



Review

Advances in superporous hydrogels

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Abstract

Superporous hydrogels (SPHs) are different from superabsorbent polymers (SAPs) in that SPHs swell fast, within minutes, to the equilibrium swollen state regardless of their size. The fast swelling property is based on water absorption through open porous structure by capillary force. The poor mechanical strength of SPHs was overcome by developing the second-generation SPH composites (SPHCs) and the third-generation SPH hybrids (SPHHs). This review examines the differences between SAPs and SPHs and describes three different generations of SPHs.

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Keywords: Superporous hydrogels; Superabsorbent polymers; Mechanical strength; Elasticity

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1. Introduction

About three decades ago, superabsorbent polymers (SAPs) were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where an excellent water-holding property was of prime importance. In 1998, superporous hydrogels (SPHs) were introduced as a different category of water-absorbent polymer systems. The original SPHs were developed into next generations of SPHs with more useful properties, such as high mechanical strength and elastic properties. In this review, evolution of SPHs is described in detail, and the differences between SPHs and SAPs are also explained.

2. SAPs vs. SPHs

SAPs, just like SPHs, are structurally cross-linked hydrophilic polymers, which have the ability to absorb considerable amounts of water or aqueous fluids (10–1000 times of their original weight or volume) in relatively short periods of time [1–3]. Depending on the manufacturing process and the materials used during preparation, the swelling rate of SAPs ranges from fraction of a minute to hours. The fast swelling, however, is mainly based on the small size of the SAP samples. On the other hand, the

swelling kinetics of SPHs is always fast regardless of the size of the final product. The porous hydrogels are prepared using several techniques, such as freeze-drying [4], porogenesis [5–7], microemulsion formation [8] and phase separation [9]. On the other hand, modern SAPs and SPHs are normally prepared utilizing a gas blowing technique in which acid-induced decomposition of a bicarbonate compound is exploited [10].

Although both SAPs and SPHs are porous in structure, they are different from each other as compared in Table 1. These differences in swelling properties are also clearly demonstrated in Fig. 1. The SPHs swell immediately upon contact with water regardless of their size in the dried state. The initial wetting of SAP particles is slower than that of SPHs, and the fast swelling is based on the small size of SAP particles. If SAPs are made into bigger size samples, swelling would not be as fast as their smaller counterparts. The unique property of size-independent fast swelling kinetics of SPHs is accounted for by their interconnected open cellular structure, as shown in Fig. 2. The open porous structure allows extremely fast absorption of water into the center of the dried matrix by capillary force.

The same monomer solution can produce different types of water-absorbing polymer networks, such as nonporous, porous and superporous structures depending on the presence of foaming agent, foaming

Table 1

General features of superabsorbent polymers (SAPs) and superporous hydrogels (SPHs)

| | SAPs | SPHs |
|-------------------------------------|--|--|
| Commonly used monomers | Acrylamide, acrylic acid, salts of acrylic acid including sodium and potassium acrylates | Acrylamide, acrylic acid, salts and esters of acrylic acid including sodium and sulfopropyl acrylates, 2-hydroxyethyl methacrylate |
| Method of synthesis | Bulk, solution, inverse suspension | Mostly aqueous solution |
| Initiating system | Thermal, redox | Mostly redox |
| Porous structure | Random closed to semiopen cells | Interconnected open cells |
| Final product | Particle | Any shape including particle, sheet, film, rod |
| Water absorption mechanisms | Diffusion (high), Capillary (low) | Diffusion (low), Capillary (high) |
| Swelling dependence on size | Size-dependent | Size-independent |
| Type of absorbed water ^a | Mostly bound | Mostly free |
| Free swelling capacity | Very high | Very high |
| Retained water under pressure | High | Low |
| Applications | Where high swelling, fast-medium rate of swelling is required | Where size-independent high and very fast swelling are required |
| Service environment | Water, saline, blood, urine | Simulated gastric fluid, simulated intestinal fluid |

^a Water in the hydrogel structure can be classified into bound, semibound and free water. While bound water is tightly attached to the hydrogel structure, the free type of water can easily be removed from the gel even under low pressures.

