Polym. Bull. (2011) 66:447–462
DOI 10.1007/s00289-010-0285-y

ORIGINAL PAPER

Synthesis and properties of silk sericin-*g*-poly(acrylic acid-co-acrylamide) superabsorbent hydrogel

Xiaobin Hu

Received: 13 February 2010 / Revised: 14 April 2010 / Accepted: 29 April 2010 /

Abstract A novel superabsorbent hydrogel has been synthesized with the crosslinking graft copolymerization of acrylic acid (AA) and acrylamide onto the chain of silk sericin. Potassium persulfate (KPS)–sodium sulfite ($NaHSO_3$) as redox initiation system and *N*,*N*′-methylenebisacrylamide (MBA) as crosslinker were used. The structure of the product characterized by Fourier transform infrared absorption spectroscopy and the surface morphology of the hydrogel were observed by scanning electron microscopy. The certain parameters of the graft copolymerization including the monomer, the initiator, the crosslinker concentration, neutralization degree of AA, reaction temperature, and time were systematically optimized to achieve a hydrogel with maximum swelling capacity (2150 g/g). The optimal conditions were initiator 8 mmol/L, MBA 2.5 mmol/L, neutralization degree of AA 75%, reaction temperature 55 °C, and time 6 h. The swelling ratio in salt solutions was also determined (in 0.9% NaCl aqueous solution: 98 g/g). In addition, the swelling capability of the hydrogel was measured in solutions with pH ranged from 1 to 13. The synthesized hydrogel exhibited a pH-dependent character. Water absorbency of the product in aqueous chloride salt solutions has the $Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+}$ order in the investigated concentration.

Keywords Acrylic acid · Acrylamide · Silk sericin · Grafting copolymer · Superabsorbent resin

---

X. Hu (✉)
Department of Chemistry, Huzhou Teachers College, 1# Xueshi Road, Huzhou 313000,
Zhejiang, People's Republic of China
e-mail: xiaobinhu001@163.com

Introduction

Superabsorbent polymers (SAPs) are slight crosslinked hydrophilic polymers that can absorb, swell, and retain thousand times of water of their weights [1]. Therefore, superabsorbents have great advantages over traditional water-absorbing materials. Because of their excellent characteristics, superabsorbents are widely used in many fields such as agriculture, horticulture, and hygienic products [2–4]. Although hydrogels made from synthetic polymers, such as polyacrylate, possess excellent water-absorbing properties, their toxicity and non-biodegradability might pose long-time environmental problems and limit their use in drug-delivery systems and consumer products [5–7]. The biodegradable polymers generally constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms. Since last decades, many attempts have been focused on grafting or blending of plastic materials with cheap and biodegradable natural biopolymers, such as agar [8], chitosan [9], cellulose [10], dextrin [11], protein [12–14], and starch [15] to produce hydrogels with a specific response to a biological environment. In order to synthesis of natural-based SAPs, an efficient approach is graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers. Free radical graft copolymerization with various monomers can carried out with different initiator systems [14–16].

Silk sericin (SS) enveloped the fibroin is a second type of silk protein, which contains 18 amino acids including essential amino acids and is characterized by the presence of 32% of serine. The total amount of hydroxy amino acids in sericin is 45.8%. There are 42.3% of polar amino acid and 12.2% of non-polar amino acid residues [17]. SS contributes about 20–30% of total cocoon weight. SS due to its proteinous nature is susceptible to the action of proteolytic enzymes present in body and hence it is digestible. This property makes it a biocompatible and biodegradable material [18]. Most of SS dissolved in wastewater from silk filature factory was discharged to environment and resulted in pollution [19]. Studies have been reported in the case of SS-based hydrogels [20–22].

In this article, a SS-*g*-poly(AA-co-AM) superabsorbent material has been synthesized in presence of a crosslinking agent in a homogeneous system. The effects of reaction variables affecting the water absorbency of the hydrogel and swelling behavior in various salt and pH solutions was investigated.

