

Improving Properties of Superabsorbent Composite Induced by Using Alkaline Protease Hydrolyzed-sericin (APh-sericin)

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A series of superabsorbent polymer composites based on sericin hydrolyzed with alkaline protease (AP) were prepared by grafting with acrylic acid (AA) and acrylamide (AM). The properties of the superabsorbent polymers (SAP) by using hydrolyzed sericin with different amount of alkaline protease (*n*Aph-sericin) were compared. It was found that the polymer prepared from 5Aph-sericin (the mass ratio of AP to sericin was 5.0 mg g⁻¹) showed the highest graft percentage and water absorbency, this phenomenon may be attributed to the change of molecular weight of resulting sericin molecules. The molecular structure of the grafted polymers was proved by thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) measurements. Comparing with PAA-AM (poly AA-co-AM) and 0Aph-sericin/PAA-AM polymer, 5Aph-sericin/PAA-AM polymer had the most excellent water retention capacity and enzyme degradability. The morphological features of the polymers with different drying methods were evidenced by SEM images. The water absorbencies of 5Aph-sericin/PAA-AM polymer prepared with freeze-drying were 896 g g⁻¹ in deionized water, 424 g g⁻¹ in tap water, and 83 g g⁻¹ in 0.9 wt% aqueous NaCl solution. POLYM. COMPOS., 35:509–515, 2014. © 2013 Society of Plastics Engineers

INTRODUCTION

Superabsorbent polymers (SAP) are highly hydrophilic hydrogels with three-dimensional networks, which can absorb aqueous solutions hundreds times of their own weight and retain water even under certain pressure [1]. Because of their excellent properties, SAP are widely used in many fields such as personal hygiene products, soil water reservoirs, tissue engineering biomaterials and coal dewatering materials, etc. [2]. Most of the traditional

SAP are based on pure monomers (such as acrylic acid, acrylamide, and sodium acrylate, etc.) for their excellent water absorbency. However, the SAP based on these monomers are too expensive by gradual depletion of petroleum resources, and could cause environmental pollution for their poor biodegradability [3]. Therefore, SAP prepared by graft copolymerization of acrylic acid-type monomers and natural polymers, such as starch, cellulose, chitosan and konjac glucomannan [4–8], have attracted considerable attentions of the researchers. Protein-based SAP have also been developed [9].

Silk derived from silkworm *Bombyx mori* is a natural protein that is mainly made of sericin and fibroin proteins. Sericin constitutes 25–30% of silk protein [10]. In recent years, sericin has been widely applied in cosmetic [11], tissue engineering [12] and enzyme immobilization [13], because of its excellent hydrophilicity, biocompatibility, and biodegradability. At present, sericin is mostly discarded in silk processing wastewater, thus results in water pollution. The exploitation of SAP based on sericin can not only enrich the type of SAP, but also reduce pollution. Moreover, a considerable cost reduction can be achieved. In our earlier work [14], the SAP based on sericin with boiling water bath was prepared, but the water absorbencies of the SAP need to be improved. The properties of sericin are closely related to its molecular weight [10]. Sericin can hydrolyze in acid and alkaline solutions, or enzymatic hydrolyze by a protease, and the size of the resulting sericin molecules depend on factors such as the amount of protease, temperature, pH, and the processing time [15]. Because of simple equipment requirement, mild reaction condition, less destroyed on the amino acids and environment friendly, enzymatic hydrolysis has been widely used in protein industries [16]. Alkaline protease (AP) is a common protease which used for sericin degumming in silk fiber processing [17]. Above all, it is expected that the properties of the SAP based on hydrolyzed sericin by AP could be improved with a moderate amount of AP.

In this work, SAP based on APh-sericin, AA and AM were prepared by free radical graft copolymerization. The

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effect of the amount of AP on graft percentage and water absorbency was investigated. Thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) measurements were used to characterize the molecular structure of the grafted polymer. Water absorbencies of 5Aph-sericin/PAA-AM polymer in three solutions prepared by oven-drying and freeze-drying was studied by comparing with 0Aph-sericin/PAA-AM and PAA-AM polymers. Morphological features of the polymers were evidenced by scanning electron microscopy (SEM) images. Additionally, water retention capacity and enzyme degradability of 5Aph-sericin/PAA-AM polymer were also examined.

