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REVIEW PAPER

Development history and synthesis of super-absorbent polymers: a review

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Abstract

Super-absorbent polymers (SAPs) refer to a three-dimensional network polymer, water-swellable, water-insoluble, organic or inorganic material that can absorb thousands of times its own weight of distilled water. It is widely used in various fields, such as: agricultural, biomedical, daily physiological products, separation technology and wastewater treatment. In the review, the development history of superabsorbent polymers since 1961 is described, and the polymerization methods of superabsorbent polymers and the wide-ranging use of this type of polymers in life are described in detail. The article introduces four basic polymerization methods, bulk polymerization, solution polymerization, suspension polymerization and radiation polymerization from the preparation methods and types. Not only the detailed methods of polymerization but also their respective advantages and disadvantages are introduced. In recent years, new progress has been made in polymerization methods, for example, in-situ polymerization to obtain an onion-like multilayer tube cellulose hydrogel. The hydrogel has super-absorbent properties, and the water swelling mechanism is briefly introduced. Finally, the latest advances in super-absorbent polymers are pointed out.

Keywords Super-absorbent polymers · Cross-linked · Swelling · Preparation

Introduction

Hydrophilic gels, known as hydrogels, are a kind of slightly cross-linked water absorbing natural or synthetic polymers which may absorb thousands of times its weight in aqueous solutions [1–3]. Hydrogel is a water-insoluble polymer material that swells in water and retains most of the water in the structure. Currently, they are widely used in biomedical fields such as be scaffolds in tissue engineering where they may contain human cells in order to repair tissue [4–7]. Hydrogels respond to the environmental stimulus such as the change of pH, temperature, and the concentration of metabolite and then release their load as a result of such a change [8]. Hydrogels can responsive to specific molecules such as glucose [9] and antigens [10] and can being used as biosensors [11, 12] as well as in drug delivery systems [13]. Contact lenses are also based on hydrogels. Agricultural application of hydrogels includes its use as granules for holding soil moisture in drought areas [14, 15].

Super-absorbent polymer is a kind of hydrogels which can absorb water as high as 500-1500 g/g whereas the absorption capacity of common hydrogels is no more than 1000 g/g [16, 17].Generally, the super-absorbent polymers can be categorized by different aspects: it can be divided into two categories based on the mechanism of water absorption: chemical and physical absorption; according to the different raw materials it can be divided into about six categories: starch [18]; cellulose such as cardiomyopathy cellulose(CMC)-based SAPs [19]; protein [20]; synthetic of polymers such as the copolymers of acrylic acid and acrylamide [21]; chitosan [22] and finally the blends and composite such as organic-inorganic hybrid materials-based super-absorbent polymers [23, 24]. It can also be classified into two types by the method of cross-linking: the formation of network structure through addition of the cross-linker, such as poly(acrylic acid) cross-linked by metal ions [25] and starch/acrylate cross-linked by N,N′-methylenebisacrylamide [26]; the self-crosslinking SAPs such as polyacrylates [27] and polyacrylamides [28].

The preparation of the first super-absorbent polymer was performed in 1961 when acrylonitrile was grafted to starch by

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Table 1 Few examples of various super-absorbent polymers with their ingredients

No.	Name of super-absorbent polymer	Monomers used	Initiator used	Cross-linker used	Name of Technique	Application
1	Oil palm empty fruit bunch graft (Acrylic Acid-co-Ac-rylamide) super absorbent composite [53]	Acrylic acid, Acrylamide, Oil palm empty fruit bunch	Ammonium Persulphate	N,N′ -methylenebisacrylamide	Graft Copolymeri-zat-iom	Promote plant growth in arid environments
2	Starch polyacrylam-ide graft co-polymer [54]	Potato starch, Polyacryla-mide	Ceric ammonium nitrate	N,N′ -methylenebisacrylamide	Graft Copolymeri-zat-iom	Increase starch viscosity and polymer stability
3	Acrylonitrile and Acrylic acid grafted on Chitosan [55]	Acrylonitrile, Acrylic acid, Chitosan	Ammonium Persulphate	N,N′ -methylenebisacrylamide	Graft Copolymeri-zat-iom	Improve the hydrophilicity of non-woven fabrics
4	Itaconic acid grafted starch [56]	Itaconic acid grafted starch	Potassium permanganateSodium bisulfite redox initiator	N,N-bismetilenacrilamide	Graft Copolymeri-zat-iom	Good water absorption
5	Dextrin-graft-Acrylic acid/ Montmorillonite [57]	Partially neutralized Acrylic acid, gelatinized Dextrin and Organic-montmorillonite powder	Ammonium persulfate / Sodium sul-fite	N,N′ -methylenebisacrylamide	Graft Copolymeri-zat-iom	Good compatibility with blood
6	Cassava starch-g-acrylamide/ itaconic acid [58]	Cassava starch, Acrylamide/ Itaconic acid	Ammonium persulphate/ Tetramethyl-ethylene diamine re-dox initiator	N,N′ -methylenebisacrylamide	Graft Copolymerizati-om	Good adsorption of heavy metal ions
7	Chicken feathers protein-g-poly (potassium acrylate)/polyvinyl alcohol semiinterpenetrating copolymer [59]	Chicken feathers protein, Acrylic acid, Polyvinyl alchol	Potassium persulfate/ Ammonium ce-rium nitrate redox initiator	N,N′ -methylenebisacrylamide	Graft Copolymerizati-om	Good water absorption and water retention