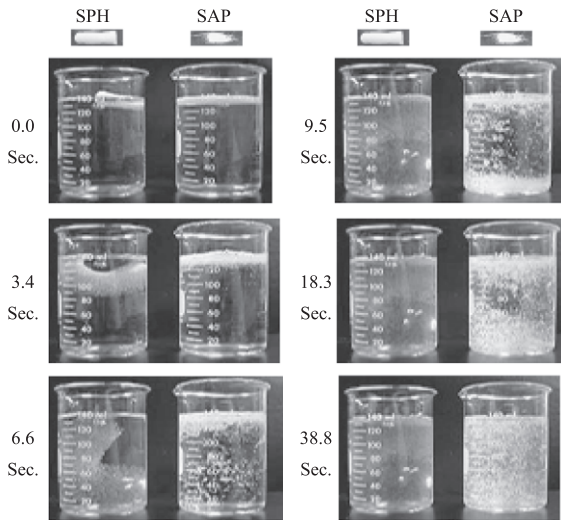


Fig. 1. Swelling kinetics of a typical superporous hydrogel (in the cylindrical shape, 2 cm length and 0.8 cm diameter) and a typical superabsorbent polymer (in the particulate shape with the particle size in a range of 0.1–1 mm).

aid and foam stabilizer, as shown in Table 2. The comparisons made in Table 2 are based on SAP and SPH prepared by using acrylamide and acrylic acid. The monomers are simultaneously polymerized (using a redox initiating system) and cross-linked in the solution containing bisacrylamide as a cross-linker. A combination of acetic acid (or acrylic acid) and sodium bicarbonate is used to make a foam structure,

which can in turn be stabilized using poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers as surfactants. Addition of foaming aid ingredients resulted in different reaction profiles as shown in Fig. 3. The reaction profile can significantly affect the swelling and physical properties of the final product. The various reaction profiles are partly due to different oxygen interferences [11–13].

3. Harmonized foaming and gelation

In the synthesis of SAPs described by the steps in Fig. 4, the following general synthetic procedure is applied regardless of the type of the materials used. Since hydrophilic monomers have a very high heat of polymerization, their bulk polymerization is normally associated with a violent exothermic reaction that results in a heterogeneous structure, so-called popcorn product with no water-absorbing properties. For this reason, the monomer is first diluted with certain amount of water to reach a desired monomer concentration (Step 1). Dilution with water also makes it easy to handle the monomers. For instance, the water-diluted glacial acrylic acid possesses superior handling properties as compared with acrylic acid because of its lower freezing temperature. Normally, the monomer is mixed with water at room temperature

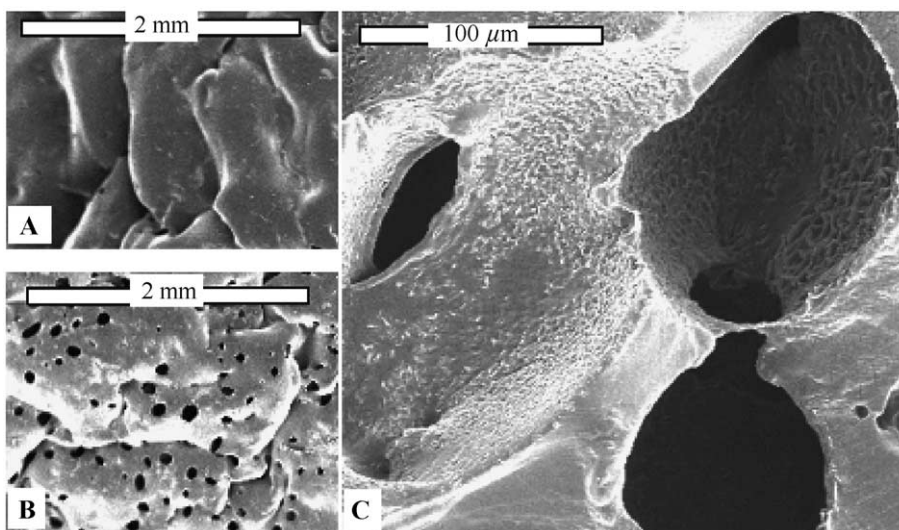


Fig. 2. Scanning electron micrographs of a nonporous SAP (A) and a corresponding SPH (B and C).