MATERIALS AND METHODS

Materials

Cocoons of the domesticated silkworm (*B. mori*) were provided by Huzhou cocoon testing station. Alkaline protease (AP) powder was obtained from Zhaodong Sun Shine Enzyme Co., Ltd. Acrylic acid (AA), acrylamide (AM), *N,N'*-methylenebisacrylamide (MBA) and ammonium persulfate (APS) were all purchased from Shanghai Bioengineering. All reagents were of analytical grade and used without further purification.

Preparation of Alkaline Protease Hydrolyzed-sericin (Aph-sericin)

The cocoons were cut into pieces (about 1 cm²) and then immersed in boiling water (the weight ratio of sericin to water is 1:30) for about 30 min to obtain the sericin solution [18]. The solution was concentrated to 10% (w/v) with a rotary evaporator (Shanghai Jiapeng Technology, China) after the filtration with a Buchner funnel and adjusted to pH 9.0 with 1.0 mol L⁻¹ NaOH solution. Then, 10 mL of concentrated sericin (1.0 g) solution was hydrolyzed by adding AP (2.5, 5.0, 7.5, and 10.0 mg) and keeping at 48°C for 2 h in a vibrator with the rotation speed of 60 rpm. The enzyme activity of AP was measured by Folin-Ciocalteu method [19], and the enzyme activity of AP was 45,783 U g⁻¹. After the hydrolyzation, the solution was treated in a water bath at 100°C for 5 min to inactivate the AP and neutralized with 1.0 mol L⁻¹ HCl solution. The resultant solution (*n*Aph-sericin) was regulated to 10% (w/v) for *n*Aph-sericin/PAA-AM superabsorbent polymer formation. The sericin solution (10% (w/v)) without AP hydrolysis (0Aph-sericin) was used for the preparation of 0Aph-sericin/PAA-AM superabsorbent polymer.

SDS-PAGE of *n*Aph-Sericin

The molecular weight distribution of *n*Aph-sericin solution was measured through SDS-PAGE electrophoresis. The concentration of *n*Aph-sericin solution was

diluted to 1% (w/v) with distilled water. The stacking gel and running gel used for electrophoresis was 5% (w/v) and 10% (w/v), respectively. The voltage of the electrophoresis was 120 V and the time was 1.5 h. After the electrophoresis, the gel was stained with Coomassie Brilliant Blue R-250 (0.1% CBB, 40% alcohol and 10% acetic acid) for 2 h and destained twice with the reagent composed of 40% alcohol and 10% acetic acid.

Preparation of *n*Aph-sericin/PAA-AM SAP

As an example, the procedure for synthesizing SAP is described in detail. A solution of AA (1.25 mL, 1.06 g mL⁻¹) with 70% neutralization percentage (neutralized with 1M NaOH solution), AM powders (0.66 g) and *n*Aph-sericin (*n* denotes 0, 2.5, 5.0, 7.5, 10.0) solution were introduced to 10 mL of deionized water in a 250 mL of three-neck flask, equipped with a stirring rod, a thermometer and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, APS (0.04 g) and MBA (0.006 g) was introduced in the mixture, the mixed solution was heated to 60°C gradually. After polymerization for 2h, the *n*Aph-sericin/PAA-AM SAP was taken out to cut into small pieces. The obtained polymer was washed with a large volume of distilled water, and poured into excess ethanol for dehydration. After extraction with acetone for 24 h to dissolve the homopolymer, the purified SAP was dried with oven-drying (60°C) or freeze-drying and stored in a desiccator for further use. The SAP prepared with oven-drying was ground into powders with the size between 100 and 200 mesh. The control sample (PAA-AM polymer) was prepared in the same procedure mentioned above, but without the addition of sericin.

Grafting Percentage and Grafting Efficiency

The grafting percentage (GP) and grafting efficiency (GE) were calculated as follows [20]:

$$GP = \frac{W_2 - W_0}{W_0} \times 100 \quad (1)$$

$$GE = \frac{W_2 - W_0}{W_1} \times 100 \quad (2)$$

where W_0 , W_1 , and W_2 are the weights of *n*Aph-sericin, the monomer (AA+AM), and *n*Aph-sericin/PAA-AM polymer after the homopolymers are removed, respectively.