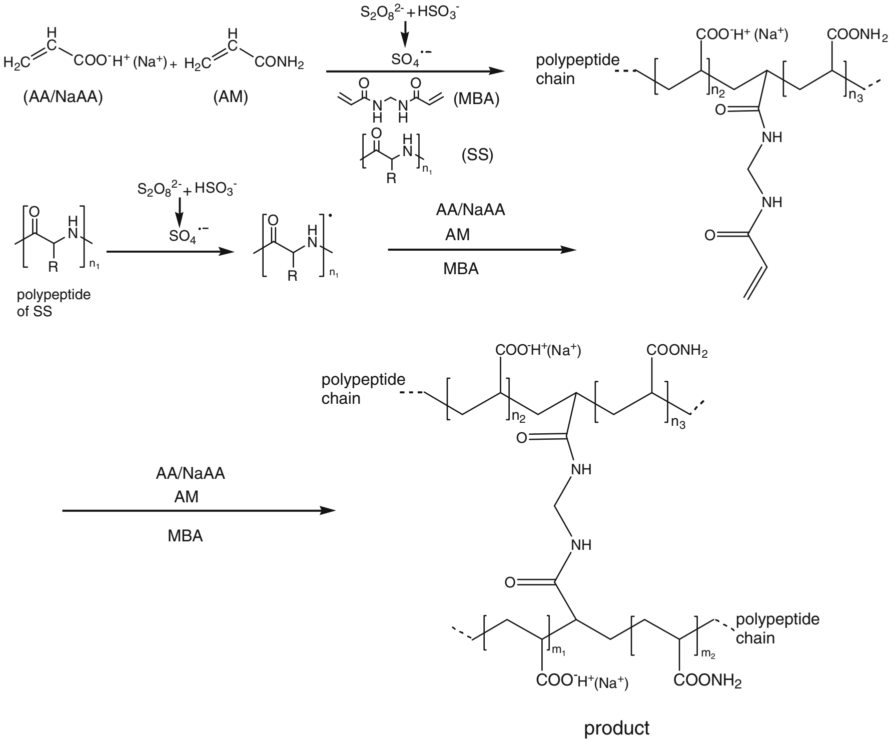
Materials and methods

Chemicals and reagents

Acrylic acid (AA), acrylamide (AM), and the crosslinker *N*,*N*′-methylenebisacrylamide (MBA) were purchased from Shanghai RichJoint Chemical Reagent Corporation Limited. AA was distilled before use. Potassium persulfate (KPS), sodium bisulfite ($NaHSO_3$), and sodium hydroxide (NaOH) (all from Nanjing Chemical Reagent Factory and analytical grade) were employed as-received. SS powder was purchased from Huzhou Xintiansibio-tech Corporation Limited and used as-received.

Synthesis of superabsorbent hydrogel

Hydrogel in this study was prepared as shown in Scheme 1. As an example, the procedure for synthesizing superabsorbent hydrogel in water is described in detail. A certain amount of AA (2.04 g, 28.3 mmol; titrated by 10% NaOH to 75% neutralization percentage), acrylamide (1.42 g, 19.8 mmol), SS (0.35 g), and crosslinker (MBA) solution (0.0026 g in 5 mL H_2O) were poured into a 100-mL beaker, which was equipped with a magnetic stirrer and placed in a digital display stable temperature water bath. The mixture was stirred until homogeneous solution was obtained. Before polymerization reaction, the solution was bubbled with pure nitrogen for 15 min to remove the dissolved oxygen; the KPS (0.043 g) and the $NaHSO_3$ (0.017 g) were added to the mixture to start the polymeric reaction. The mixture was bubbled with pure nitrogen for another 5 min and then airproofed. The temperature of mixture was increased rapidly and controlled to a setting value (55 °C) within a few minutes. After the reaction of a certain time (6 h), the product was cut into small pieces and then put into 100 mL dried ethanol for 2 h for removal of most of the water. Then the ethanol was decanted and another 100 mL fresh ethanol was added. The particles were allowed to stand for 4 h in ethanol to be



Scheme 1 Proposed pathway for the synthesis of SS-*g*-poly(AA-co-AM)

dewatered. After that, the product was dried in a vacuum oven at 50 °C for 10 h and then the small particles were grinded into powder by using an agate mortar. The powdered superabsorbent hydrogel was stored in desiccator.

Morphology of the hydrogel

The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of palladium gold alloy and imaged in an SEM instrument (HITACHI S-3400 N, 30 kV).

Fourier transform infrared spectroscopy analysis

Infrared spectroscopy (IR) spectra of SS, poly(AA-co-AM), and the product SS-*g*-poly AA-co-AM superabsorbent hydrogel were recorded on a Nexus 870 Fourier transform infrared spectroscopy (FTIR) spectrophotometer (KBr disk). Infrared spectra were carried out in the region of 4000–400 cm^{-1}.

Swelling measurements

A weighted quantity of dry sample (50 mg) was introduced into a 500-mL beaker. The 400 mL distilled water or saline solution was added to the beaker. The fully swollen hydrogel was separated from the unabsorbed water until absorption equilibrium was reached and excess water was drained by using filter paper for 15 min. Then, the hydrogel was weighted. Relative water absorbency was calculated by

$$q = (m_2 - m_1)/m_1 \tag{1}$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. The q value was calculated as grams of water per gram of sample.

Swelling in salt solutions

Absorbency of the hydrogel was evaluated in 0.15 M solutions of NaCl, KCl, $MgCl_2$, and $CaCl_2$ according to the above-described method for swelling measurement in distilled water. In addition, swelling capacity of the hydrogel was measured in different concentrations of NaCl, $CaCl_2$, and $AlCl_3$ salt solutions.

Swelling kinetics

For studying the rate of absorption of the hydrogel, a certain amount of sample (50 mg) with average particle sizes between 40 and 60 mesh was poured into a weighed tea bag and immersed in 400 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the above-mentioned method.

Results and discussion

The mechanism for graft copolymerization is shown in Scheme 1. At first, the redox reaction of KPS and sodium bisulfite produced sulfate anion-radicals. Then the anion-radicals attacked the double bond of monomers (AA and AM) to form corresponding radicals. With the increase in chain initiated by free radicals, the micro radicals formed from the monomers (AA and AM) attack the SS to produce SS-*g*-poly(AA-co-AM) chain. On the other hand, sulfate anion-radicals abstract hydrogen from one of the functional groups (i.e., –COOH, –SH, –OH, and –NH_2) in side the chains of the SS to form corresponding radicals. These radicals initiate partially neutralized AA and AM grafting onto polypeptide chain of SS led to a graft copolymer. In addition, crosslinking reaction was occurred in the presence of a crosslinker (MBA), so that a three-dimensional network was obtained.