Table 2
Typical formulations for aqueous solution polymerization of SAPs and SPHs

| Starting material | Role | Nonporous SAP | Porous SAP | SPH |
|--|-----------------|--|--|--|
| Acrylamide, acrylic acid ^a | Monomer | √ | √ | √ |
| Bisacrylamide | Cross-linker | √ | √ | √ |
| Deionized water | Solvent | √ | √ | √ |
| Ammonium persulfate | Oxidant | √ | √ | √ |
| Tetramethyl ethylenediamine | Reductant | √ | √ | √ |
| Glacial acetic acid | Foaming aid | | √ | √ |
| Sodium bicarbonate | Foaming agent | | √ | √ |
| PEO–PPO–PEO block copolymers | Foam stabilizer | | | √ |
| Starting reaction temperature (°C) | | 25 | 25 | 25 |
| Reaction | | Within 30 s (after 15 s of inhibition period), the reaction temperature rises from 25 to about 75 °C with the rate of about 2 °C/s. | Within 66 s (after 80 s of inhibition period), the reaction temperature rises from 25 to about 65 °C with the rate of about 1 °C/s. | Within 78 s (after 70 s of inhibition period), the reaction temperature rises from 25 to about 55 °C with the rate of about 0.7 °C/s. |
| Reaction product after synthesis | | Solid rigid hydrogel | Solid flexible unstable foam | Solid flexible stable foam |
| Comparative swelling capacity (g/g) | | 9 | 20 | 33 |
| Comparative swelling retardation period ^b (min) | | 185 | 55 | 1 |

Data provided in the table are for a reaction system containing acrylamide 50 wt.% (500 μ L), acrylic acid (50 μ L), bisacrylamide 1 wt.% (100 μ L), deionized water (750 μ L), Pluronic® F127 10 wt.% (50 μ L), ammonium persulfate 20 wt.% (40 μ L), tetramethylethylenediamine 20 v/v% (50 μ L), acetic acid (30 μ L) and bicarbonate (35 mg).

^a Acrylic acid can also be used as a foaming aid.

^b Swelling retardation is the time by which about 60% of the ultimate or equilibrium swelling capacity is achieved.

under gentle mixing. To produce ionic superabsorbents, monomers, such as acrylic acid, may be neutralized to some degree, normally to 75 mol% (Step 2), followed by addition of a cross-linker (Step 3). Since neutralization can be accompanied by the sudden release of significant amounts of heat, a double-surfaced reactor equipped with external or

internal cooling jackets or coils may be used. All modern superabsorbent polymers are produced to possess large amounts of pores necessary to acquire fast water absorption property. This property can normally be achieved by generating gas bubbles. To produce a foam during polymerization, foaming aid such as glacial acetic acid and acrylic acid are added

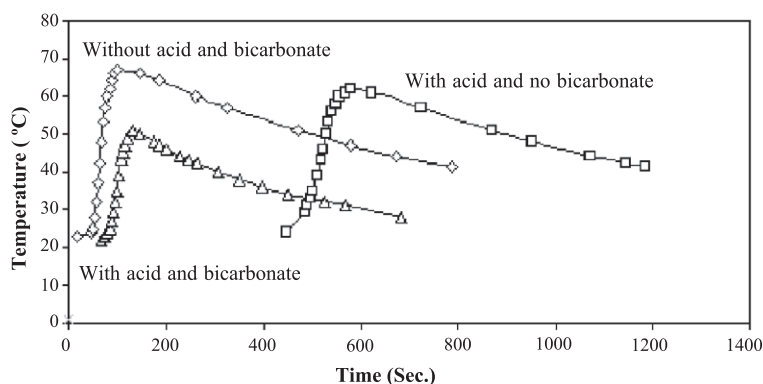


Fig. 3. Typical time-dependent temperature changes during cross-linking polymerization of acrylamide/acrylic acid monomers. Bisacrylamide was used as a cross-linking agent.

