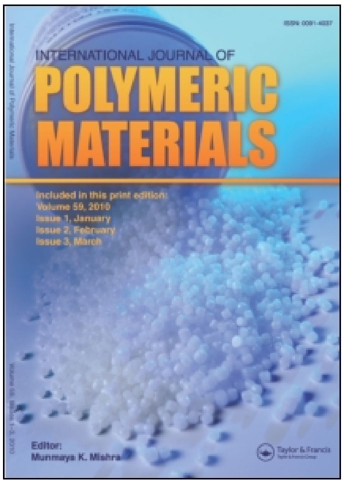

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Synthesis and Swelling Properties of Hydrolyzed Cottonseed Protein Composite Superabsorbent Hydrogel

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A novel protein-based superabsorbent hydrogel was synthesized by graft copolymerization of hydrolyzed cottonseed protein (HCP) and acrylic acid (AA) monomer. This hydrogel was synthesized by solution-based copolymerization, using N,N-methylene bisacrylamide as a crosslinking agent, potassium persulphate and sodium sulfite as the initiators. The effects of the certain variables of the graft copolymerization on the swelling capacity of the hydrogel were measured and its swelling properties in different solutions were investigated as well. This new approach is a promising method in utilizing hydrolyzed cottonseed protein in the production of a superabsorbent polymer with excellent water absorbency and potential use in various applications.

Keywords acrylic acid, hydrolyzed cottonseed protein, superabsorbent hydrogel, swelling

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INTRODUCTION

Superabsorbent polymers or hydrogels are crosslinked polymer networks with strong hydrophilic groups that can absorb and hold large amounts of water. Due to their excellent characteristics, superabsorbent polymers are widely used in various fields in items such as disposable diapers, feminine hygiene products, hospital products, soil for agriculture and horticulture, food packaging and biomedical products [1–4].

Although most of the commercially available superabsorbent polymers are full synthetic partially neutralized crosslinked poly(acrylic acid), there has been increasing interest in the synthesis and applications of natural-based superabsorbent polymers. One reason may be the advantage of natural-based superabsorbent polymers in environment-friendly, biocompatible and biodegradable aspects, which have great potential in medical and pharmaceutical fields. Another reason is the cost savings of replacing increasingly exhausted petroleum resources with natural materials.

These natural-based superabsorbent hydrogels can be divided into two main groups according to their original sources, namely, the copolymers based on polysaccharides and based on proteins [2]. Superabsorbent hydrogels from various polysaccharides such as cellulose [5,6], starch [7–9], pectin [10], carrageenan [11,12], and chitosan [13–15], have been reported by several researchers, but only a few studies have been reported on protein-based superabsorbent hydrogels [16–19].

One method to obtain protein-based superabsorbent hydrogel is crosslinking after introducing hydrophilic groups into a protein molecule by direct acylation. Hwang and Damodaran reported a method of modifying lysyl residues of soy protein isolate with ethylenediaminetetraacetic dianhydride (EDTAD) and then crosslinking with glutaraldehyde to get a biodegradable hydrogel [17,18]. Similar methods were employed by Rathna in fish protein [20,21]. And a catamenial absorbent system of hollow and flexible crosslinked microcapsules of soybean protein with a maximum absorption of 2000% was obtained by a modified crosslinking method with succinylchloride [19]. These methods can produce a biodegradable hydrogel, but the water absorbent capacity is not very high because the modified groups in the protein are limited and the acylation process is hard to perform well due to the low acylation efficiency.

Another method is graft polymerization of vinylic monomers onto protein backbones and crosslinking of the copolymer, and it is more efficient to modify protein by increasing the hydrophilicity than by the acylating method. Pourjavadi and coworkers reported a few protein-grafted poly-acrylate hydrogels using animal proteins like collagen, gelatin or their hydrolyzed forms [16,22,23], and the water absorbency of hydrolyzed collagen-based hydrogel reached 920 g/g [16]. These results encourage us to utilize this modification method in vegetable proteins like cottonseed protein. To the best of our knowledge, the preparation of a superabsorbent polymer from hydrolyzed cottonseed protein through grafting modification by vinyl monomers has not yet been reported.