Measurement of Water Absorbency

Dry superabsorbent polymer sample (W_0 , 0.1 ± 0.001 g) was sealed in a tea bag (100 mesh screen) and immersed in an adequate medium solution (400 mL deionized water, 200 mL tap water, or 100 mL 0.9 wt% aqueous NaCl solution) at room temperature for 12 h to

reach the swelling equilibrium. Then, the swollen polymer sample including the wet tea bag was taken out from the medium solution and weighed (W_2) after removing the excess water by hanging at room temperature for 30 min. The weight of the wet tea bag was measured (W_1) after washing off the swollen polymer sample. The equilibrium swelling capacity (Q_{eq}) was calculated according to the following equation:

$$Q_{eq}(\text{g/g}) = \frac{W_2 - W_1 - W_0}{W_0} \quad (3)$$

Instrumental Analysis

Thermo gravimetric measurements were performed using a thermal gravity analysis (TGA) instrument (DTA-60A, Shimadzu, Japan) under nitrogen atmosphere. The scanning temperature range and the heating rate were 50–600°C and 10°C min⁻¹, respectively. The Fourier transform infrared (FTIR) spectra were recorded on a FTIR-8400S spectrometer (Shimadzu, Japan) in the 4000–400 cm⁻¹ region with a spectra resolution of 4 cm⁻¹ in the absorption mode, with using KBr pellets. The morphology of the SAP was observed with scanning electron microscopy (SEM). SAP powder was sputter-coated with a gold ion sputter (Hitachi E-1010, Japan) in a vacuum and imaged in an SEM instrument (Hitachi S-3000N, Japan).

Measurement of Water Retention

A weighted quantity (W_0) of SAP was immersed in deionized water at room temperature to reach swelling equilibrium. The swollen polymers were hung for 15 min in a tea bag to remove excess water, weighed (W_1), and placed in an oven at 25 or 60°C. The relative humidity in the oven was constant at ~40.0%. The samples were weighed every 2 h or every day (W_i). The water retention capability (R_{IT}) was calculated by the following equation:

$$R_{IT} = \frac{W_i - W_0}{W_1 - W_0} \quad (4)$$

Data were the means of three repeated measurements.

Enzyme Degradability

SAP powder (W_0 , 0.5 ± 0.001 g) was sealed in a tea bag (100 mesh screen) and then immersed in a beaker containing 200 mL 0.01% (w/v) AP solution. The pH of AP solution was adjusted to 9 with 1.0 mol L⁻¹ NaOH solution. Then, the solution was kept in a vibrator at 48°C for 24 h with the rotation speed of 60 rpm. After degradation, the tea bag containing SAP was taken out, washed with deionized water until the soluble substances were removed and dried in an oven (60°C) to constant weight (W_2). The rate of enzyme degradation (R_{ed}) of SAP was determined by the following equation:

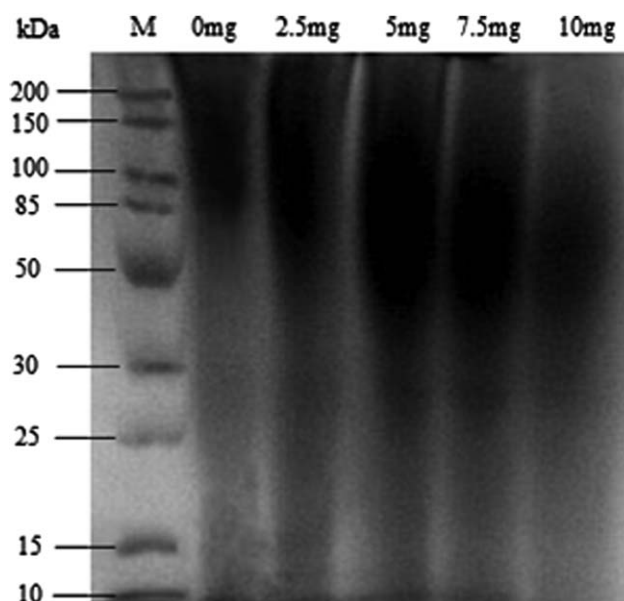


FIG. 1. SDS-PAGE of marker and *n*Aph-sericin samples: marker (lane M); 0Aph-sericin (lane 0 mg); 2.5Aph-sericin (lane 2.5 mg); 5Aph-sericin (lane 5 mg); 7.5Aph-sericin (lane 7.5 mg); 10Aph-sericin (lane 10 mg). The Marker protein was a standard ladder protein with the range of molecular weight from 10 to 200 kDa.

$$Red = \frac{W_0(W_2 - W_1)}{W_0} \times 100 \quad (5)$$

where W_1 is the dry weight of a tea bag.