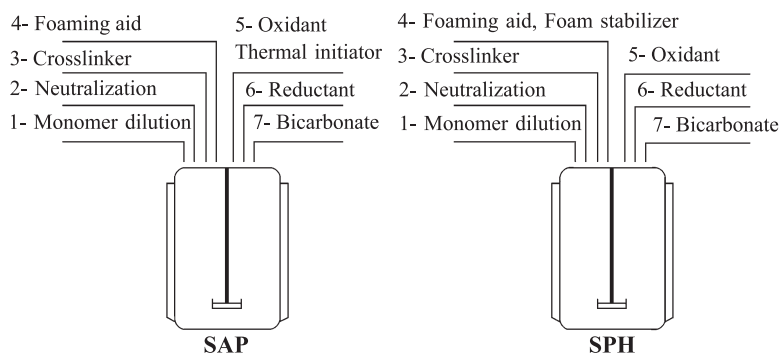


Fig. 4. Synthetic steps in the production of SAPs and SPHs.

to the monomer solution (Step 4). To promote polymerization, redox couples of ammonium persulfate/sodium metabisulfite or potassium persulfate/sodium metabisulfite and thermal initiators, such as ammonium persulfate or potassium persulfate, are normally used. Oxidant and reductant are added to the monomer solution under gentle mixing (Steps 5–6). Lastly, to generate gas bubbles, acid-dependent foaming agent, such as sodium bicarbonate, is added (Step 7).

To produce SPH polymers, a foam stabilizer is added during the process (Step 4 in Fig. 4). Since the foam stability is essential for producing homogeneous SPHs, surfactants, such as PEO–PPO–PEO triblock copolymers, are used during the synthesis. The aqueous surfactant solution is added to the monomer solution and mixed under gentle mixing. Another unique step in the synthesis of SPHs is using redox couple initiators (Steps 5–6). Almost all SPHs are produced using an oxidant/reductant couple, while SAPs are produced via both thermal and redox

systems. Depending on the monomer(s) used, the redox couple may be different. For instance, for the monomer system of acrylic acid and potassium acrylate, the redox couples of persulfate/diamine and bisulfite/persulfate are effective for acid-rich and salt-rich monomer systems, respectively.

The reactions involved in the preparation of SAPs and SPHs are cross-linking polymerization (which is also known as gelation) and foaming. Dispersion and dissolution of the bicarbonate (Step 7 in Fig. 4) increases the pH of the reaction medium to a level at which the initiator decomposes faster. As the formation of initiator radicals reaches a certain level, the polymerization reaction proceeds rapidly and the reacting mixture becomes viscous over time. At the same time, bicarbonate interacts with the acid component of the system to produce CO_2 gases required for the blowing process. The two processes, i.e., gelation and foaming processes, need to be conducted in such a way to enable harmonized foaming and gelation. As shown in Fig. 5, this harmonization is a basic element

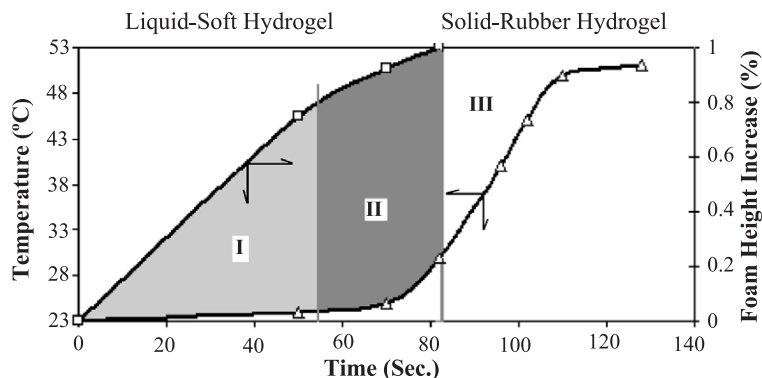


Fig. 5. Typical harmonized gelation and foaming processes in the synthesis of superporous hydrogels.

for successful preparation of very homogeneous SPHs. Stage I in Fig. 5 is assigned to a foaming of about 80% while the gelation process has not begun as indicated by no temperature rise. In Stage II, the rest of the foaming process takes place as the reaction temperature rises to a certain level (5–10 °C increase of the reacting mixture). The foam consistencies at Stages I and II are fluid and soft solid, respectively. With no foam development beyond this point (Stage III), the gelation proceeds and foam turns to solid flexible rubber as the temperature reaches to its maximum.