Generally, vegetable protein is regarded as functional and nutritional ingredients in food or feed. But the application of cottonseed protein in these fields is limited because of the toxicity of gossypol, protein denaturation due to high temperature and chemical reaction between lysine and gossypol during oil extraction processing. In China, most of the cottonseed meal has to be used as fertilizer or substrates for edible mushrooms while only 5–10 percent is used as feed material, leading to the waste of this valuable protein resource.

In the present study, a HCP-PAA superabsorbent hydrogel was synthesized by grafting copolymerization of HCP and acrylate monomers and simultaneously crosslinking to form a HCP-PAA hydrogel. The reaction variables affecting the water absorbency of the hydrogel and the swelling properties of the synthesized hydrogel were investigated as well.

EXPERIMENTAL

Materials

Hydrolyzed cottonseed (HCP) was purchased from China Cotton-Unis Bioscience Co., Ltd., Beijing, China. Acrylic acid (AA), potassium persulfate (KPS) and sodium bisulfite (SBS) were of analytical grade from Tianjin Yongda Chemical Reagent Developing Center, Tianjin, China. N,N′-methylene bisacrylamide (NMBA) was of analytical grade from Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China. Sodium hydroxide was of analytical grade and purchased from Tianjin Baishi Chemical Industry Co., Ltd., Tianjin, China. All other reagents were of analytical grade and used without further purification. Distilled water was used for the hydrogel preparation and swelling measurements.

Synthesis of HCP-PAA Superabsorbent Polymer

The typical procedure for the HCP-PAA hydrogel synthesis process is as follows: NMBA (0.015 g in 5 mL H_2O) was added into partly neutralized (75 mol%) AA (10 g) by certain amounts of 7.5 N NaOH solution with stirring. Hydrolyzed cottonseed protein (1.0 g) was dissolved in 25 mL distilled water at pH 10 with 0.1 N NaOH solution and filtered to remove its insoluble substance. Then the initiator (0.25 g, $m_{KPS}:m_{SBS} = 2:1$) was added to the HCP solution at a desired temperature in a thermostat water bath. After stirring for 10 min, the two solutions were mixed and the mixture was kept in water bath for 2 h. The resulting hydrogel product was scissored and put into excess absolute ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted and the product hydrogel was kept in 100 mL fresh absolute ethanol for 24 h. Finally, the hydrogel was dried in oven under vacuum at 80°C to a constant weight. The hydrogel was prepared after the dried product was milled and screened.

Swelling Measurement (Tea Bag Method)

Water absorbency is expressed in grams of water retained in the swollen hydrogel by a gram of the dried hydrogel. A weighed hydrogel sample (0.1–0.5 g) in a nylon bag (200 mesh screen) was immersed entirely in 500 mL distilled water or other solutions to swell for 24 h, then the nylon bag was hung in the air for 15 min to remove the excess solution. The equilibrium water absorbency of hydrogel was calculated according to the following equation:

$$Q\ (g/g) = (m_2 - m_1)/m_1 \qquad (1)$$

where Q is water absorbency and m_2 and m_1 are weights of swollen and dry hydrogel sample, respectively.

Swelling Kinetics

The swelling kinetics of the hydrogel samples (0.5 ± 0.001 g) with various particle sizes were poured into weighed nylon bags (200 mesh screen) and immersed entirely in 200 mL distilled water. The water absorbency of the hydrogels was measured at different time intervals by the above-mentioned method.

FTIR Spectroscopy

The structure of the sample was characterized in KBr pellets using a FTIR spectrophotometer (Bruker EQUINOX55). The superabsorbent hydrogel powder (1–2 mg) was mixed with KBr powder (20–30 mg) and pressed into discs for inspection. Transmittances were recorded at wave numbers between 4000 cm^{-1} and 450 cm^{-1}.