RESULTS AND DISCUSSION

Molecular Weight Distribution of *n*Aph-Sericin

Molecular weight distribution of sericin hydrolyzed with different amount of AP (*n*Aph-sericin) was tested through SDS-PAGE electrophoresis and the results are shown in Fig. 1. Each sericin sample with or without AP hydrolysis (*n*Aph-sericin, lane 0–10 mg) has a continuous band, indicating the molecular weight distribution. Comparing with the marker protein (lane M), the molecular weight of 0Aph-sericin (lane 0mg, without AP hydrolysis) was mainly at 85–200 kDa and even higher. However, the molecular weight of sericin gradually decreased with the increasing amount of AP (lane 2.5–10 mg). 2.5Aph-sericin (lane 2.5 mg) sample exhibited a relatively wider molecular weight distribution with a range between 50 and >200 kDa. When the amount of AP increased to 5 mg (lane 5 mg, 5Aph-sericin), the molecular weight was ranged from 30 to 200 kDa. 7.5Aph-sericin (lane 7.5 mg) showed a range at 30–150 kDa. While little bands of 10Aph-sericin were observed and mainly at 30–100 kDa, revealing that sericin was mostly hydrolyzed to peptides <10 kDa. The degradation of sericin indicated that the length of sericin molecular chain gradually shortened, and larger number of sericin molecules emerged with the increasing amount of AP.

TABLE 1. Effect of the amount of AP on grafting efficiency and grafting ratio of *n*Aph-sericin/PAA-AM superabsorbent polymers.

Amount of AP (mg)	Grafting percentage (%)	Grafting efficiency (%)
0	115.2 ± 6.3	57.6 ± 3.2
2.5	129.5 ± 6.8	64.8 ± 3.1
5.0	140.1 ± 8.9	70.1 ± 4.5
7.5	121.3 ± 7.5	60.7 ± 3.7
10.0	102.7 ± 5.4	51.4 ± 2.7

Effect of the Amount of AP on Grafting Percentage and Grafting Efficiency

Table 1 shows the effect of the amount of AP on the grafting percentage and grafting efficiency of *n*Aph-sericin/poly(acrylic acid-*co*-acrylamide) (*n*Aph-sericin/PAA-AM) polymer. When the amount of AP was 5 mg, the polymer has the highest grafting percentage and grafting efficiency. Protein was proposed to graft with the monomers (AA and AM) through the radicals of protein initiated by the hydroxyl radicals [21], indicating that the grafting percentage and grafting efficiency related to the amount of protein radicals.

When the amount of AP was lower than 5 mg, the number of hydroxyl radicals of sericin increased with the increasing amount of AP, therefore, grafting percentage and grafting efficiency increased. When the amount of AP was higher than 5 mg, lower molecular weight induced higher hydroxyl radical scavenging activity of sericin [22]. Therefore, less radicals of sericin appeared, grafting percentage and grafting efficiency decreased with the increasing amount of AP.

Effect of the Amount of AP on Water Absorbency

Figure 2 shows water absorbency of APh-sericin/PAA-AM polymers prepared from hydrolyzed sericin by different amount of AP. The water absorbency in deionized water of SAP based sericin without AP hydrolysis (0 mg AP) was 483 g g⁻¹, while the water absorbency gradually increased and then decreased with the increasing amount of AP. When the amount of AP was 5 mg, the highest water absorbency (627 g g⁻¹) of the polymer obtained. These results indicated that water absorbency of the polymer related to the amount of AP.

Water absorbency of SAP usually depends on the extensibility of the polymer network. Excellent extensibility of the network can provide high water absorbency of polymer. Sericin without AP hydrolysis has the highest molecular weight and its long chains fold and entangle to form a complex structure, which hindered the extensibility of polymer chains, thus influenced the water absorbency. This phenomenon has also been observed in the graft copolymerization of starch and the monomers [23]. When hydrolyzed with AP (<5 mg), the molecule chains of sericin become shorter and show improving mobility