4. Postsynthesis treatment

Since no foam stabilizer is normally used in the synthesis of SAPs, the foam spontaneously collapses under its weight and shrinks into a smaller volume. Therefore, pore structures are not preserved in a controlled manner. Consistency of the hydrogel after its formation can affect the foam stabilization. For instance, polymerization of highly concentrated monomer solutions results in sudden gelation of the reacting mixture to a brittle and solid product. Thus, mobility of the polymer chains is prevented and hence the pores could be preserved to some extent. The foamed product is then dried and mechanically ground. The ground mass, which is a mixture of

granules and particles of different sizes, is screened in order to obtain a desired particle size distribution. It is these small granules and particles that provide superabsorbent property.

In case of SPHs, the as-synthesized foamed product is soaked into a nonsolvent, usually ethanol, to be dehydrated. For complete dehydration, a number of fresh batches of ethanol can be used. Dehydration using ethanol helps to stabilize the foamed product and prevent it from shrinking. Complete dehydration results in a solid, brittle porous product, which is white in color because of heterogeneous combination of polymer and pores. Ethanol can be removed from the stabilized product by a short drying process. The final product can be ground into a particle shape (like superabsorbent particles), sliced into absorbent sheets, or machined into any shape and size. Comparison of postsynthesis steps of SAPs and SPHs are shown in Fig. 6.

In the synthesis of SAPs, conversion or reaction may continue during the final drying process and its extent depends partly on the gel consistency after its formation. Therefore, the swelling properties of the final dried polymers are critically affected not only by the inhibition period events, but also by drying. On the other hand, in the synthesis of SPHs, the gels are dehydrated in ethanol almost immediately after the gel formation. Accordingly, SPHs are obtained in the dry

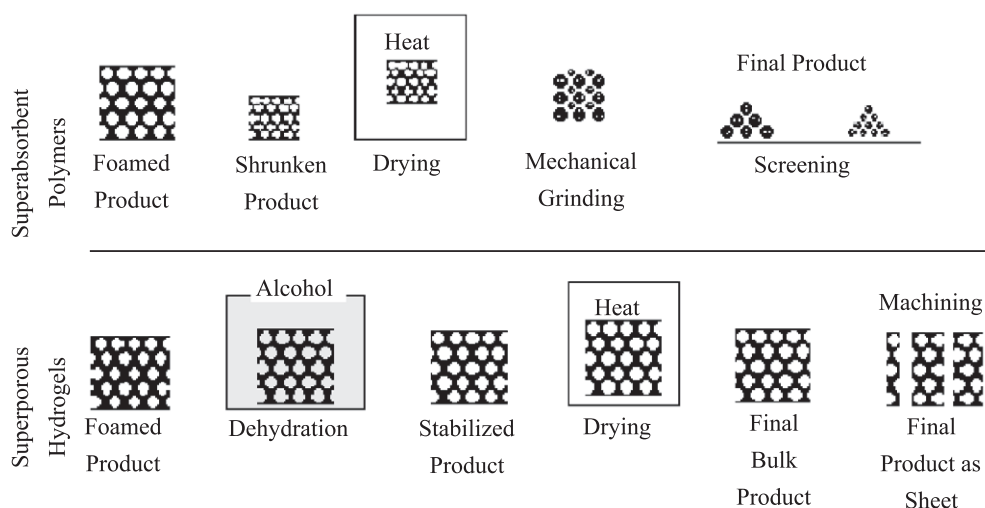


Fig. 6. Postsynthesis steps of SAPs and SPHs.

and brittle state after dehydration. During dehydration, the residual monomers and other soluble fractions are washed out of the SPHs. As a result, the polymerization process for the final product is limited to the time of gel formation. Likewise, the kinetic chain length, polymer sol content and its final consistency are defined as obtained immediately after the gel formation. This indicates that events during the gelation or exothermic period are much more critical in the synthesis of SPHs than in the synthesis of SAPs. Effects of the formulation variables on gelation process are shown in Fig. 7 for the acrylamide-based superporous hydrogel [13]. Dilution of the monomer solution with water or foaming aid has significant impact on the temperature rise. Addition of water and foaming aid also has significant effects on the inhibition period and exothermic period.