RESULTS AND DISCUSSION

FTIR Spectra of the CP and the Copolymer

The synthesized copolymers were characterized by the functional groups using the FTIR technique. The IR spectra for PAA and the graft copolymer HCP-PAA are presented in Figure 1. The infrared spectrum of the copolymer shows peaks corresponding to the functional groups of the monomer units in

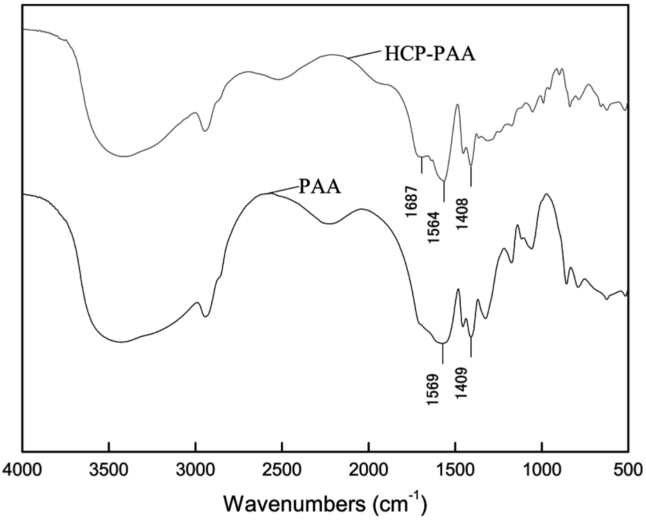

Figure 1: FTIR spectra of PAA polymer and HCP-PAA copolymer.

polymeric chains. The observed peaks at 1569 cm^{-1}/1409 cm^{-1} in PAA correspond to the $-C=O$ stretching of acrylate units and shift to 1564 cm^{-1}/ 1408 cm^{-1} in HCP-PAA after grafting copolymerization. The new absorption peaks at 1687 cm^{-1} in HCP-PAA are due to the $-C=O$ stretching of the amide bands, which are characteristic of the $-CONHR$ group in the polypeptide of HCP. A comparison of the IR spectra indicates the grafting copolymerization of AA monomer onto the HCP backbone.

Effect of Reaction Parameters on Water Absorbency

The water absorbency of the polymer shows a relation to the crosslinked density, ionic osmotic pressure and affinity of the hydrogel with water. The swelling ratio Q of a crosslinked polymer can be expressed by the following equation according to Flory's theory [24]:

$$Q^{5/3} = [(i/2V_uS^{1/2})^2 + (1/2 - X_1)/V_1]/(V_e/V_0) \qquad (2)$$

where Q, V_e/V_0, $(1/2 - X_1)/V_1$, V_u, i/V_u, and S are the water absorbency, the crosslinking density of polymer, the affinity between the polymer and external solution, the volume of structural unit, the fixed charge per unit volume of polymer, and the ionic strength of the external solution, respectively. The first term on the right-hand side of Eq. (2) represents the osmotic pressure and the second term represents the hydrophilic ability of the function groups. It is well-known that the water absorbency of a superabsorbent polymer depends on hydrophilic groups in the network, the crosslinking density, and ionic strength of the external solution. To improve the swelling capacity of the copolymer, the effects of the reaction parameters on water absorbency in distilled water and dilute NaCl solution, such as the amount of HCP, initiator, crosslinker, degree of neutralization and reaction temperature, were investigated.

Effect of HCP Content

The effect of HCP content in the copolymer on swelling is shown in Figure 2. As the weight ratio of HCP to AA increases, the water absorbency diminishes in distilled water. The swelling of the superabsorbent polymer is caused by the electrostatic repulsion of the ionic charges of its network, and the hydrophilic units contribute to the ionic charges in the swelling polymeric structure according to Flory's network theory [24]. Although there are many hydrophilic groups in the HCP molecule, those groups in CP are relatively less hydrophilic and the amount of those groups is fewer compared to that of $-COO^-$ group in poly-AA. Thus the water absorbing capacity decreases. But in NaCl solution, this decline trend is much milder because the functional groups in HCP, like amino- and hydroxyl- groups, are nonionic hydrophilic groups which can reduce the ionic strength inside the hydrogel network while swollen in an electronic solution, and improve the water absorbency in some degree.