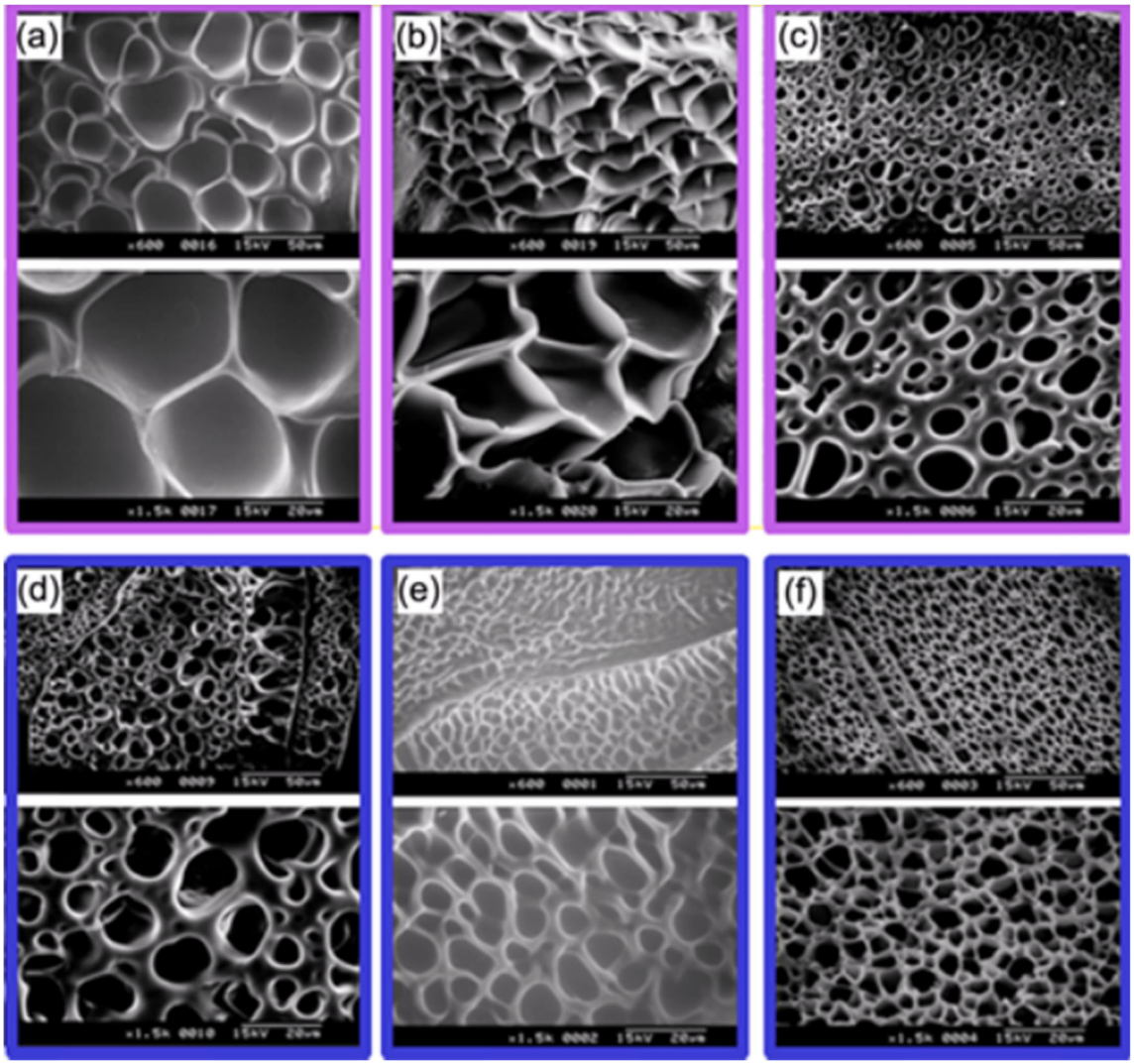

Fig. 1 SEM images of different HEMA hydrogels [67]

Russell [29], followed by Fanta investigated that the super-absorbent polymer based on starch derivatives possessed excellent water absorbing capacity and could retain them under a certain pressure [30, 31]. In the 1970s, the first SAP was developed in the Northern Regional Laboratory of the US Department of Agriculture, which was synthesized from starch-graft-hydrolyzed acrylonitrile products [32]. In 1978, Japan began the commercial production of SAP for female napkins [33]. After further developments, in 1980s, Germany and France employed SAP materials in baby diapers [34]. In late 1990,world production of SAP resins reached one million tons. Leading SAP manufactures are the Amcol (Chemdal), Stockhausen, Hoechst, Sumitomo, Colon, Nalco and SNF Floerger Companies etc. [35]

A series of papers have been published in the reviews for SAP hydrogel materials. In general, people mainly focused on the synthetic methods and properties of the hydrogel. Chemical and physical method of preparing agricultural hydrogels were reviewed by Kazanskii and Dubrovskii [36]. Bouranis et al. reviewed the synthetic polymers as soil conditioners [37]. Super absorbents obtained from shellfish waste have also been reviewed [38]. Ichikawa and Nakajima have reviewed the super absorbent materials based on the polysaccharides and proteins [39]. Athawale et al. reviewed the super-absorbent resin through gelatinized starch grafted copolymerization with acrylic acid [40]. Buchholz et al. has elucidated the cross-linked starch-based super-absorbents via partially neutralized poly(acrylic acid) grafted copolymerization with starch [41]. Dayal et al. reported a series of synthesises on acrylic superabsorbents, included solutions polymerization and suspension polymerization [42]. In a unique article published in 1994, Ricardo Po et al. [43] surveyed the water-absorbent polymers in accordance with the patent literature. Stanford Research Institute SRI has published a paper on industrial production of acrylic SAPs [44]. So far, there are several books worth mentioning about synthetic SAPs that detail the phenomenon of