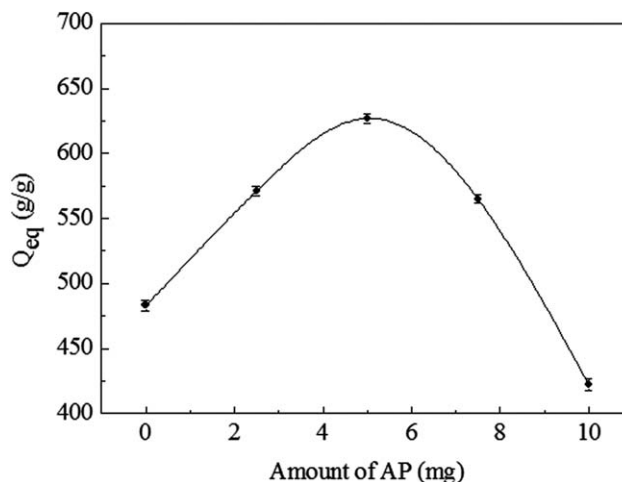


FIG. 2. Effect of the amount of AP on the water absorbency of *n*Aph-sericin/PAA-AM SAP.

and extensibility. Therefore, the water absorbency of the polymer increased with the increasing amount of AP. When the amount was higher than 5 mg, the distance between the crosslink points of the polymer chains became shorter with the increasing amount of AP, therefore, water absorbency of the polymer decreased.

Thermal Property Analysis

Thermo gravimetric analysis (TGA) results of the polymers and sericin are employed to characterize the thermal properties and it shown in Fig. 3. PAA-AM polymer showed two loss stages, obviously different from sericin with three loss stages. Total weight loss percentage of 0Aph-sericin/PAA-AM (69.71%) and 5Aph-sericin/PAA-AM (79.02%) polymers were higher than PAA-AM (53.56%), but lower than sericin (95.57%). These results indicated the thermostability of *n*Aph-sericin/PAA-AM polymer was between that of PAA-AM polymer and sericin, revealed that sericin was successfully grafted with poly (acrylic acid-*co*-acrylamide) (PAA-AM) chains. The total weight loss percentage of 5Aph-sericin/PAA-AM

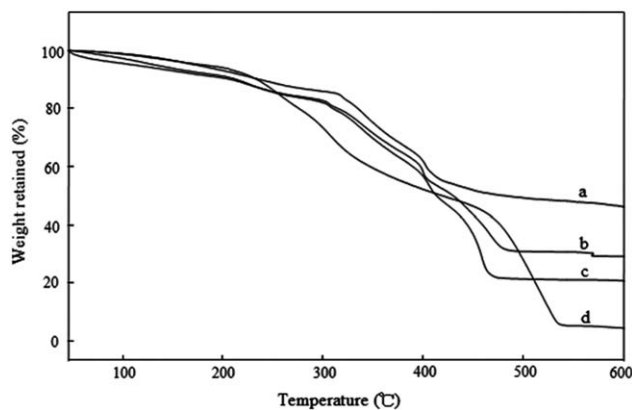


FIG. 3. TGA curves of (a) PAA-AM polymer; (b) 0Aph-sericin/PAA-AM polymer; (c) 5Aph-sericin/PAA-AM polymer; (d) sericin.

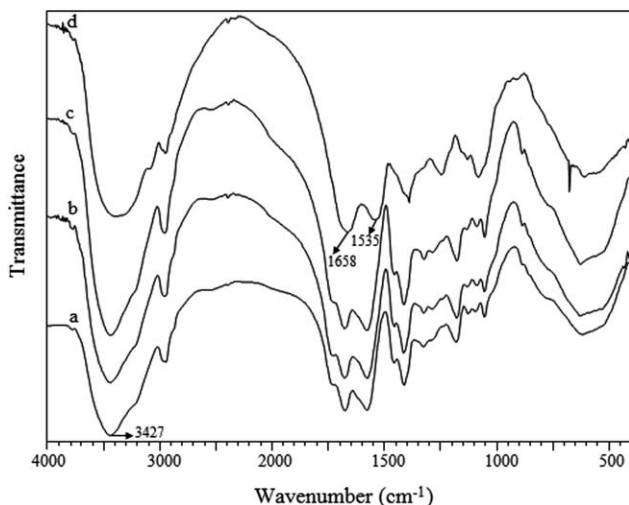


FIG. 4. FTIR spectra of (a) PAA-AM polymer; (b) 0Aph-sericin/PAA-AM polymer; (c) 5Aph-sericin/PAA-AM polymer; (d) sericin.

polymer was higher than that of 0Aph-sericin/PAA-AM polymer, this phenomenon may be attributed to larger number of sericin molecules of 5Aph-sericin/PAA-AM polymer.

