irradiation copolymerization showed the optimized water absorption of 2507 g/g in distilled water and 658 g/g in 0.9 wt% NaCl solution, respectively. This was due to a large number of hydrophilic functional groups (-OH, $-NH_2$ and -COOH groups) and moderately sized holes in the three-dimensional network. The product also showed a good water retention capability with 39% and 0.5% after centrifugation (6000 rpm) for 60 min and drying at $60^{o}C$ for 70 h, respectively [43]. Low salt-sensitivity, good water absorbency and excellent water retention capability enabled maize bran-PAA wide potential applications.

4.2. Polyacrylamide (PAM)

Polyacrylamide (PAM) is secondly commonly used synthetic SAP after PAA. It has similar water absorbency to PAA. However, low salt-tolerance and poor mechanical properties severely hampers its application. Thus many strategies have been proposed to enhance comprehensive performance of PAM.

To explore the effect of different kinds of clays on poly(AM-co-vinyl alcohol) copolymeric superabsorbent materials, the poly(AM-co-vinyl alcohol)/clay composites were synthesized and the addition of 2 wt% Cloisite®30B clay showed the best water absorbency ratio of 5,455%. Though its water absorbency may be lower than neat PAM, it exhibited good acid and alkali resistance. In 1 M HCl, the swelling was reduced by 46%, while in 1 M NaOH, the swelling was reduced by 37% in comparison to that in double distilled water after 24 h. Moreover, this materials exhibited positive re-swelling, which made it absorb more water than previous time [44].

To increase the water absorbency of PAM, a starch-g-PAM superabsorbent was prepared and showed the maximum absorption of 1452 g/g and 83 g/g for distilled water and 0.9 wt% NaCl solution, respectively [45]. On this basis, when grafted

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hydrophobic monomer sodium 2-acrylamido-tetradecanesulfonate ($NaAMC_{14}S$) to copolymerization of soluble starch and AM, the obtained soluble starch-g-poly(AM-co-$NaAMC_{14}S$) exhibited the maximum water absorbency of 2537 g/g in distilled water and 93 g/g in 0.9 wt% NaCl solution, indicating that $NaAMC_{14}S$ has great potential to enhance the water absorbency of superabsorbent resin. Moreover, after adding $NaAMC_{14}S$, the mechanical properties of SR-14 have considerably improved due to hydrophobic association. This study also found that the introduction of NaOH-induced hydrolysis to the last stage of gel polymerization can enhance the water absorbency of the AM system [46].

4.3. Copolymer of acrylic acid and acrylamide (P(AA-co-AM))

Generally, the most common SAP in the market is copolymer of acrylic acid and a small amount of acrylamide (P(AA-co-AM)), which is often expressed as “SAP” in the literature [47]. As a result of good water absorbency, large water retention capacity and easy accessibility, P(AA-co-AM) has been widely applied to industries including agriculture, commodity as well as medicine and health. At the addition level of 1.5 wt% P(AA-co-AM), the water absorption of sulphoaluminate planting concrete enhanced 74% than the reference, and the water release rate decreased by 26% at 180 h [48]. However, its water absorbency should be further improved to reduce the amount of indegradable P(AA-co-AM) used.

To achieve this, many researches are devoted to compounding inorganic particles with P(AA-co-AM). For example, TiO_2-P(AM-AA) was prepared by photocatalytic surface initiated polymerization, which has effectively solved the problems such as uneven dispersion of inorganic particles in organic phase and weak interfacial combination of organic and inorganic. IR and XPS detection showed that mechanism of this method is that TiO_2 produced free radicals on its surface under UV irradiation, promoting AM and AA monomers to occur in situ copolymerization reaction on the surface of TiO_2. A three dimensional network was fabricated after adding crosslinking agent. Results showed that the maximum water absorbency of the product reaches 942 g/g in deionized water and 70 g/g in 0.9 wt% NaCl solution [49]. $Ca(OH)_2$

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nanoparticles can also enhance the swelling ratio of AA-AM copolymer. The maximal swelling ratio of the resulting PAM/PAA/$Ca(OH)_2$ reaches high up to 5580 g/g at pH=7 and 328 K and the water retention ratio remains over 60% after maintaining 3 days in the open air at 298K with humidity around 40%. Furthermore, a good water absorbing capacity for this SAH sample can also be obtained in 0.9 wt% NaCl solution and 0.5-20 wt% urea solution [50], which is expected to lead to applications in many fields, such as agriculture, wastewater treatment and hygienic products.