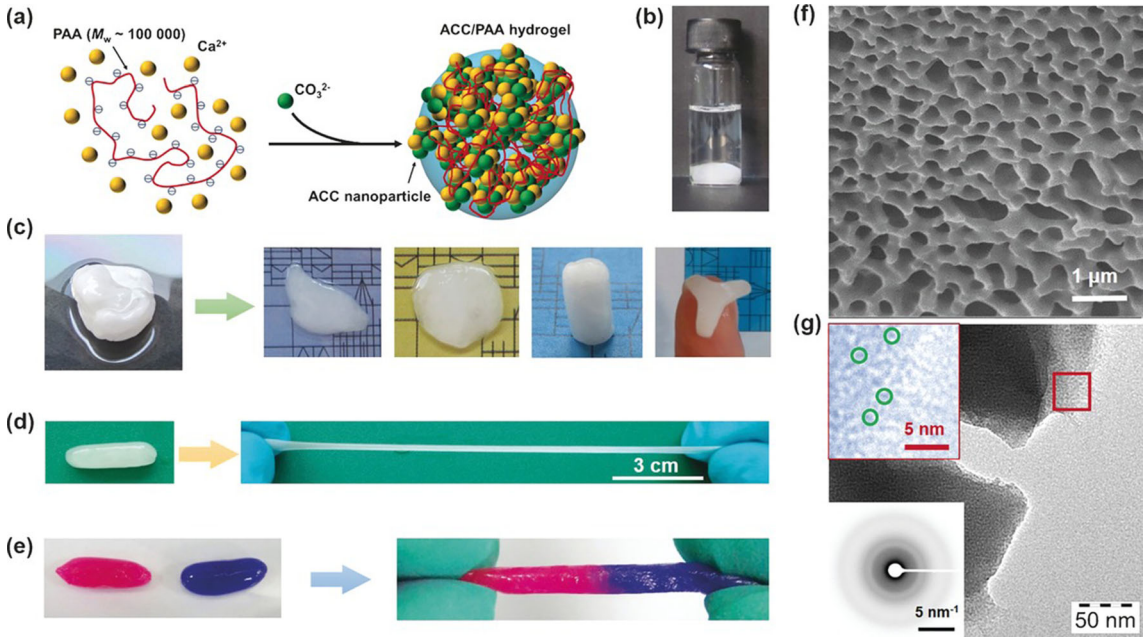

Fig. 2 (a) Depicted the synthesis of the ACC/PAA supramolecular hydrogel (b-e) Its various properties (f and g) Its SEM and TEM images [69]

synthesis [45–47]. In 2002, a book focusing on the high water absorption of fibers and textiles was published [48]. R. Dhodapkar et al. reviewed the superabsorbents on removal of dyes from aqueous solutions [49]. Ma Jianzhong et al. reported briefly the recent progress in the cellulose-based superabsorbent hydrogels via investigated different preparation approaches, the materials that employed in synthetic and promising applications and future research [50]. Laftah et al. [51] comprehensive discussed the classification, main properties and applications of superabsorbent polymer hydrogels.

Preparation methods

Most of the SAPs are synthetic or of petrochemical origin [52]. They are produced from many monomers, acrylic acid (AA), its salts and acrylamide are most widely used, some examples of SAP are listed in Table 1.

Various synthetic methods are employed to synthesis the super-absorbent polymers. In general, they can be classified into two types: chemical synthesis methods and physical methods. Chemical synthesis methods include bulk polymerization, solutions polymerization/cross-linking, suspension polymerization and polymerization by radiations. More over, physical methods refer to freeze/thaw cycle technology and cross-linked by a hydrogen bond. It is worth noting that new technologies such as interface contact technology [60] and in situ polymerization [61] are also used in preparation of SAPs.

Chemical synthesis methods

Chemical synthesis methods are widely used in preparation of super-absorbent polymers. The typical synthesis methods are detailed stated below.

Bulk polymerization

Bulk polymerization, is also known as mass polymerization, is the simplest technique that monomers are polymerized by initiators, light, heat or radiation without the presence of solvents and dispersants [62]. High rate and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases markedly and the heat result from polymerization is hard to spread. These problems can be avoided by using the lower temperature and low concentration of initiators in the case of producing a lot of heat [63]. The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity without complex devices. Poly (2-hydroxyethyl methacrylate) and poly(-acrylic acid) SAPs are prepared by these techniques. 2-hydroxyethyl methacrylate (HEMA) hydrogel has stronger mechanical properties than other polymer. It can be strengthened by bulk polymerization, co-polymerization with hydrophobic monomers and rigid cyclic monomer modification methods [64]. Poly(acrylic acid) is a polymeric substance containing carboxylic groups and linear CH_2-CH_2 chains. In earlier reports [65–68], its has a simple structure and has been used as a model compound for the study of natural

biopolymers. Shin et al. [67] reported a copolymer, it was prepared by sodium acrylate and hydroxyethyl methacrylate grafted bulk co-polymerization. From SEM we can observe the morphology of the hydrogel was a porous network structure and the average size of pores are several μm (Fig. 1.) The size of pores and pressure sensitive adhesion force was adjustable according to HEMA content and cross-linking agent content. Sun et al. reported a facile route for an amorphous $CaCO_3$-based hydrogel consisted of small calcium carbonate nanoparticles that physically cross-linked by poly(acrylic acid). The hydrogel has many outstanding characters such as shapeable, stretchable, self-healable and reversible with shear-thinning and thixotropic properties [69]. As showed in Fig. 2. The hydrogel formed free-standing, rigid, and transparent objected with remarkable mechanical performance upon drying. By swelling in water, the material can completely recover the original hydrogel status. The new synthesized super-absorbent hydrogel may be with widely application in various fields.