Surface morphology of the hydrogel

The surface structure of the hydrogel was observed using SEM (Fig. 1b) and the micrograph of the optimized hydrogel sample compared with that of SS (Fig. 1a). While the SEM photograph of SS does not show any porous structure, the structure of the SS-*g*-poly(AA-co-AM) was highly porous. To our knowledge, water absorbency capacity of superabsorbent is related to the porous structure and level of crosslinking. This kind of porosity in the structure of an SS-*g*-poly(AA-co-AM) can give higher water absorbency.

FTIR analysis

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 2 shows the FTIR spectra of the SS, poly(AA-co-AM), and SS-*g*-poly(AA-co-AM). The band observed at 1656, 1662, and 1662 cm^{-1} in Fig. 2a–c, respectively, can be attributed to C=O stretching in carboxamide (–$CONH_2$) and carboxylate (–COO^-) functional groups of substrate backbone and hydrogel. On the other hand, the characteristic absorption bands at about 1660 and 1400 cm^{-1} can be attributed to the overlapping of carboxamide I and III band with symmetric and asymmetric stretching modes of carboxylate anions. The broad band at 3200–3600 cm^{-1} is due to stretching of O–H and N–H groups. Absorption bands at 2941 cm^{-1} in Fig. 2a, 2944 cm^{-1} in Fig. 2b, and at 2941 cm^{-1} in Fig. 2c correspond to the –C–H stretching vibration. The peaks observed at 1538, 1565, and 1564 cm^{-1} in Fig. 2a–c, respectively, can be attributed to the N–H bending vibration (carboxamide II band).

Although the stretching band of C=O stretching in carboxamide (–$CONH_2$) and carboxylate (–COO^-) functional groups overlapped with the C=O stretching band of the SS portion of the copolymer, the shape of the signal of C=O groups around

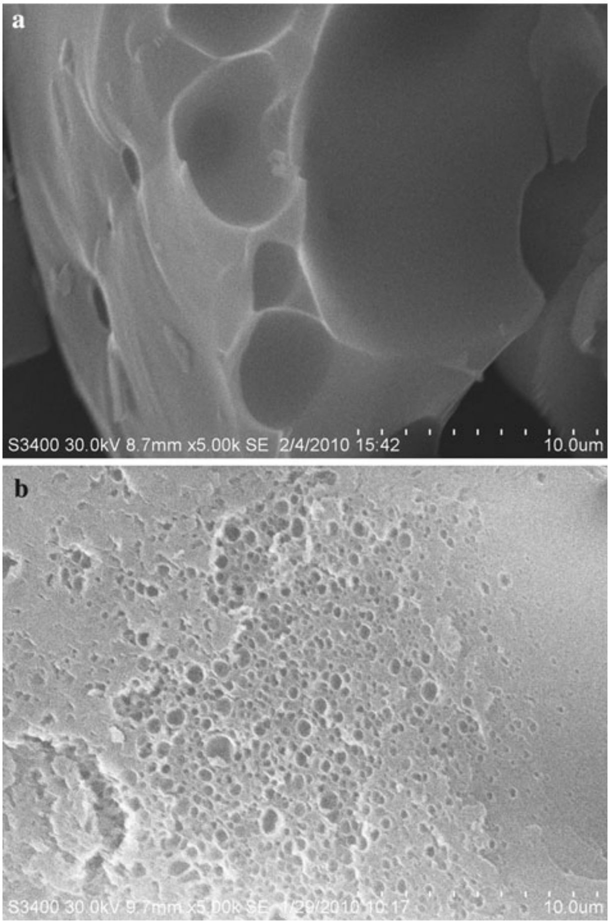


Fig. 1 **a** SEM photograph of SS. **b** SEM photograph of optimized superabsorbent hydrogel

1662 cm^{-1} (in Fig. 2a) and N–H bending vibration (carboxamide II band) around 1564 cm^{-1} and their change to a very obvious signal (in Fig. 2a) can be explained by the presence of SS-*g*-poly(AA-co-AM) polymer network.

Effect of initiator concentration

The swelling capacity as a function of initiator concentration (0.0025–0.020 mol/L) was investigated in this series of experiments (Fig. 3). Too low concentration of the initiator results in low polymerization efficiency and incomplete polymerization. A part of monomers probably cannot take part in the polymerization reaction. The strength and the crosslinking density are not sufficient, so the swelling capacity is not high. With the increasing of initiator amount, the swelling rate of hydrogel is increased. The optimized initiator amount with the highest water absorbency (2150 g/g) is at about 8 mmol/L. The reduction of swelling after using higher