FTIR Measurements

The molecular structure of the polymers was confirmed by FTIR measurements. Figure 4a–d shows the FTIR spectra of PAA-AM, 0Aph-sericin/PAA-AM, 5Aph-sericin/PAA-AM polymers and sericin, respectively. In the spectrum of PAA-AM polymer (Fig. 4a), the characteristic peak at 3427 cm^{-1} was attributed to the —NH stretching vibration of the AM unit, which overlapped with the —OH groups of the sericin and acrylate units [20, 24]. According to Fig. 4d, the peak at 1658 cm^{-1} indicated C=O stretching (carboxamide I band) and that at 1535 cm^{-1} indicated N—H bending vibration (carboxamide II band), which are the typical absorption bands of the sericin [25].

Comparing *n*Aph-sericin/PAA-AM polymers (the spectra of b and c) with PAA-AM polymer, *n*Aph-sericin/PAA-AM polymers shows the similar spectrum to PAA-

AM polymer, This result indicated the good compatibility of sericin and PAA-AM molecules in the graft copolymerization, which were consistent with the TGA results. In the *n*Aph-sericin/PAA-AM polymers, the typical peak of sericin and PAA-AM was indistinguishable, maybe because that the molecule structure of sericin changed into a new molecular structure, which overlapped the typical peaks of PAA-AM chain. These FTIR results indicated that the PAA-AM chains were successfully grafted onto the chains of sericin.

Water Absorbency with Different Methods in Different Solutions

The 5Aph-sericin/PAA-AM polymer has the highest graft percentage (Table 1) and water absorbency (Fig. 2). More examinations on 5Aph-sericin/PAA-AM polymer by comparing with 0Aph-sericin/PAA-AM and PAA-AM polymers were carried out. Figure 5 shows water absorbency of the SAP in three swelling medium solutions (deionized water, tap water, 0.9 wt% aqueous NaCl solution). Water absorbency of all the samples is the highest in deionized water, lower in tap water, the lowest in 0.9 wt% aqueous NaCl solution, which could be observed in other polymers [26]. This is attributed to the decreased electrostatic repulsion of polymer chains, which may be due to the higher ionic strength of the swelling medium solution.

Regardless of the samples dried by oven-drying (Fig. 5a) or freeze-drying (Fig. 5b), water absorbency of 5Aph-sericin/PAA-AM polymer was higher than that of 0Aph-sericin/PAA-AM polymer but lower than that of PAA-AM polymer, which was consistent with the result shown in Fig. 2. The water absorbency of 5Aph-sericin/PAA-AM polymer was lower than PAA-AM polymer, which was due to the functional groups of sericin and PAA-AM molecules. There are many nonionic groups (—OH) in the side chain of sericin molecular, while there are many ionic groups (—COOH) in the side chain of PAA-AM molecular [27]. Therefore, the electrostatic repulsion and

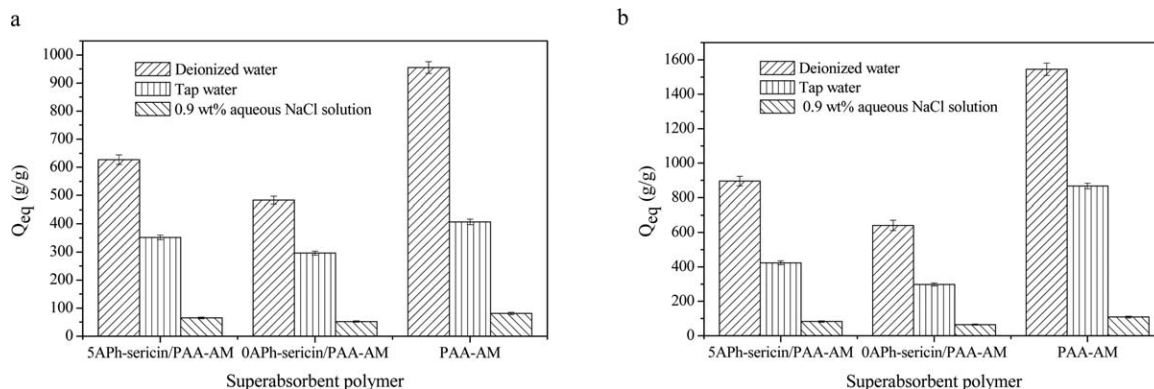


FIG. 5. Water absorbency of superabsorbent polymers prepared by (a) oven-drying and (b) freeze-drying in three types of medium solution (deionized water, tap water and 0.9 wt% aqueous NaCl solution).