Effect of Initiator Content on Absorbency

Figure 3 shows the effect of the initiator content on the water absorbency. The water absorbency increases as the initiator content increases from 1.2 to

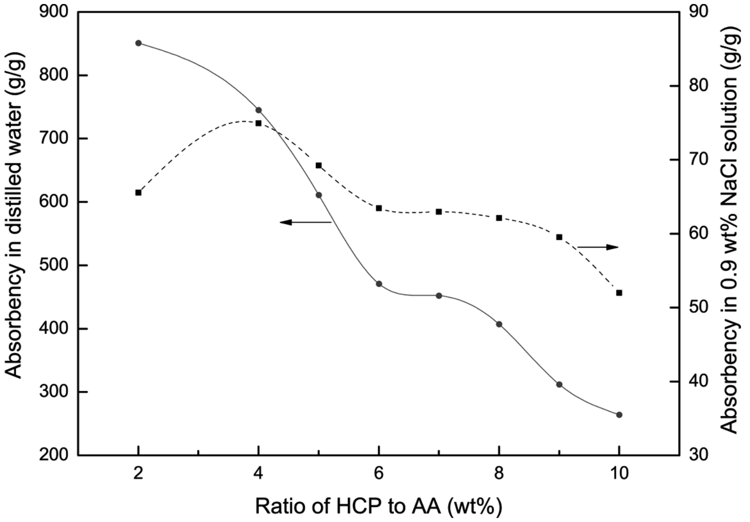

Figure 2: Effect of HCP content on the absorbency of copolymers.

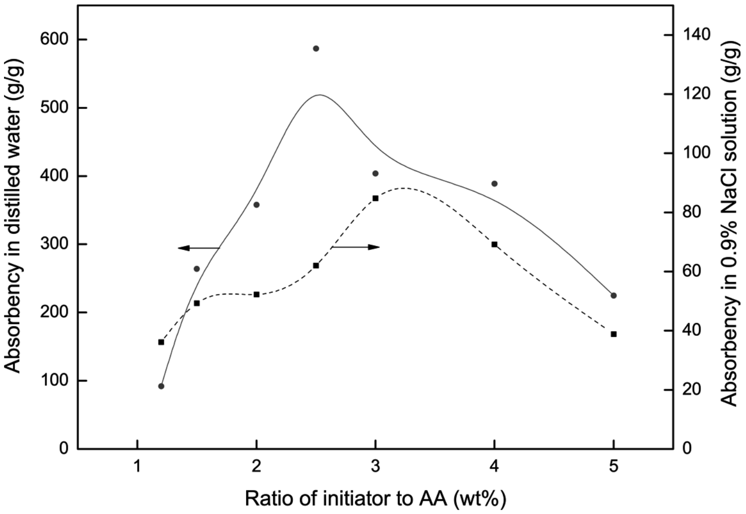

Figure 3: Effect of initiator on the absorbency of copolymers.

2.5 wt% (based on the amount of AA) and decreases with a further increase in the content of initiator. KPS/SBS is a redox initiator couple in free-radical chain polymerization. In free-radical polymerization, the creation of free radicals and active points increase as the initiator increases, and it benefits the copolymerization and the formation of three-dimensional networks. With a small amount of radicals in the free-radical polymerization, the network cannot form efficiently and results in the decrease of the water absorbency. However, a further increase of initiator will cause high quantities of produced free radicals which may cause a decrease of the molecular weight and high crosslink density, leading to the decrease of water absorbency. Similar results can been seen in NaCl solution except that the maximum absorbency occurs when the initiator content is 3.0 wt%. This might be because the network can not spread sufficiently due to the ionic effect of the external solution, and the influence of molecule weight is not significant in the saline solution compared with that in distilled water.

Effect of Crosslinker Content on Absorbency

The amount of crosslinker affects the crosslinking density of the network directly which has a decisive effect on the water absorbency of the copolymer. The effect of crosslinker content on water absorbency is shown in Figure 4. The water absorbency increases with the increase of crosslinker content from 0.1 wt% to 0.15 wt% (based on the amount of AA) and decreases with further increase of crosslinker content. When the content is less than 0.15 wt%, the absorbency of the copolymer decreases because there are several water-soluble materials in the network due to the low crosslinking density. As the