Solutions polymerization

Solution polymerization reaction is an important method in the synthesis of polymers. The polymerization is initiated thermally, by UV-irradiation, and by a redox initiator system or catalyst. If the resulting polymers can soluble in water, we called it homogeneous solution polymerization; the precipitation polymerization occurs when the polymers can't soluble in aqueous, we also call it heterogeneous polymerization. Compared with bulk polymerization, it is easy to control the temperature and the molecular weight of the product. The viscosity in the system is lower than bulk polymerization. The best example is preparation of poly(2-hydroxyl ethyl methacrylate) [70]. Poly(2-hydroxy ethyl methacrylate) (PHEMA) contains one carbonyl (C=O) and one hydroxyl (OH) groups on each side chain. The OH group acts as both proton donor and proton acceptor, while the C=O group as only proton acceptor [71]. Thus, both OH···OH and C=O···HO types of hydrogen-bonds are acceptable in PHEMA. Not only dimer structure (OH···OH) but also aggregates structure (···OH···OH···OH···) have been found in many systems including liquid alcohol and solid polymers. The mechanisms are shown in Fig. 3. By this method, a great variety of hydrogels have been synthesized. Katiyar et al. [72] reported fullerene (C60) containing cross-linked poly (2-hydroxyethyl methacrylate) polymers was synthesized by free radical polymerization. He used benzoyl peroxide (BPO) as an initiator and propylene glycol dimethacrylate as a cross-linker. The SAPs can become pH-sensitive or temperature-sensitive by using methacrylic acid [73] or N-isopropyl acrylamide [74] as monomers. Graft polymerization is a common method of solution polymerization. It refers to grafting monomer

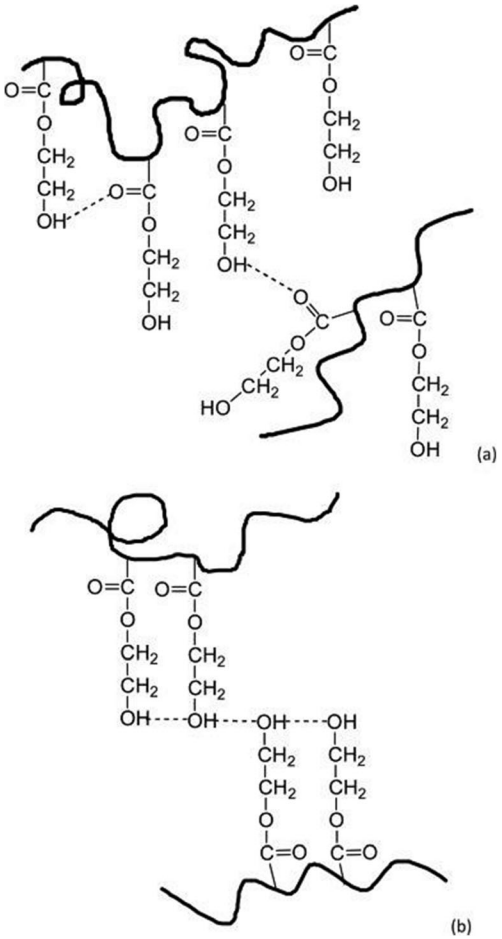

Fig. 3 Types of hydrogen bonds in PHEMA. Hydrogen bonds between hydroxyl (OH) and carbonyl (C=O) groups in the same or different macromolecular chain (a) and OH aggregates (b) [72]

molecules onto natural polymers, such as chitosan [75], starch [76], cellulose [77], pectin [78]and so on. The properties of the polymers are optimized by grafting monomers. In 2018, wang et al. grafted polyacrylic acid with chitosan as the main body by means of free radical solution polymerization to obtain a hydrogel with 3D structure granularity. When pH = 2.0–3.0, it has good adsorption performance for antibiotics [79]. Pakdel et al. published a review chitosan-based hydrogels, detailing six different types of hydrogels and their use in wastewater treatment. Hydrogels can absorb harmful substances such as heavy metal ions, dyes, and antibiotics in wastewater [80]. Pectin is a kind of polysaccharide with carboxyl group. This method which synthesizing superabsorbent resin with pectin grafted acrylic acid can not only improve the absorption capacity, but also reduce the environmental pollution [81]. Utilized The graft polymerization of soluble starch and acrylamide sythesized a low-cost ion exchange resin for removing chromium ions and nickel ions in water efficiently. The reserch showed that the process of resin adsorption of heavy metal ions can be explained by ion exchange process [82].