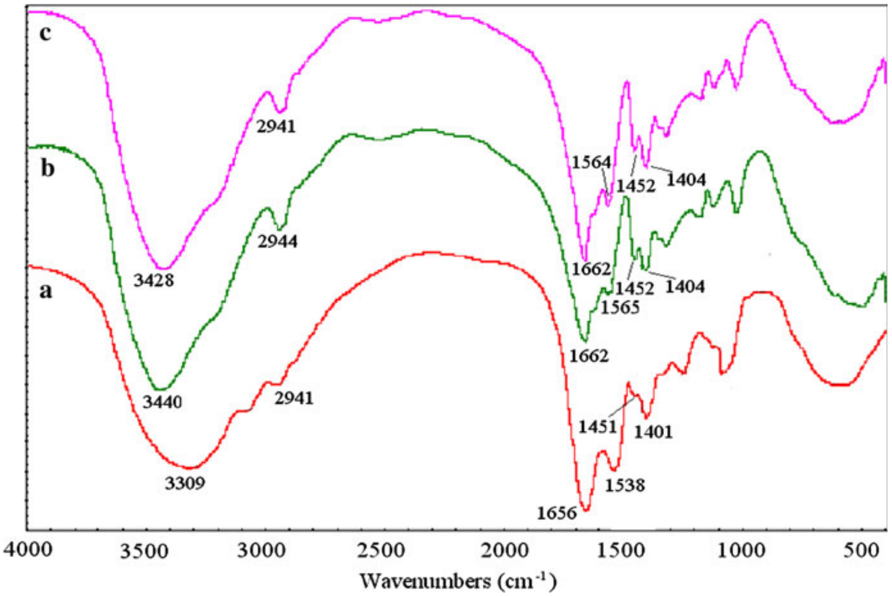


Fig. 2 FTIR spectra of (*a*) SS, (*b*) poly(AA-co-AM), (*c*) SS-*g*-poly(AA-co-AM)

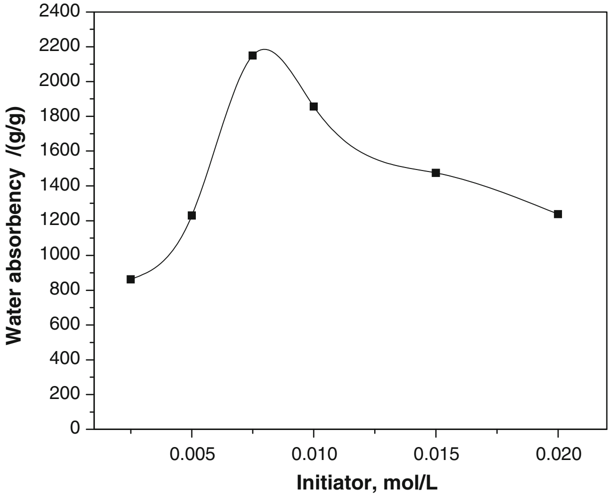


Fig. 3 Effect of initiator concentration on swelling capacity of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, AA 1.6 mol/L, AM 1.1 mol/L, MBA 2.5 mmol/L, 55 °C, 6 h

concentration of initiator may be attributed to too much free radicals and an increase in chain termination reactions via bimolecular collision resulting in too much short chain polymer and consequently undeveloped network in the polymer. In addition, the free radical degradation of SS backbones by sulfate radical-anions is an additional reason for swelling-loss at higher initiator concentration [23, 24].

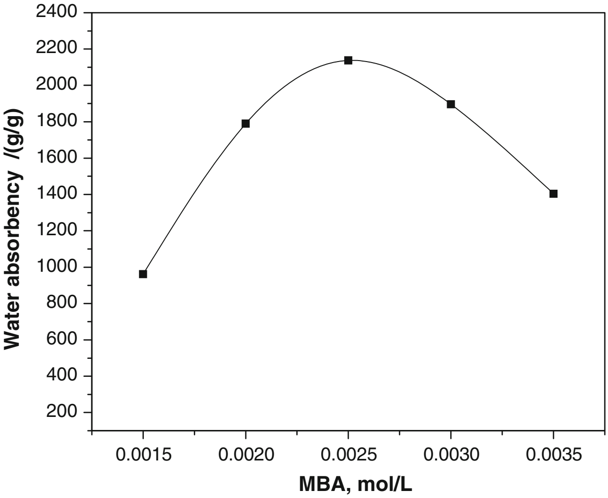


Fig. 4 Effect of crosslinker concentration on swelling capacity of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, AA 1.6 mol/L, AM 1.1 mol/L, initiator 8 mmol/L, 55 °C, 6 h

Effect of crosslinker concentration

Figure 4 demonstrates the effect of MBA concentration on water absorbency of the synthesized hydrogels. Different amounts of MBA (0.0015–0.0035 mol/L) were used and the maximum of swelling was achieved at 0.0025 mol/L of MBA. At a lower level of MBA, a slimy gel is formed and the less crosslinking resulted in an insufficient three-dimensional network in the polymer. The water cannot hold effectively in the loose network by hydrogen bond. It is well known that a higher crosslinker concentration increases the extent of crosslinking of the polymeric chains. The polymer particles cannot expand adequately as water moves into the network and the free space of the network unit in the polymer significantly decreased due to the too tight crosslinking. Consequently, the swelling capacity is decreased after reaching a maximum. Similar behaviors have been reported by other researchers [25].