5. Water absorption mechanisms

Regardless of the synthetic method, various grades of SAPs are normally prepared as nonporous to porous particles. Nonporous hydrogels can find applications where high mechanical strength properties are required, as in agriculture when the hydrogel is applied in deep soil and should withstand the associated pressure. They can also be used in applications where the rate of water absorption is not primary. The outermost dry layer of granular particles is first moistened upon contact with water

to result in two phases of partially swollen and dry polymer. Diffusion of water continues through the partially swollen layer towards the core. In case of porous SAPs, pores created on the surface and in the bulk of the polymer enhance water absorption by capillary forces. The industrial grade SAPs are produced in desired range of particle sizes to fulfill the requirements for specific applications. This can be achieved because of the resistance of the bulk polymer to the mechanical forces applied during grinding. Unlike SAPs, SPHs swell very fast regardless of their size, and this is due to the interconnected porous structure. The interconnected structural pores provide water absorption into the center of the SPHs by capillary force.

6. New generations of SPHs

The fact that SPHs absorb water very fast even in large sizes makes them useful in the development of gastrointestinal platforms. The fully swollen SPHs, however, are mechanically very poor to meet the requirements for certain applications for which very high mechanical property (in their swollen state) is highly demanded. To distinguish SPHs with different properties, SPHs are divided into three different generations. The conventional (i.e., the first generation) SPH is characterized by fast swelling, high swelling ratio and weak mechanical properties. On the other hand, the second-generation SPHs

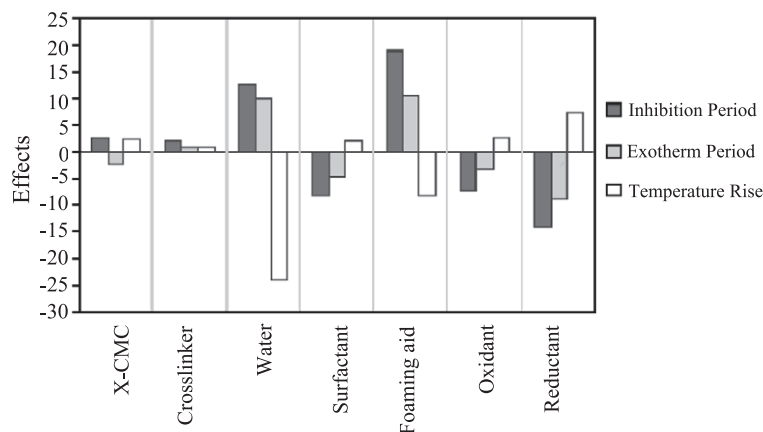


Fig. 7. Effect of the formulation variables on the SPH synthesis.

(SPH composites) are characterized by fast swelling, medium swelling ratio and improved mechanical properties. The third-generation SPH hybrids (SPHHs) possess elastic properties that can be highly useful in the development of gastrointestinal devices, as well as in other pharmaceutical and biomedical applications.

7. The first-generation SPHs: Conventional SPHs

The most commonly used monomers for synthesis of the first generation of SPHs are highly hydrophilic acrylamide, salts of acrylic acid and sulfopropyl acrylate. The dried SPHs are hard and brittle, but the hydrophilic nature of the polymer results in moisture-induced plasticization of the rigid structures into soft and flexible structures. The dried SPHs swell fast to a large size, larger than a few hundred times of their own volume in the dried state. Due to extremely small fraction of the polymer in the swollen state, the swollen SPHs are sometimes difficult to handle without breaking. When the SPHs are dried, the porous structure become collapsed or shrunken due to the surface tension of water pulling the polymer chains together during the drying process. To avoid this problem, water inside SPHs is replaced with alcohol (e.g., ethanol). The low surface tension of alcohol prevents the porous structure from collapsing during drying.

The CSPHs are fragile against bending or tensile stresses. Their structures are easily broken apart even under very low pressures. The lack of desirable mechanical properties of the conventional SPHs triggered the development of the second-generation SPH composites.

8. The second-generation SPHs: SPH composites

A composite is a matrix of a continuous phase having a dispersed phase incorporated within. Composite structures are generally made to attain certain properties, which cannot otherwise be achieved by each matrix alone. For making SPH composites, a matrix-swelling additive or a composite agent is utilized. A composite agent used in SPH composites is a cross-linked water-absorbent hydrophilic polymer that can absorb the solution of monomer, cross-linker, initiator and remaining components of the SPH synthesis. Upon polymerization, the composite agent serves as the local point of physical cross-linking (or entanglement) of the formed polymer chains. During the polymerization process, each composite agent particle acts as an isolated individual reactor in which cross-linking polymerization occurs. As the cross-linking polymerization proceeds throughout the solution, individual swollen composite agent particles are connected together through polymer chains connecting them. The presence of composite agent in SPH composites