Suspension polymerization

Suspension polymerization is a method of preparing spherical SAP microparticles with size range of 1 μm to 1 mm. In the suspension polymerization, the initiators were dissolved in the aqueous to form a droplet shape and the polymerization is initiated by radicals generate from thermal decomposition of an initiator. The mechanism of suspension is similar with bulk polymerization. Yu et al. [83] synthesized super-absorbent polymer via inverse suspension polymerization used corn starch, acrylic acid and acrylamide as raw materials, cycloexane as continuous phase, N,N′-methylenebisacrylamide as cross-linking agent, potassium persulfate as initiator. The average particle size of polymer decreased with increased the dosage of Span65/Span80 dispersant. In suspension polymerization, the monomers may be enwrapped by the particles and hard to remove. Some SAPs microparticles of poly(hydroxyethyl methacrylate) have been prepared by this method. Cao et al. [84]reported a method to synthesis microspheres by grafting poly(N,N-dimethylacrylamide) (PDMA) from the surface of magnetic poly(2-hydroxy ethyl methacrylate) (PHEMA). The microspheres were rendered magnetic, which offers benefits such as quick and easy manipulation and/or separation from complex mixtures using a magnet, it is shown in Fig. 4. Cole et al. [85] investigated cellulose-graft-polyacrylamide/hydroxyapatite composite hydrogels of different weight ratios were prepared through a suspension polymerization method. The technique is shown in Fig. 5. The hydroxyapatite powders were embedded in the hydrogel matrix through ionic cross-linking of species OH^-, Ca^{2+}, PO_4^{3-} and amide groups of acrylamide and/or hydroxyl groups in the cellulose backbone. The swelling behaviors of the composite hydrogels were investigated under varying conditions of time, temperature and pH. The optimized swelling capacity in standard conditions was found to be 5197% per gram of the hydrogel [86].

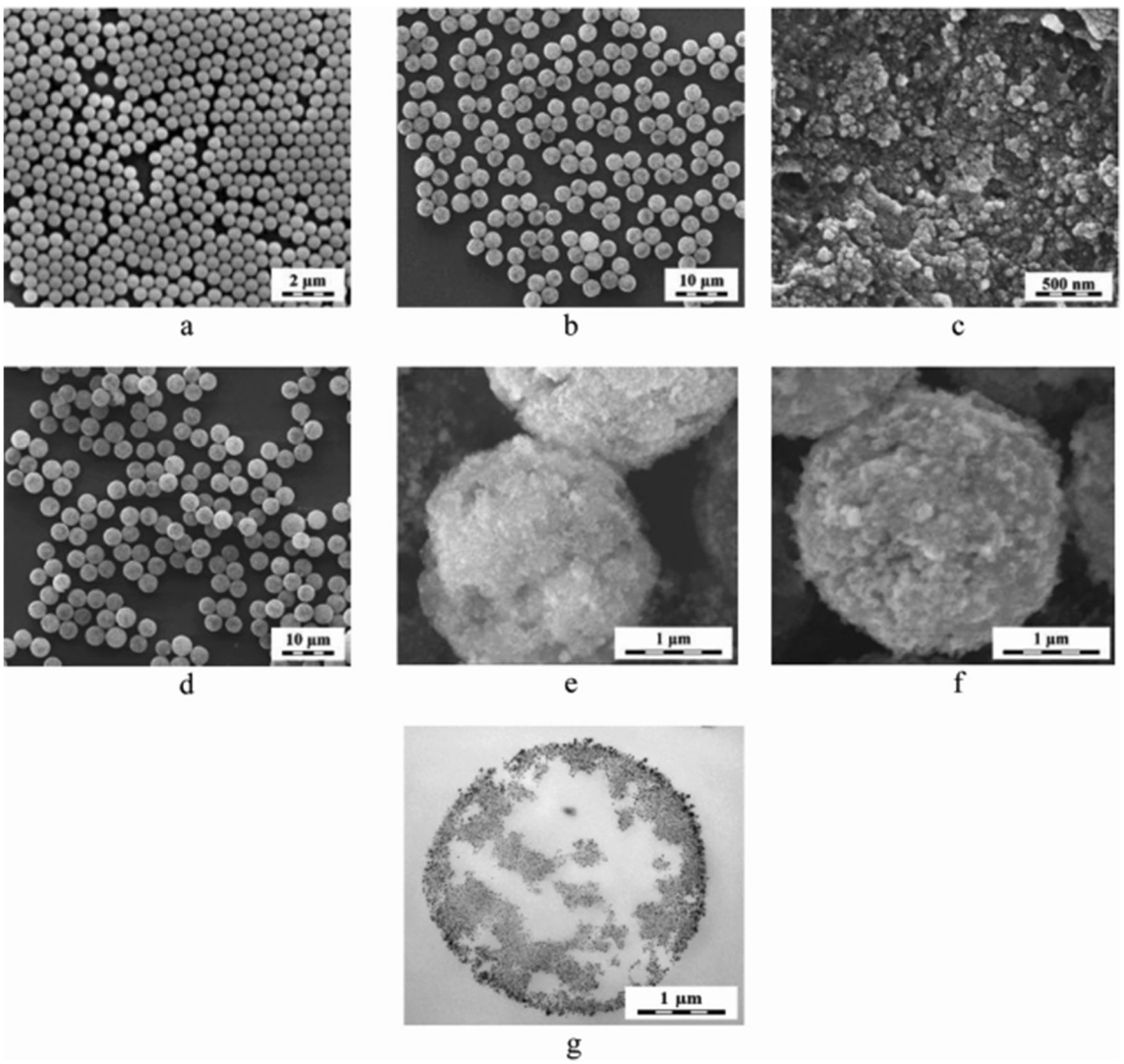

Fig. 4 SEM of various synthesized microparticles [85]