Effect of monomer concentration

The effect of monomer concentration on the water absorbency of the hydrogel was investigated by varying the AA and acrylamide concentration from 15 to 40% of the total weight of the reaction system, while the amount of SS was kept constant (0.35 g) and the mass ratio of AA to acrylamide kept unchanged (1:0.7). As shown in Fig. 5, with increasing monomer concentration up to 20% (the ratio of SS/monomers is 1/10, w/w), the water absorbent capacity increases and then decreases slowly with further increase in monomer amount. The maximum absorbency is obtained at 1.6 mol/L of AA and 1.1 mol/L of AM. The initial increase in water absorbency can be attributed to a higher monomers content improve the density of

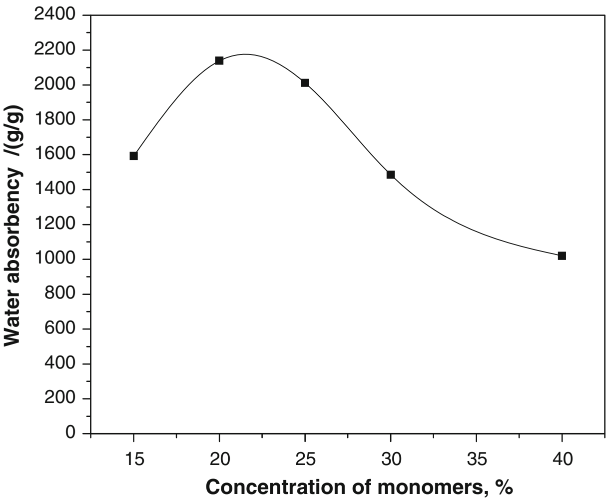


Fig. 5 Effect of the monomer concentration on water absorbency of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, initiator 8 mmol/L, MBA 2.5 mmol/L 55 °C, 6 h

hydrophilic groups (–COO^-, –COOH, –$CONH_2$) in the hydrogel, which cause a stronger absorption of water. The subsequent decrease after maximum absorbency may be attributed to high density of monomers resulting in a rapid polymerization and too high crosslinking degree in product; at the same time, an increase in viscosity of the reaction medium hinders the movement of the macroradicals and monomer molecules and causes more homopolymerization than graft copolymerization. Similar conclusions were reported by other researchers [26].

Effect of neutralization percentage of AA

Figure 6 demonstrates the effect of neutralization degree of AA on water absorbency of the synthesized hydrogel. Different neutralization percentages of AA (from 60 to 85%) were used and the maximum of swelling was achieved at 75% of neutralization degree. Without the neutralization stage, the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and consequently the water absorbency is decreased (Fig. 6). With the increase in the neutralization percentage, the screen effect of Na^+ shielding the charge of the carboxylate anions increased and thus prevents effective repulsion between carboxylate anions. So, the swelling rate of the synthesized hydrogel decreased at high neutralization percentage of the carboxylic acid groups [27].

Influence of reaction temperature

Figure 7 demonstrates the effect of the reaction temperature on swelling of SS-*g*-poly(AA-co-AM) hydrogels. It has been observed that the water absorbency of the hydrogels increased initially when increasing the reaction temperature up to 55 °C,

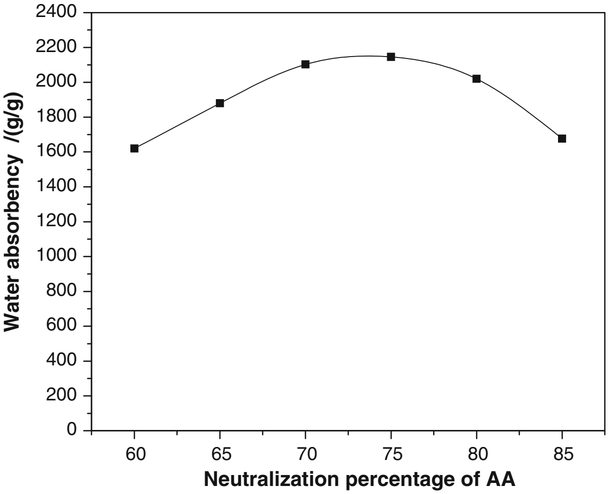


Fig. 6 Effect of the neutralization degree of AA on water absorbency of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, AA 1.6 mol/L, AM 1.1 mol/L initiator 8 mmol/L, MBA 2.5 mmol/L, 55 °C, 6 h

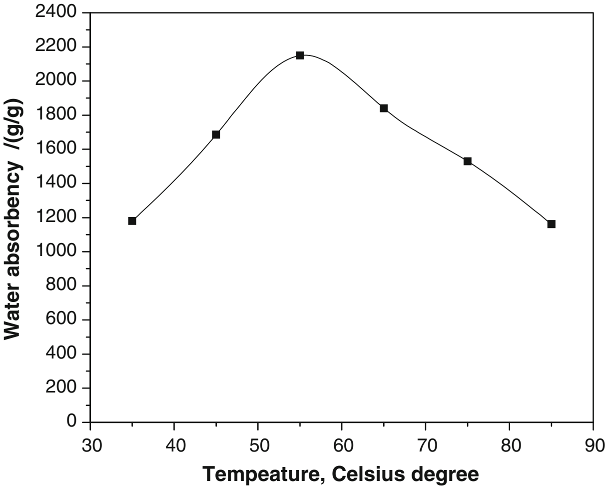


Fig. 7 Effect of the reaction temperature on water absorbency of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, AA 1.6 mol/L, AM 1.1 mol/L, initiator 8 mmol/L, MBA 2.5 mmol/L, 6 h

but decreased later as shown in Fig. 7. The swelling capacity for hydrogel is 1161 g/g at 85 °C. When temperature is too low, the polymerization reaction rate is correspondingly slow, the reaction time must be prolonging, but the high temperature accelerates the dissociation of KPS. So, beyond the optimum temperature, an increase in the temperature favors the increasing of radical centers, causing high crosslinking degree in the hydrogel. So, the swelling capacity of the hydrogel is decreased.