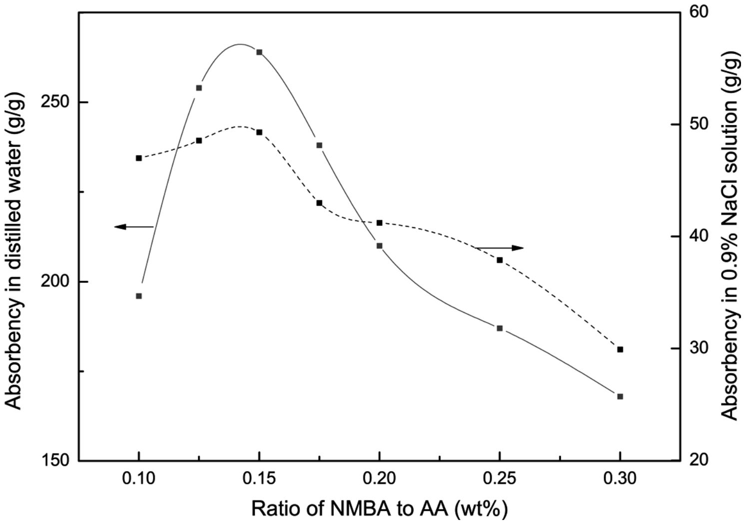

Figure 4: Effect of crosslinker content on the absorbency of copolymers.

crosslinker content increases, the water absorbency increases as the crosslinking density increases from more crosslinked points in polymeric chains and the three-dimensional structure improves successfully to hold water in the network. However, when the crosslinker content increases more than 0.15 wt%, the increased crosslinking density results in a decrease in the space of the copolymer networks because many more crosslinking points may occur, leading to shorter molecule chains between two crosslinking points. Thus the water absorbency decreases drastically.

Effect of Reaction Temperature on Absorbency

The effect of reaction temperature on the water absorbency is presented in Figure 5. With increasing temperature, the water absorbency of the hydrogel gradually increases and reaches a maximum at 70°C, after which the water absorbency decreases slowly. As we know, the rate of decomposition of thermal initiator KPS increases with the increase of temperature and produces more free radicals in free-radical polymerization. And a higher temperature will also enhance the diffusion of AA monomer and HCP molecules. Thus, higher temperatures favor the formation of a sufficient network and result in a higher water absorbency of the copolymer. However, when the reaction temperature increases above 70°C, radical termination and chain transfer reactions are dominant in the copolymerization, which leads to a decreased molecular weight and high crosslinking density of the copolymer, and the water absorbency decreases. In addition, the effect of self-crosslinking in the copolymer under high temperature may be another reason for the lower swelling [25].

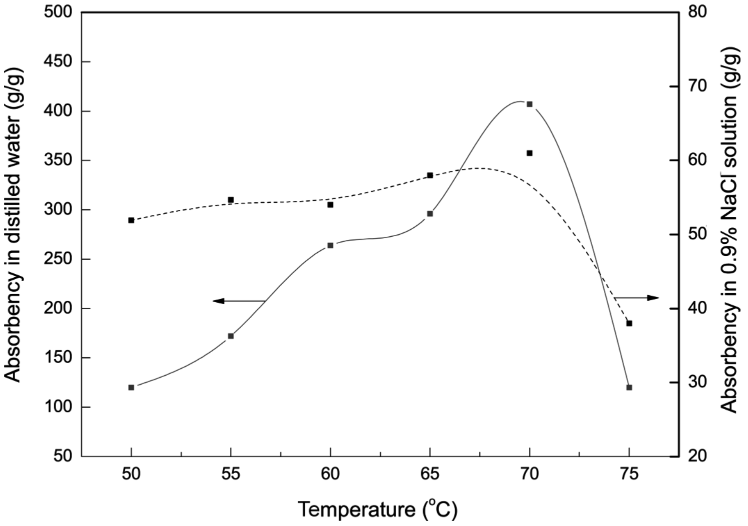

Figure 5: Effect of reaction temperature on the absorbency of copolymers.

Effect of the Neutralization Degree (ND) of AA on Absorbency

It is known that the electrostatic repulsion originated by the negative carboxyl groups attached to the polymer chains fascinates the swelling of the hydrogel network. As the charge density on the polymer chains increases, the electrostatic repulsion of carboxyl anions in the three-dimensional network will lead to the increase in water absorbency. When AA is neutralized with sodium hydroxide, the carboxylic acid group turns into a carboxylate group and the charge density on the polymer chains increases, resulting in the increase of water absorbency. Figure 6 depicts the effect of neutralization degree of AA on the water absorbency of the copolymer. It can be seen that the water absorbency increases with the increase of ND from 65 to 75 mol%. However, a further increase in ND above 75 mol% caused the decrease of water absorbency. It might be the screen effect of the negative charges of carboxyl groups which affected the dissociation of the sodium acrylate and reduces the electrostatic repulsion and osmotic pressure, leading to the decrease of water absorbency [26,27].