It is worth mentioning that the load of soil can significantly reduce the water retention capacity of SAPs. For a 30 cm deep layer of soil of bulk density of 1.3 $g \cdot cm^{-3}$, after 1 h, this value amounted to 5 g/g, and for the control sample without load, this value amounted to more than 200 g/g. At the same time, loads also prolong the swelling time of P(AA-co-AM). The rate parameter (time required to reach 63% of maximum absorption capacity) increased from 63 min for the control sample to more than 300 min for the load of 3.8 kPa [51]. Considering poor saline-absorbency under load and worse swollen gel strength of P(AA-co-AM), a surface modification was employed using the glycerol-lactic acid-based star-shaped modifier (SM). Results showed that the implementation of surface treatment decreased the water absorbency both in deionized water and saline solution without load due to higher-surface crosslinking density, while increased the saline-absorbency under load by 28% due to higher elastic modulus [52].

4.3. Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) is a synthetic hydrophilic polymer with medium water holding capacity, which can degrade with the help of bacterial enzymes. The water evaporation of soil that sprayed with 30% PVA aqueous solution was reduced by 13% compared to sprayed with water [53]. Though the water absorbency of PVA is inferior to PAM, PVA with the appropriate degree of alcoholysis have more beneficial influence on plant growth in sandy soil compared with PAM, indicating that harmful competition of water absorption between plants and water retaining agent may bring

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about adverse effect [54]. Therefore，the comprehensive properties should be considered in practical applications, including appropriate water absorbency and retention, degradability and so on.

Constructing semi-IPN by linear PVA is a general method to ameliorate the comprehensive performances of PVA based water retention agents. For example, 3 wt% PVA was added into hemicelluloses-g-AA/bentonite matrix (HAB) and a semi-IPN was formed to enhance swelling properties. The maximum absorbency in the distilled water and 0.9 wt% NaCl solution of HAB-PVA was 1200 and 150 g/g, respectively, while the absorbency of HAB was 850 and 120 g/g, respectively [55], which affirmed PVA's role in promoting water absorption. Olad et al. added the linear polymer PVA and cellulose nanocrystals (CNC) when synthesized starch-graft-poly(AA-co-AM) and received a superabsorbent hydrogel composite with a semi-IPN structure. This hydrogel composite also exhibited a high equilibrium swelling ratio (922 g/g) and saline absorbency under load [56]. When linear PVA that grafted with ammonium polyphosphate (APP) was semi-interpenetrated with corn stalks (CSC)-g-AA, the resulting CSC-g-AA/PVA-APP not only showed good water absorbency of 303 g/g in distilled water, which was about 15% higher than the control group CSC-g-AA/APP, but also had the function of slow release of N and P. The slow release experiment indicated that the cumulative N and P release rates of CSC-g-AA/PVA-APP were 64 and 54% after 25 days in soil, by contrast CSC-g-AA/APP were 76 and 73% [57].

PVA can also be chemically cross-linked with other components to prepare good water retention agents. For example, a super-absorbent material was fabricated by electrospinning the natural polysaccharide pullulan (PULL) with PVA and montmorillonite (MMT) clay to form nonwoven webs, which were then heat treated at 150^{o}C for 4 min. Results showed that ether bonds were formed between PULL and PVA. And these degradable and green eco-friendly hybrid nanofibers exhibited a water absorbency of 143 g/g in distilled water and 40 g/g in a 0.9 wt% NaCl solution. Under extremely dry conditions, the PULL/PVA/MMT webs exhibited the ability to

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retain 43% distilled water and 38% 0.9 wt% NaCl solution after being exposed to the atmosphere for one week. Moreover, the presence of PVA also increased the thermal stability and mechanical strength of the product [58]. Another superabsorbent prepared by cross-linking PVA and borax and then adding *Moringa oleifera*, displayed maximum swelling ratio of 1163 g/g in deionized water and 290 g/g in 0.9 wt% NaCl solution. Furthermore, it still maintained excellent water retention capacity under high temperature [59].

4.4. Others

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Polyurethane (PU) foam is widely used in many fields. It has high mechanical strength but low water absorbency. Thus, the composite of PU foam and sodium polyacrylate (PNaA) was prepared to combine the advantages of both. Results showed that the content of 5.5 wt% PNaA could achieve water absorption of 891% and water retention of 408% (96h), which increased twice and eleven times respectively compared to the pure PU foam. And the strength of the composite enhanced a lot compared with the pure PNaA [60].

Interestingly, waste plastics made with a mixture of 35% disposable lunch boxes (mostly PP), 15% shopping bags (mostly HDPE), 40% waste plastic film (mostly LDPE) and 10% waste plastic foam (mostly PS), could be transferred into a water retaining agent through graft polymerization in an inverse emulsion system [61]. The results showed that its maximum water absorbing capacity for distilled water and tap water was 343 and 125 g/g, respectively. Moreover, the resulting samples showed excellent water retention capacity with 299 g/g water absorbing capacity after ten swelling-deswelling cycles. Compared with other synthetic polymer based water-retention agents, this agent has the advantages of lower production cost, higher strength and better reusability, which made it a promising water-retention agent to achieve sustainable and effective utilization of limited water resource. Water absorbency and retention capacity of various synthetic SAPs based agricultural water retention agents are summarized in Table 2.