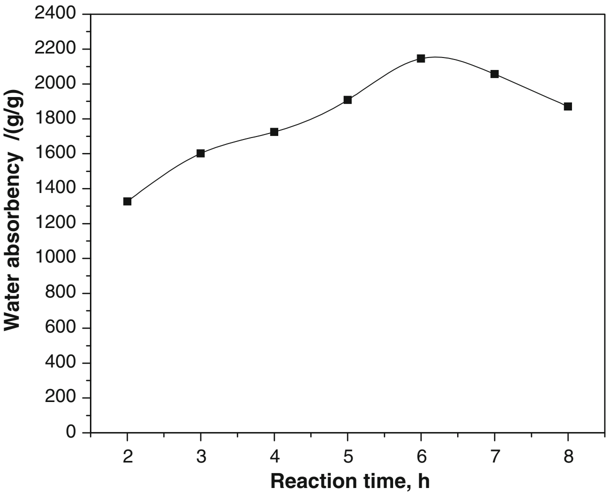


Fig. 8 Effect of the reaction time on water absorbency of the SS-*g*-poly(AA-co-AM). Reaction conditions: SS 0.35 g, AA 1.6 mol/L, AM 1.1 mol/L, initiator 8 mmol/L, MBA 2.5 mmol/L, 55 °C

Influence of reaction time

The reaction time is another factor affecting the structure and water absorbency of hydrogel. From Fig. 8, it is obvious that the water absorbency of the hydrogel increases and then decreases with the reaction time prolonging. Usually, higher reaction temperature resulting in shorter reaction time is accorded with the general rule of polymerization reaction. Because the reaction is free radical polymerization, at the beginning of the reaction the main reaction is chain propagation. So, crosslinking degree increases with the time. But beyond the optimum time, an increase in the time causes a too high crosslinking degree in the hydrogel and thus a decreased swelling capacity.

Swelling kinetics

A Voigt-based equation (2) [28] is applied to describe the swelling behavior of SAP in water.

$$S_t = S_e(1 - e^{-t/\tau}) \tag{2}$$

where S_t (g/g) is the swelling at time t, S_e is equilibrium swelling (power parameter, g/g), t is the time (min) for swelling S_t, and τ (min) is the “rate parameter.” For calculating the “rate parameter,” by using the above formula (after a natural logarithm transfer), one can plot Ln $(1 - S_t/S_e)$ versus time (t). The slope of the fitted straight line (slope $= -1/\tau$) gives the rate parameter. Figure 9 displayed the swelling capacity of the hydrogel in distilled water at consecutive time intervals. At the beginning, the rate of water absorbency sharply increases and then began to level off. The equilibrium swelling was established after 30 min approximately. A

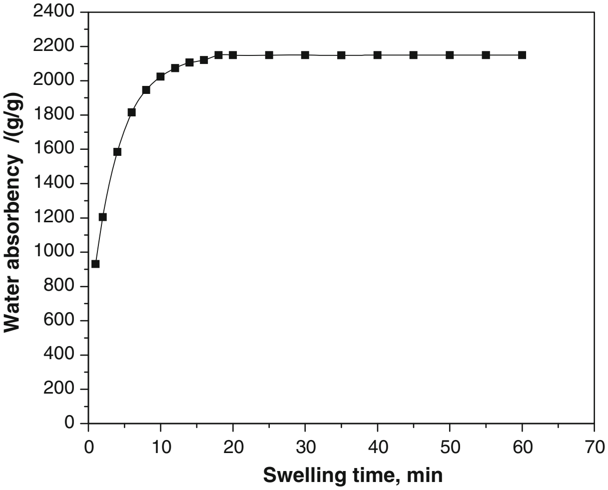


Fig. 9 Swelling kinetics of the SS-*g*-poly(AA-co-AM) powder (40–60 mesh)

power–law behavior is obvious from Fig. 9. The data may be well fitted with the Eq. 2. According to Fig. 9 and using Eq. 2, the "rate parameter" for swelling of the hydrogel (40–60 mesh) in water is 3.9 min. Since the τ value is a measure of swelling rate (i.e., the lower the τ value, the higher the rate of swelling), it can be used for comparative evaluation of the rate of water absorption of hydrogels on the condition that the particle size of the comparing samples are the same or, at least, in the same range.