Optimized Synthetic Conditions

By studies under different conditions, it was found that the optimum synthetic conditions for the copolymer with high HCP content and swelling capacity are as follows: the mass ratio of HCP, the initiator and the cross-linker to AA are 10 wt%, 2.5 wt%, and 0.15 wt%, respectively, the degree of

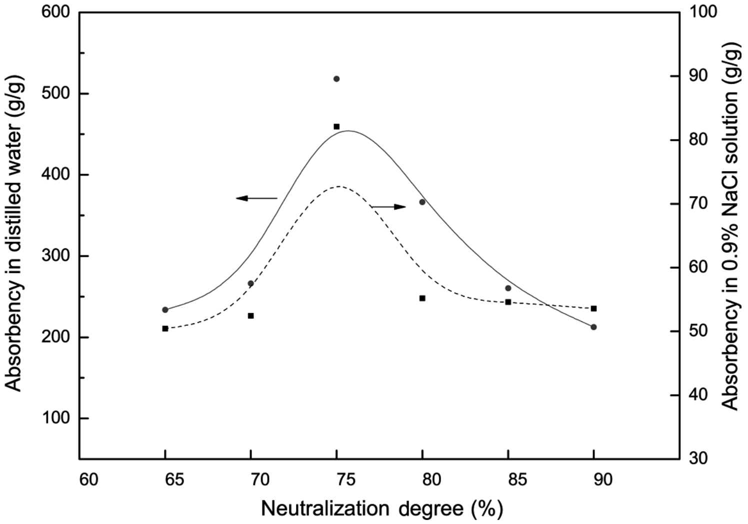

Figure 6: Effect of neutralization degree on the absorbency of copolymers.

neutralization of AA is 75 mol% and the reaction temperature is 70°C. The water absorbency of the obtained copolymer reaches 890 g/g in distilled water.

Effect of NaCl Concentration on Swelling

The effect of different NaCl concentrations on the water absorbency of the copolymer is depicted in Figure 7, which clearly shows that the water absorbency diminishes as the NaCl concentration increases. According to Flory's theory [24], this diminishing trend of water absorbency can be attributed to the decrease of the osmotic pressure difference between the HCP-PAA superabsorbent and the external saline solutions with the increasing of ionic strength. In addition, the screening effect of the counter-ions from the external solution on the fixed anionic groups of the network itself reduces the electrostatic repulsion force, resulting in the decrease of the osmotic pressure difference and water absorbency [28,29].

Effect of pH on Swelling

The effect of pH of the swelling media on the water absorbency was investigated in different pH solutions ranged from 3 to 12. No buffer solutions were used and NaOH (0.01 mol/L) or HCl (0.01 mol/L) solutions were used to reach the desired basic and acidic pH. The results depicted in Figure 8 indicate that the water absorbency decreases as the pH of the swelling media changed from 7 to 3 or from 7 to 12 and the maximum water absorbency (890 g/g) is obtained at pH 7. One explanation of this phenomenon can be attributed to the ionic

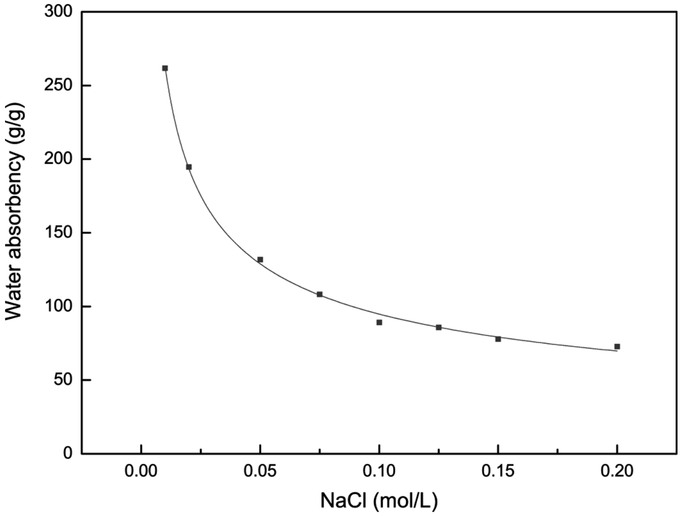

Figure 7: Absorbency of copolymer in various concentration of NaCl solution.