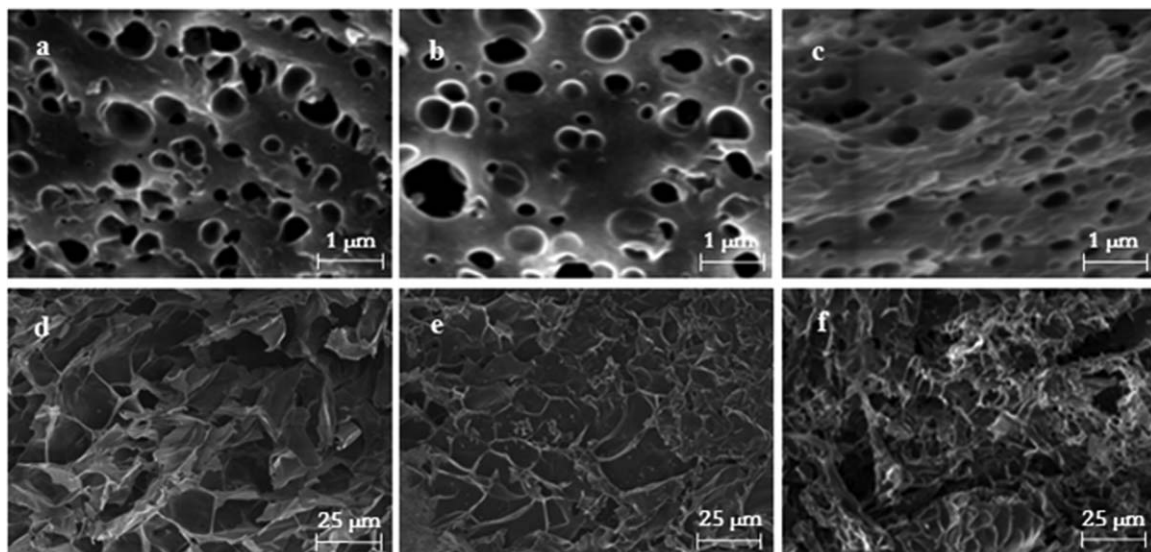


FIG. 6. SEM images of superabsorbent polymers prepared by oven-drying: (a) 5Aph-sericin/PAA-AM polymer; (b) 0Aph-sericin/PAA-AM polymer; (c) PAA-AM polymer, and freeze-drying: (d) 5Aph-sericin/PAA-AM polymer; (e) 0Aph-sericin/PAA-AM polymer; (f) PAA-AM polymer.

extensibility of *n*Aph-sericin/PAA-AM chain was less than PAA-AM chain, which caused the lower water absorbency.

The water absorbencies of the 5Aph-sericin/PAA-AM polymer prepared with freeze-drying were 896 g g^{-1} in deionized water, 424 g g^{-1} in tap water, and 83 g g^{-1} in 0.9 wt% aqueous NaCl solution. And the polymer prepared with oven-drying was 627 g g^{-1} in deionized water, 352 g g^{-1} in tap water, and 65 g g^{-1} in 0.9 wt% aqueous NaCl solution. The water absorbencies of the polymers with freeze-drying are higher than oven-drying, it is because that the samples prepared with free-drying showed interconnecting pores as shown in Fig. 6, however, they are more costly and less practicable in processing.

Morphological Analyses

Figure 6 shows the SEM images of the SAP prepared with oven-drying and freeze-drying, the porosity of

5Aph-sericin/PAA-AM polymer was higher than 0Aph-sericin/PAA-AM polymer but lower than PAA-AM polymer. The pore structure related to the water absorbency of polymers, higher porosity can lead to higher water absorbency [28]. Therefore, it could be concluded that 5Aph-sericin/PAA-AM polymer had higher water absorbency than 0Aph-sericin/PAA-AM polymer but lower than PAA-AM polymer, which was consistent with the results shown in Fig. 5. In addition, samples prepared with freeze-drying showed interconnecting pores, which leads to higher water absorbency as shown in Fig. 5.