Effect of salt solution on the swelling

In general, there are two main aspects that affect the swelling ratio of SAP. One is the characteristic of the SAP (i.e., the elasticity of the network, the constitution of the monomers, the presence of hydrophilic functional groups, the crosslinking degree); another is the characteristic of the external solution (i.e., the charge number, ionic strength, ionic radius). The swelling capacity of ionic hydrogels in salt solutions is significantly decreased compared to the values in distilled water. The osmotic pressure theory is developed to explain the well-known phenomenon. The ions attached to the polymer network are immobile and considered to be separated from the external solution by a semi-permeable membrane. When the hydrogel is placed in pure water, the osmotic pressure is much higher than that of the hydrogel in salt solution (i.e., NaCl). Equation 3 is applied to describe the relationship between swelling and concentration of salt solution [29]:

$$\text{Swelling} = k[\text{salt}]^{-n} \tag{3}$$

where k and n are constants for an individual superabsorbent. The k-value gives the swelling at a high concentration of salt and the n value is a measure of salt sensitivity. In this series of experiments, the swelling capacity was measured in various salt solutions (Figs. 10 and 11). According to Figs. 10 and 11, the

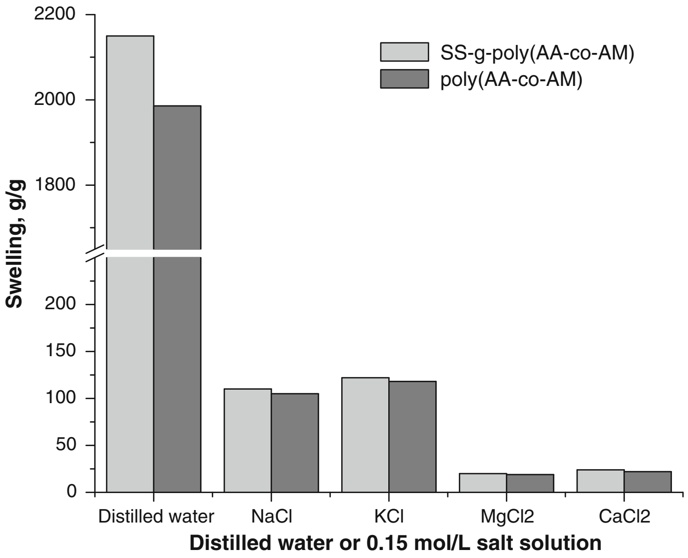


Fig. 10 Swelling capacity of the SS-*g*-poly(AA-co-AM) and poly(AA-co-AM) in distilled water and different chloride salt solutions (0.15 M)

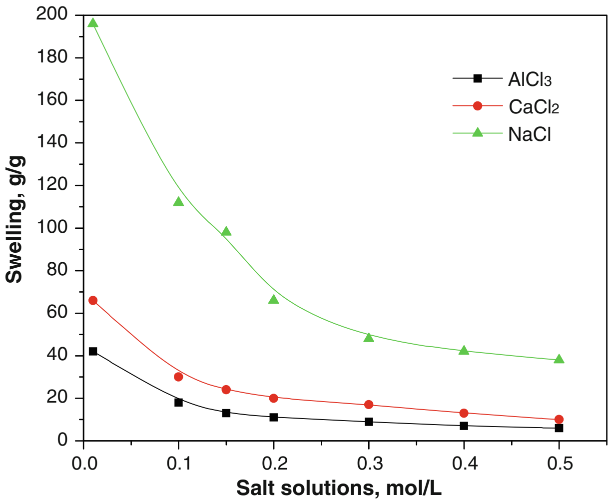


Fig. 11 Swelling capacity variation of the SS-*g*-poly(AA-co-AM) in saline solutions with various concentrations

decrement in swelling amounts is strongly dependent on the type and concentration of salt added to the swelling medium. For example, the water absorbency of a hydrogel is very susceptible to the presence of NaCl in the solution (Fig. 10). In Fig. 11, it is shown that, at the same concentrations of salt solutions, the absorbency decreased with an increase valence charge of the metal cations from Na^+ to Ca^{2+}

and Al^{3+}. A charge screening effect and “ionic crosslinking” are the main explanations for the intense loss of swelling [30]. With increasing cation charge, the ionic strength of the medium and the ionic crosslinking at the surface of the particles are increased and the swelling capacity consequently decreases.

In these experiments, the poly(AA-co-AM) was also synthesized in almost the same conditions as SS-*g*-poly(AA-co-AM) except for the addition of SS. The swelling capability of the synthesized poly(AA-co-AM) hydrogel was measured and compared with that of the SS-*g*-poly(AA-co-AM) in distilled water and 0.15 M different salt solutions. It is shown in Fig. 10 that the absorbency of SS-*g*-poly(AA-co-AM) was higher than that of poly(AA-co-AM). Small part of SS addition slightly improved the water absorbency of the hydrogel synthesized in the given conditions. That maybe owing to the strong hydrophilicity of SS resulted from the hydrophilic functional groups like hydroxyl (–OH), carboxamide (–$CONH_2$), and carboxylate (–COO^-) radicals in it.

Swelling variation with pH

Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, the equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranging from 1.0 to 13.0 (Fig. 12). Since the swelling capacity of all “anionic” hydrogels is appreciably decreased by the addition of counter-ions (cations) to the swelling medium, no buffer solutions were used. Therefore, aqueous stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach the desired basic and acidic pHs, respectively. Maximum swelling was obtained at pH 7. Under acidic pHs, most of the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and consequently swelling amounts are decreased. Furthermore, some additional attractive interactions, like H–O hydrogen bonding, lead to more