strength changing at different pHs. The ion strength of the swelling solution is the lowest at pH 7, while the ion strength increases when the pH of the solution deflects from pH 7. Thus, as the pHs decrease from 7 to 3 or increase from 7 to 12, the ion strength will increase gradually and result in the eliminated anion-anion repulsion and the ion osmotic swelling pressure decrease, and ultimately reduce the equilibrium water absorbency of the hydrogel. Another reason is that an anionic-type superabsorbent polymer normally

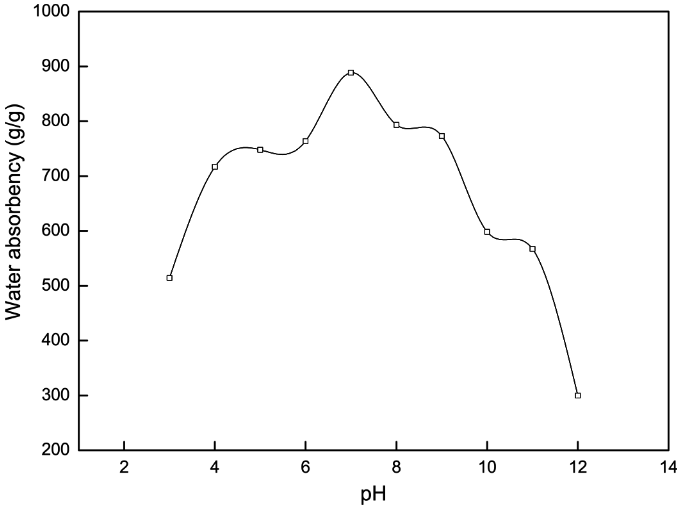

Figure 8: Absorbency of copolymer in solution with various pH value.

ionizes at a high pH but unionizes at a low pH. Under low pH, most of the carboxylate anions are protonated, the electrostatic repulsion forces causing the network relaxing are weakened and therefore the water absorbency decreases. At a higher pH around 7, the ionization of the carboxylic groups in the network increases and the concentration of anionic groups in the polymer network increases, resulting in an appreciable increase in the water absorbency. However, in the basic solutions at higher pH, the "charge screening effect" of excess cations in the external solution prevents the carboxylate anions' dissociation and reduces effective electrostatic repulsion, resulting in the loss of water uptake. In addition, the occurrence of interpolymer hydrogen bonds will increase the crosslinking density and also lead to decreased water uptake at low pH [30]. Similar swelling behaviors have been reported in other hydrogel systems [16,22,28].

Swelling Kinetics

A high swelling rate is important for the superabsorbent polymer as well as water uptake capacity in practical applications, especially in hygiene products. Several factors such as the type of polymerization, monomer composition, swelling capacity, particle size and distribution can affect the swelling rate of the superabsorbent polymer greatly [31]. Figure 9 illustrates the swelling kinetics of the synthesized copolymer particle samples of different sizes in distilled water. It can be seen that the swelling rate of synthesized hydrogel sharply increases initially to a certain extent and then begins to level off. Each curve follows an exponential relationship model which can be fitted with a

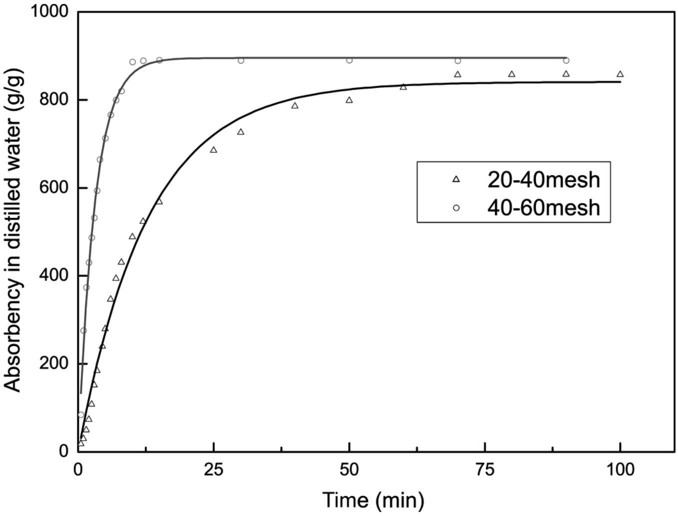

Figure 9: Swelling kinetics of the copolymer.