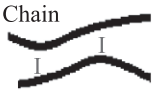

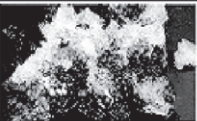

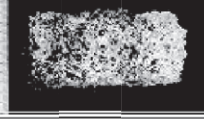


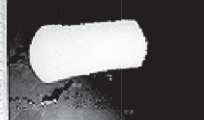

| | Structure | Swelling Property | Mechanical Property |
|-------------------|--|---|--|
| First Generation | Polymer Chain  |  |  |
| Second Generation | Composite Agent  |  |  |
| Third Generation | Hybrid Agent  |  |  |

Fig. 8. Structural, swelling and mechanical properties of various SPH generations.

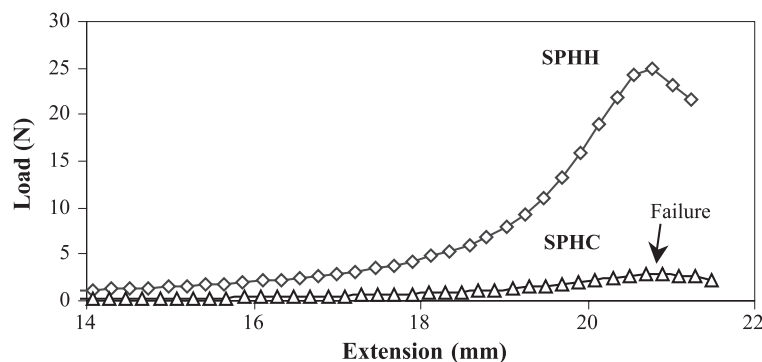


Fig. 9. Quantitative mechanical properties of SPH hybrid (SPHH) and SPH composite (SPHC). Data were obtained by Chatillon TCD-200 digital mechanical tester.

results in improved mechanical properties over conventional (i.e., the first generation) SPH, but the SPH composites are still brittle and thus break into pieces upon application of stresses. This modification over conventional SPHs resembles modification of superabsorbent polymers through surface cross-linking. Overall, this type of modification results in a higher modulus polymer network in the swollen state, which is susceptible to failure under the brittle fracture mechanism. For many years, this second generation of SPHs have been an attractive research tool for peroral and intestinal drug delivery applications [14–16].

9. The third-generation SPHs: SPH hybrids

To synthesize SPHs with very high mechanical or elastic properties, the third generation of SPHs was developed based on SPH hybrids. Unlike SPH composites wherein a pre-cross-linked matrix-swelling additive is added, SPH hybrids are prepared by adding a hybrid agent that can be cross-linked after SPH is formed. The hybrid agent is a water-soluble or water-dispersible polymer that can form cross-linked structure (in a manner similar to forming interpenetrating network) through chemical or physical cross-linking. Examples of hybrid agents are polysaccharides including sodium alginate, pectin, chitosan or synthetic water-soluble hydrophilic polymers such as poly(vinyl alcohol). Once the second network is formed, the whole system becomes similar to interpenetrating polymer net-

works. An example of SPH hybrids is the synthesis of acrylamide-based SPH in the presence of sodium alginate, followed by the cross-linking of alginate chains by calcium ions. One of the unique properties of SPH hybrids is that the gels are highly elastic in the swollen state. As compared with conventional SPHs and SPH composites, SPH hybrids are not easily breakable when stretched. The elastic and rubbery properties make SPH hybrids a choice for various applications where resilient gels are preferred. The resiliency of the fully water-swollen SPHs has never previously been observed. Elastic water-swollen SPH hybrids can resist various types of stresses, including tension, compression, bending and twisting. General structural, swelling and mechanical properties of different generations of SPHs are shown in Fig. 8.

As in Fig. 9, an SPH hybrid (SPHH) of alginate polyacrylamide could withstand compression forces of up to 25 N, while its SPH composite (SPHC) counterpart (cross-linked carboxymethylcellulose-polyacrylamide) failed under 2 N force. The mechanical property of the first-generation polyacrylamide SPH was not sufficient under testing conditions to be evaluated by the mechanical tester.

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