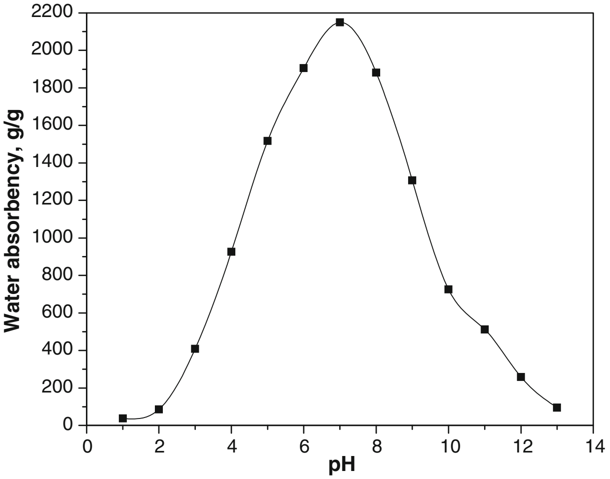


Fig. 12 Effect of pH of solutions on water absorbency of the SS-*g*-poly(AA-co-AM)

decreased absorbencies. At higher pHs, some of the carboxylate groups are ionized and the electrostatic repulsion between –COO$^-$ groups causes an enhancement of the swelling capacity. The reason of the swelling loss for the highly basic solutions (pH $>$ 8) is a “charge screening effect” of excess Na$^+$ in the swelling media, which shields the carboxylate anions and prevents effective anion–anion repulsion. Similar swelling pH dependencies have been reported for other hydrogel systems [30–33].

Conclusion

A novel superabsorbent hydrogel by both crosslinking and graft copolymerization of AA and AM monomer onto SS in a homogeneous aqueous solution was synthesized. The surface morphology of the hydrogel was observed by SEM. The swelling characteristics of the superabsorbent hydrogel are described. Different parameters including initiator, crosslinker, monomers, and neutralization degree were studied and the hydrogel with highest water absorbency was obtained. The optimum reaction conditions to obtain maximum water absorbency (2150 g/g) were found to be: AA 1.6 mol/L, AM 1.1 mol/L, initiator 8 mmol/L, MBA 2.5 mmol/L, neutralization degree of AA 75%, reaction temperature 55 °C, and time 6 h. Swelling measurement of the synthesized hydrogel in different salt solutions and pH were also studied and a normal behavior was observed. In addition, because of the use of SS, it is expected that the resulted SAP shows more compatibility with environment.

References

1. Zou XX (2002) Superabsorbent materials. Chemical Industry Press, Beijing
2. Chen L, Xie ZG, Zhuang XL, et al (2008) 72:342
3. Chu M, Zhu SQ, Huang ZB et al (2008) J Appl Polym Sci 107:3727
4. Abd El-Rehim HA (2005) Radiat Phys chem 74:111
5. Hoffman AS (1996) In: Salamone JC (ed) Polymeric materials encyclopedia, vol 5. CRC Press, Boca Raton, FL, p 3282
6. Haselbach J, Berner T, Wright H et al (2000) Regul Toxicol Pharm 32:332
7. Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology. Wiely-Vch, New York
8. Pourjavadi A, Farhadpour B, Seidi F (2009) J Polym Res 16:655
9. Wang Q, Zhang JP, Wang AQ (2009) Carbohydr Polym 78:731
10. Pourjavadi A, Ghasemzadeh H, Mojahedi F (2009) J Appl Polym Sci 113:3442
11. Ding X, Li L, Liu PS et al (2009) Polym Compos 30:976
12. Marandi GB, Hosseinzadeh H (2007) Polym Compos 15:395
13. Tang QW, Wu JH, Lin JM et al (2009) J Mater Res 24:1653
14. Zohuriaan-Mehr MJ, Pourjavadi A, Salimi H et al (2009) Polym Adv Technol 20:655
15. Shogren RL, Willett JL, Biswas A (2009) Carbohydr Polym 75:189
16. Pourjavadi A, Kurdtabar M, Mahdavinia GR et al (2006) Polym Bull 57:813
17. Padamwar MN, Pawar AP (2004) J Sci Ind Res 63:323
18. Komatsu K (1996) In: Salamone JC (ed) Polymetric materials encyclopedia, vol 10. CRC Press, New York
19. Fabiani C, Pizzichini M, Spadoni M et al (1996) Desalination 105:1

20. Ahn JS, Choi HK, Lee KH et al (2001) J Appl Polym Sci 80:274
21. Wu W, Wang DS, Wang LQ (2009) Chem J Chin Univ 30:830
22. Wu W, Li WJ, Wang LQ et al (2006) Polym Int 55:513
23. Hsu SC, Don TM, Chiu WY (2002) Polym Degrad Stab 75:73
24. Sanli O, Pulat E (1993) J Appl Polym Sci 47:1
25. Kabiri K, Zohuriaan-Mehr MJ (2003) Polym Adv Technol 14:438
26. Pourjavadi A, Soleyman R, Barajee GR (2008) Starch/Starke 60:467
27. Sugahara Y, Takahisa O (2001) J Appl Polym Sci 82:1437
28. Omidian H, Hashemi SA, Sammes PG, Meldrum IG (1998) Polymer 39:6697
29. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, New York
30. Wu JH, Lin JM, Wei YL (2005) High water-absorption and water-retention materials. Chemical Industry Press, Beijing
31. Pourjavadi A, Sadeghi M, Hosseinzadeh H (2004) Polym Adv Technol 15:645
32. Mercade-Prieto R, Sahoo PK, Falconer RJ et al (2007) Food Hydrocolloid 21:1275
33. Pourjavadi A, Hosseinzadeh H, Sadeghi M (2007) J Compos Mater 41:2057