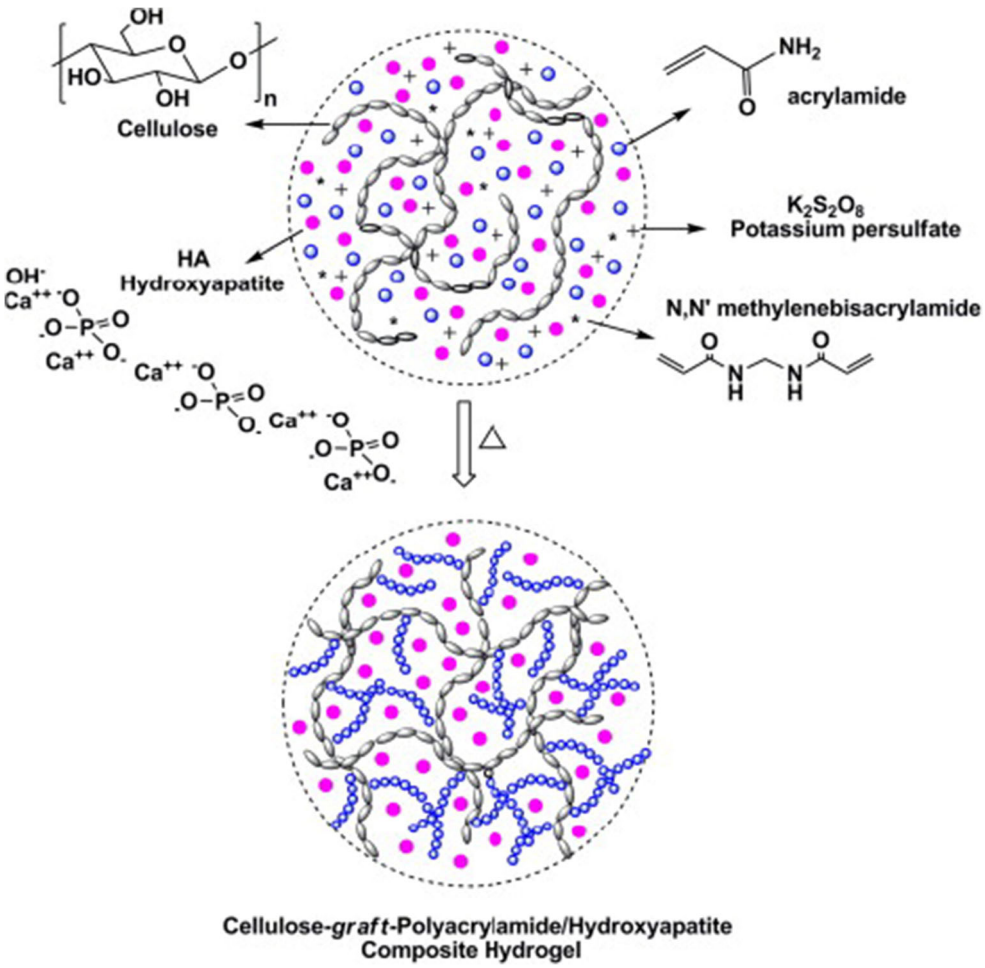

Fig. 5 Illustration for the synthesis of cellulose-graft-polyacrylamide/hydroxyapatite composite hydrogels [86]

Polymerization by radiations

The irradiation polymerization technology was first used in polymerization of liquid ethylene. The radiation, like alpha, beta, gamma rays and electron beams had been used as an initiator to synthetic the SAPs. The radiations of aqueous polymer solutions results in the formation of radicals on the polymer chains [87]. Also, radiolysis of water molecules results in the formation of hydroxyl radicals, which also attack the polymer chains, resulting in the formation of macro radicals. Recombination of the macro radicals on different chains results in the formation of covalent bonds, so finally a cross-linked structure is formed without any initiators and catalysts residue in system. The reaction can be carried out at a very low

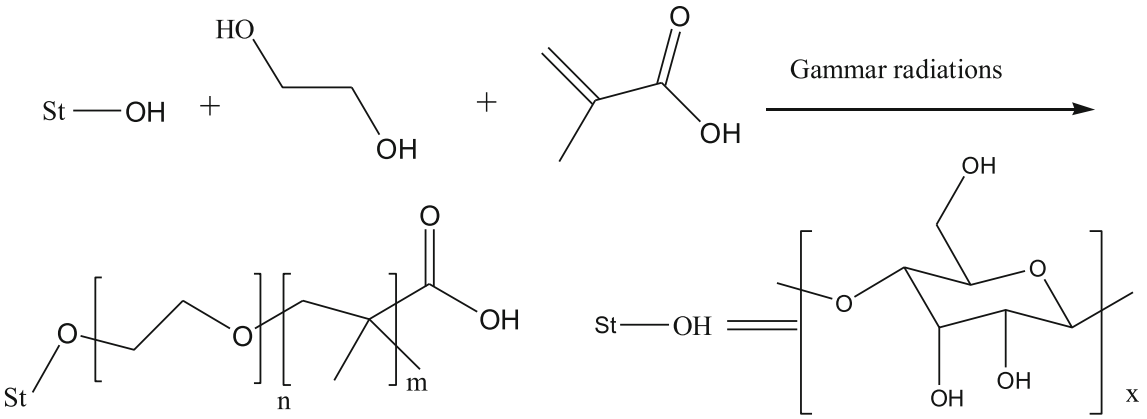

Fig. 6 Synthesis of St-g-PEG-co-PMAA hydrogel [93]