Table 2. Water absorbency and retention of various synthetic SAPs based water retention agents

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Water retention agents	WA^a (g/g)	WA^b (g/g)	WR	Reference
Kaolin-g-P(AA-co-AM)-UF	-	68 (tap water)	32%, 16 d, soil with 1 wt% materials	[36]
LLDPE-g-PAA/montmorillonite	800	50	-	[37]
CS-g-PAA/bent/PVP/Urea	1018	71	20%, 10 d, at RM, soil with 1 wt% materials	[38]
poly(AA-co-AMPS)/SH	1380	117	-	[39]
poly(AA-co-AMPS)/chitosan/SH	1097	103	77%, 5 h at 30°C	[40]
NaHMC-g-P (AA-co-AMPS)/ laterite	1329	140	73%	[41]
HPC-g-P(AA-co-AMPS)/laterite	1427	143	97%, 14 h at 35°C	[42]
AA-g-maize bran	2507	658	0.5%, 70 h 60°C	[43]
Poly(AM-co-vinyl alcohol)/Cloisite®30B	55	40	60%, 40 h at 30^{o}C	[44]
Starch-g-PAM	1452	83	-	[45]
Starch-g-poly(AM-co-NaAMC$_{14}$S)	2537	93	-	[46]
TiO2-P(AM-AA)	942	70	-	[49]
PAM/PAA/Ca(OH)2	5580 (55^{o}C)	42	60%, 3 d at 40% humidity	[50]
HAB-PVA	1200	150	63%, 8 h at 80^{o}C	[55]
Starch-graft-poly(AA-co-AM)/PVA/CNC	922	52 (0.3 psi)	15%, 0.1 M NaCl	[56]
CSC-g-AA/PVA-APP	303	-	-	[57]
PULL/PVA/MMT	143	40	43%, 7 d	[58]
Moringa oleifera gum/PVA	1163	290	31%, 5 h at 60^{o}C	[59]
Mixed waste plastics	343	-	53%, 6 h at 40^{o}C	[61]

(^{a}: water absorbency in distilled water under optimal conditions; ^{b}: water absorbency in 0.9 wt% NaCl solution under optimal conditions; WA: water absorbency; WR: water retention)

5. Conclusion and summary

With the advance of science and technology, more and more excellent polymer water-retention agents have been prepared. In this paper, the research progress of natural and synthetic polymer based water-retention agents in recent 10 years is reviewed. Both natural polymer based water-retention agents and synthetic polymer based water-retention agents have their own advantages and disadvantages. Water-retention agents based on natural polymers, such as cellulose, starch and chitosan, have an obvious advantage of great degradability. Nevertheless, large

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quantity of natural polymer-based water-retention agent is necessary to maintain the water retention effect due to its low water absorption rate. On the other hand, although water-retention agents based on synthetic polymers, such as polyacrylicacid and polyacrylamide, show the advantages of low cost, long service life and high water absorption rate, their degradation products may have an adverse effect on the environment and plant growth. Thus many studies combined natural and synthetic polymers to achieve an excellent comprehensive performance.

From the above we were informed that owing to a large number of hydrophilic groups and three-dimensional crosslinked network structure, polymer water-retention agents exhibit huge water absorbency and strong water-retention capacity even under certain pressure. Therefore, introducing functional groups with strong hydrophilicity and constructing specific network structures, such as IPN, semi-IPN and copolymer network, could dramatically increase water absorption and water retention capacity of polymer based water-retention agents. This paper provided a lot of inspiration in preparing superior polymer water-retention agents for posterity, which has profound significance to the development of agriculture.

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6. Future scope

In the future, preparing a water-retaining agent with a broad agricultural application prospect should consider not only its water absorption and water retention in soil, but also its saline-alkali resistance, mechanical strength, reusability, degradability, safety, cost and so on. However, almost all SAPs have a considerably lower water absorbency in saline solution than in distilled water. And their three-dimensional network structures are easier to be destroyed if they were soaked in saline solution for a long time. The degradation product may be against the growth of corps. In addition, most SAPs show a worse water absorbency under load, which results in that the effect in actual application is not as good as in experiments.

Besides, present test conditions about water retention capacity, such as temperture, humidity and test duration, are different in various research, resulting in no uniform standard to compare water retaining property. Furthermore, superior water absorbency and water retention capacity of neat materials may not represent same excellent effect on soil moisture under water deficiency. Therefore, many factors should be considerded when design potential SAPs used in agriculture.

Declaration of competing interest

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

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Superabsorbent polymers (SAPs) can improve water use efficiency in agriculture.
According to their source, SAPs can be classified as natural and synthetic polymers.
Representative achievements in the design and modification of SAPs are introduced.
Future trends and rational design for SAPs with desired properties are concluded.

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Declaration of competing interest

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