Water Retention Property

Figure 7 shows the water retention capacity of SAP at 25 and 60°C. Water retention decreased significantly as the temperature and time increased. These results are attributed to the interacting of H-bonding and Vander

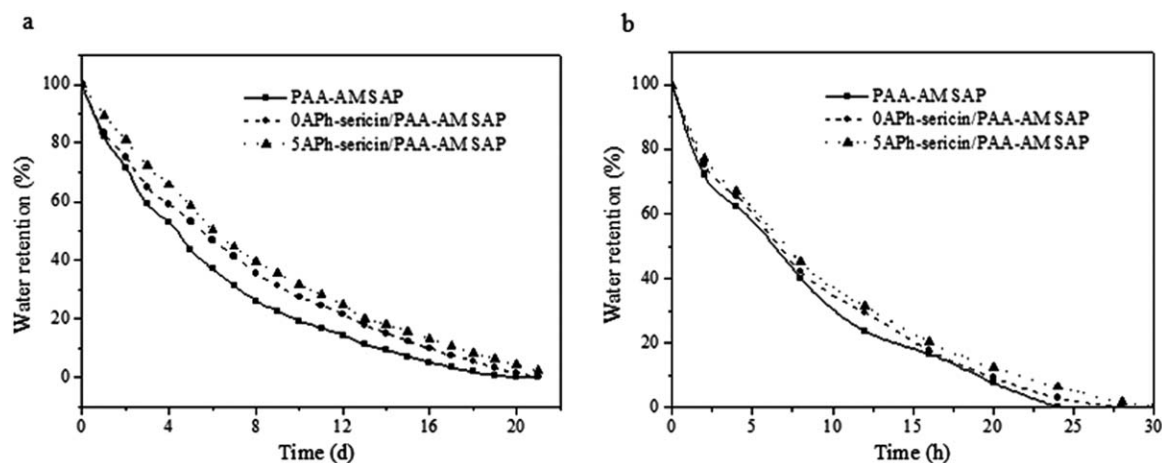


FIG. 7. Water retention capacity of the SAP at (a) 25°C and (b) 60°C.

TABLE 2. Enzyme degradation percent of the SAP.

Superabsorbent polymers	Enzyme degradation percent (%)
5APh-sericin/PAA-AM SAP	40.1 ± 3.6
0APh-sericin/PAA-AM SAP	29.7 ± 3.3
PAA-AM SAP	11.2 ± 2.9

Waals force between water molecules and the SAP in the swollen gel [20]. Water retention capacity of 5APh-sericin/PAA-AM polymer was higher than that of 0APh-sericin/PAA-AM and PAA-AM polymers. When kept at 25°C for 12 days, water retention of 5APh-sericin/PAA-AM, 0APh-sericin/PAA-AM and PAA-AM polymers was 25.6, 21.6, and 14.4 wt% (Fig. 7a), respectively. When kept at 60°C for 12 h, water retention of 5APh-sericin/PAA-AM, 0APh-sericin/PAA-AM and PAA-AM polymers was 31.3, 29.5, and 23.7 wt% (Fig. 7b), respectively. The results indicated 5APh-sericin/PAA-AM polymer has the best water retention property.

Enzyme Degradation Property

Table 2 shows enzyme degradation percent of 5APh-sericin/PAA-AM, 0APh-sericin/PAA-AM and PAA-AM polymers. These results revealed that 5APh-sericin/PAA-AM polymer possesses a better degradation property than 0APh-sericin/PAA-AM and PAA-AM polymers, which may be attributed to the larger number of sericin molecules in 5APh-sericin/PAA-AM polymer, this result was in correspondence with TGA results, as shown in Fig. 3.

CONCLUSIONS

In this work, a series of superabsorbent composites (*n*APh-sericin/PAA-AM polymers) based on *n*APh-sericin and the monomers (AA and AM) were prepared through radical graft copolymerization. SDS-PAGE results showed that the molecular weight of *n*APh-sericin decreased with the increasing amount of AP. Graft percentage and water absorbencies of *n*APh-sericin/PAA-AM polymers related to the amount of AP and reached to the highest when the mass ratio of AP to sericin was 5 mg g⁻¹. The molecular structure of the grafted polymers had been proved by thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) measurements. Comparing 5APh-sericin/PAA-AM polymer with 0APh-sericin/PAA-AM and PAA-AM polymers, water retention capacity and enzyme degradability were the most excellent, porosity was the highest. These results are useful for the development of sericin-based functional materials with better properties.

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