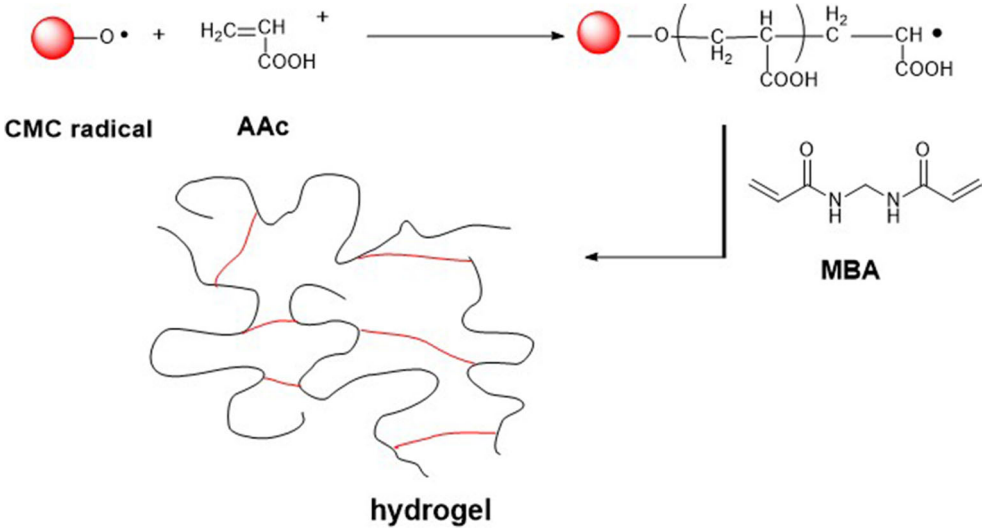

Fig. 7 General mechanism for the radical cross-linking of CMC/AAc mixture in the presence of MBA [94]

temperature. Examples of polymers cross-linked by the radiation method are poly(vinyl alcohol) [88], poly(ethylene glycol) [89]and poly(acrylic acid) [90]. Kasinee et al. [91] studied that super-absorbent polymer was synthesized by radiation-induced grafting of acrylamide onto carboxymethyl cellulose in the presence of a cross-linking agent, N,N′-methylenebisacrylamide. The results showed that, in an aqueous solution, swelling ratio decreased with increasing dose and increasing content of AM. In salt solution, swelling ratio decreased with increasing ionic strength. Zhang et al. synthesized St-g-PAM cross-linked with N,N-methylbisacrylamide (MBA) with 10 MeV electron beam irradiation at room temperature. The optimum dose was found to be 8 kGy, the optimum ratio of AM to AGU was 4.5 and the optimum ratio of MBA to AM was 0.4. The resultant product showed excellent absorbance and was categorized as super-absorbent polymer [92]. Similarly, El-Mohdy et al. synthesized starch-graft-poly(ethylene glycol)-co-poly(methacrylic acid) (St-g-PEG-co-PMAA) hydrogel from water soluble starch, ethylene glycol (EG) and methacrylic acid (MAA) using g initiations as radical initiators [93]. The synthetic route is given in Fig. 6.

Salmawi et al. [94] reported gamma irradiation to initiate preparation of a novel superabsorbent polymer used carboxymethyl cellulose as raw materials and grafted with acrylic acid and clay montmorillonite. The general mecanism of sythesis the SAP is given in Fig. 7.

Grafting induced by radiations is useful, because it requires less time than grafting induced by chemicals thus prevents the waste of time [95]. In general, facile technique, not any initiators or cross-linkers, no waste products, and relatively low operating costs makes the irradiation technique a suitable choice for the synthesis of SAPs [96] (Table 2).

Physical synthesis method

Physical synthesis methods are molecular assembly by cross-linking hydrogen bonds or ionic bonds between polymers. The super-absorbent polymers can be prepared at low temperatures, in contrast to methods used at ambient temperatures. The super-absorbent polymers are polymerized by strong hydrogen bonding. This strong hydrogen bonds may be formed during one of the stages of the freeze/thaw cycles: ether during freezing of the initial system, during storage of the samples in the frozen state and during thawing of the frozen specimens [97]. Guan et al. [59] prepared a novel hydrogels were prepared from hemicelluloses, polyvinyl alcohol (PVA), and chitin

Table 2 Comparison of three chemical synthesis of SAPs

The type of polymerization	Characterization
Bulk polymerization	The technique is simplest and easy to get high rate and degree of polymerization; but its viscosity s high and the heat hard to spread.
Solution polymerization	Easy control; the polymerization rate is also high and it is safe and harmless
Suspension polymerization	Easy to preparespherical SAP microparticles.
Irradiation polymerization	Fast heat, clean and with high efficiency.