Voigt-based equation as follows [31]:

$$Q_t = Q_e(1 - e^{-t/\tau}) \tag{3}$$

where Q_t (g/g) is the degree of swelling at time t, Q_e is the equilibrium swelling (g/g), t is time (min) for swelling Q_t, and τ (min) stands for the swelling rate parameter. The swelling rate parameters were found to be 12.9 and 3.1 min for the copolymers with particle sizes of 20–40 mesh and 40–60 mesh, respectively. Absorption of water for the copolymer with particle size of 40–60 mesh is rapid, requiring approximately 12 min to reach maximum uptake, while it takes 40 min for particles with diameters between 20–40 mesh. This is attributed to that higher surface area and contact area with water of the smaller particles results in a faster permeation rate for water.

Water Retention Test

In general, superabsorbent polymers have excellent water retention capacity. There are two ways to accelerate a swollen hydrogel to lose water, namely, under pressure or heat, in order to investigate the water retention capacity of the hydrogel. The result of the water retention capacity test carried out in a hot air oven at temperatures of 60°C and 80°C is presented in Figure 10. It can be seen from Figure 10 that the hydrogel can retain 50% of the water it absorbed before for 9 h and 17 h at temperature 60°C and 80°C, respectively. In addition, the hydrogel could hold 71.6% of the initial

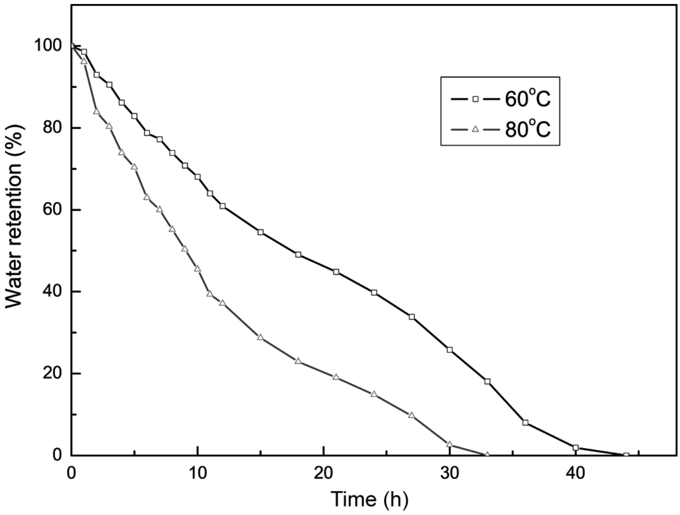

Figure 10: Water retention capacity of the copolymer at high temperature.

absorbing water after centrifugation under 4000 rpm for 10 min. These results indicate that the hydrogel has good water retention capacity under pressure or heat.

CONCLUSION

A superabsorbent hydrogel based on hydrolyzed cottonseed protein was synthesized by solution polymerization of HCP and partly neutralized AA, using NMBA as a crosslinking agent, and KPS and SBS as a redox initiator system. The effects of the certain variables of the graft copolymerization on the swelling capacity of the hydrogel were measured. The optimum conditions were obtained as follows: the mass ratio of HCP, the initiator and the crosslinker to AA are 10 wt%, 2.5 wt%, and 0.15 wt%, respectively, the degree of neutralization of the AA is 75 mol% and the reaction temperature is 70°C. In addition, the swelling properties of the synthesized hydrogel in solutions with various pHs and saline solution were investigated and the maximum water absorbency (890 g/g) was obtained at pH 7. Swelling kinetics and the water retention test show that the hydrogel can reach swelling equilibrium in 12 min and can hold water under press and heat. This new approach shows a promising method in utilizing natural hydrolyzed cottonseed protein in the production of superabsorbent hydrogel which has excellent water absorbency and potential in various applications.

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