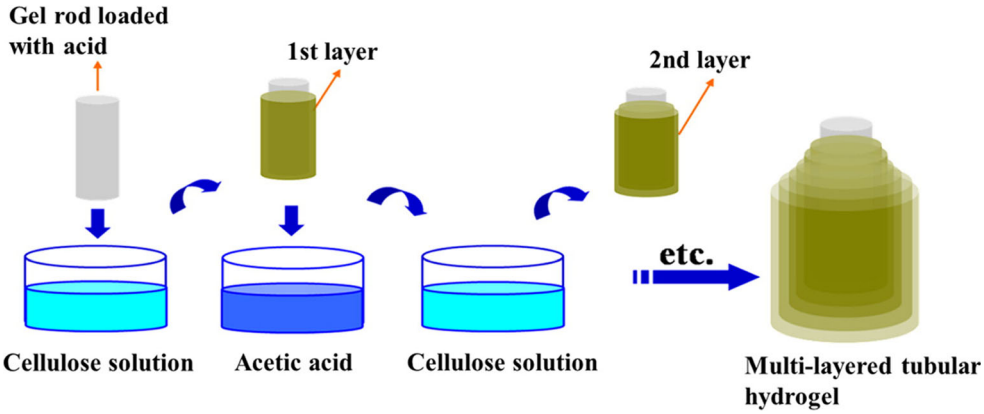

Fig. 8 Preparation Process of the Multi-Layered Cellulose Hydrogel [100]

nanowhiskers through 0, 1, 3, 5, 7, and 9 times of freeze/thaw cycles and concluded that the increase of freezing/thawing cycles made the structure of the hydrogel become more stiff, thermal property become more stable, crystalline degree become higher, whereas after 3 times of freeze/thaw cycle, the equilibrium swelling ratio of hydrogels decreased due to the formation of the lamellar structure. Kuo et al. [98] compared the thermal properties and hydrogen bonding of poly (vinylphenol) (PVPh) and bisphenol A (phenoxy) polyhydroxyether (phenoxy) polymer blends, and measured them by differential scanning calorimetry Method (DSC), Fourier transform infrared spectroscopy (FTIR) and solid-state nuclear magnetic resonance techniques have shown that the tendency of hydrogen bonding between PVPh and phenoxy is more favorable than the internal hydrogen bonding of PVPh and phenoxy.

New methods

In these years, scientists explored some new methods to synthesis super-absorbent polymers such as rapid contact technology between solid and liquid and in situ polymerization. For example, He et al. [99] prepared a novel onion-like and multilayered tubular cellulose hydrogels through fast contact of solid−liquid interface. The preparation process of the multilayered cellulose hydrogels is shown in Fig. 8. Zhong et al. [100] reported a facile one-pot in situ polymerization method for the preparation of tough and highly stretchable physical hydrogels via dual cross-linking composed of vinyl-hybrid silica nanoparticles (VSNPs) as multivalent covalent cross-linking and hydrogen bonding as physical cross-linking. Poly(acrylic acid) nanocomposite physical hydrogels (NCP gels) are obtained without adding any organic chemical cross-linkers (Fig. 9).

Swelling mechanism

It is necessary to understand the reasons why super-absorbent polymers swell. There are several factors such as networks parameters, nature of the solution, hydrogels structure (porous or poreless), and drying techniques influence the process of swelling, all of which contribute to the final swelling capacity [101]. As shown in Fig. 8.

Hydrogen bonds are electrostatic interactions between molecules, occurring in molecules that have hydrogen atoms attached to small electronegative atoms such as N, F, and O. The hydrogen atoms are attached to the non-bonding electron pairs (long pairs) on other neighboring electronegative atoms [102]. In water, the electronegative

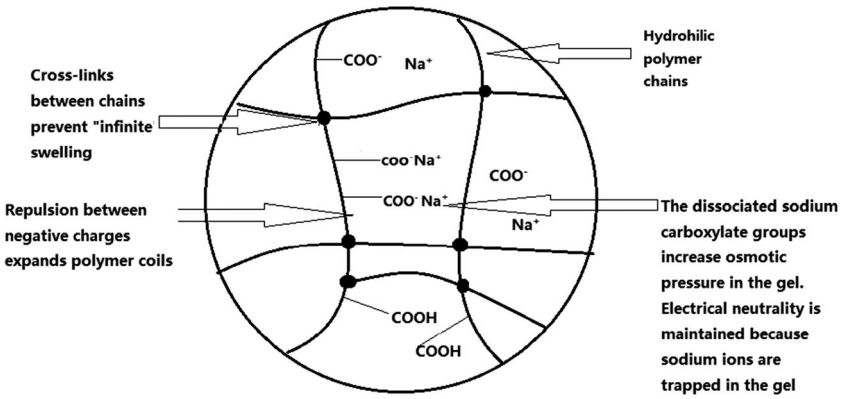

Fig. 9 A diagrammatic representation of neutralized super-absorbent polymer network, showing the charged polyacylate and acidic group [101]

atom is oxygen that pulls the hydrogen's electrons towards itself setting up a dipole in the molecule. The positive hydrogen atoms are attached to the oxygen long pairs on other water molecules. Oxygen has two lone pairs of electrons and each is capable of hydrogen bonding to two other water molecules [103]. These effects decrease the energy and increase the entropy of the system. Due to the hydrophilic nature of SAP the polymer chains have a tendency to disperse in a given amount of water, which leads to a higher number of configurations for the system and increases entropy [104, 105].

Outlook

This review summarizes recent advances in the preparation of super-absorbent polymers and focuses on the synthesis of superabsorbent polymers. Super-absorbent polymer refers to a three-dimensional network polymer, an organic or inorganic material that is swellable in water but insoluble in water, capable of absorbing up to about 5000 times its weight in an aqueous solution. It has a variety of preparation methods, and many people have now prepared a wide variety of different super-absorbent polymers. However, the preparation mechanism of SAPs still need to be further investigated and the swell kinetics in different media requires deeper investigation. Because more theoretical studies may help us better understand the SAPs and make full use of them. In order to improve the heat resistance and stability of SAP, we can add inorganic super-absorbent polymers, which are still under study.

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