Available online at www.sciencedirect.com
SCIENCE DIRECT®

Carbohydrate Polymers 62 (2005) 74–79

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Rapid synthesis of a superabsorbent from a saponified starch and acrylonitrile/AMPS graft copolymers

Tong Qunyi[a,*], Zhang Ganwei[b,*]

[a]School of Food Science and Technology, Southern Yangtze University, Huihe Road 170, Wuxi, Jiangsu 214036, China
[b]Department of Biology, Huanggang Normal College, Huangzhou, Hubei 438000, China

Received 30 July 2004; revised 30 May 2005; accepted 20 July 2005
Available online 8 September 2005

Abstract

In this work, superabsorbents comprising the graft polymer of acrylonitrile and AMPS onto starch were prepared using a manganic pyrophosphate redox initiation system. The addition of AMPS results in a gradual saponification time decrease for the graft polymer, then the total synthesis time decrease of superabsorbents. The effect of KOH volume, KOH concentration, saponification temperature on the water absorbency of superabsorbent was investigated using response surface methodology (RSM). The maximum response at the optimal saponification conditions can be obtained. The water absorbency was 1345 g/g dry superabsorbent, using the following saponification conditions: KOH volume 203.7 ml, KOH concentration 0.51 mol/l, saponification temperature 92.6 °C. The shortest saponification time is 17 min, then the total synthesis time of superabsorbents is 2.5 h.

Keywords: Starch; Acrylonitrile; 2-acrylamido-2-methylpropanesulfonic acid (AMPS); Manganic pyrophosphate; Supwerabsorbent; Response surface methodology

1. Introduction

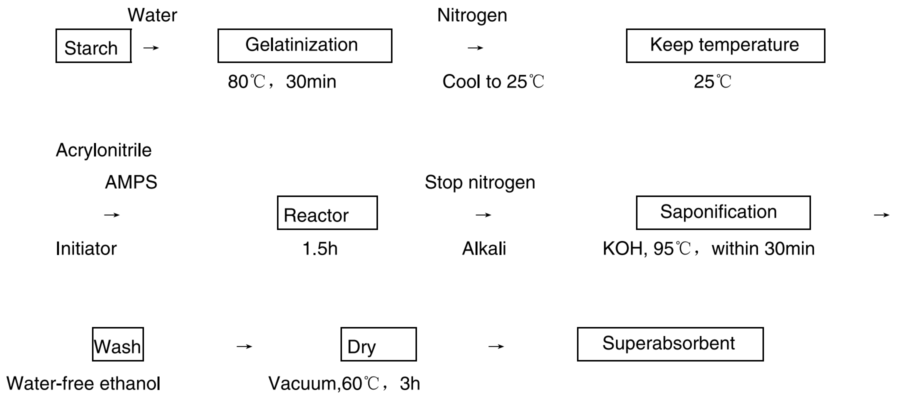
Superabsorbents can absorb a large amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their superior properties, they have found extensive product applications such as disposable diapers, feminine napkins, soil for agriculture, horticulture, drilling additives, water-blocking tape and drug delivery systems (Fanta & Burr, 1969; Hebeish, Beliakova & Bayazeed, 1993; Sakiyama, Chu, Fujii, & Yano, 1993; Shiga, Hirose, Okada, & Kurauchi, 1992; Wu, Wei, Lin, & Lin, 2003; Yoshida, Asano, & Kumakura, 1989) Superabsorbents have been widely studied since the first superabsorbent was developed by the US Department of Agriculture in 1961 (United States Department of Agriculture, 1961). The grafting copolymers of many hydrophilic monomers such as acrylamide (AM) (Hebeish, El-Rafie, & Higazy, 1996), acrylic acid (AA) (Fanta, Stout, & Doane, 1978) and acrylonitrile (AN) (Pourjavadi and Zohuriaanmehr, 2002) onto starch have been utilized to prepare superabsorbents. Among the superabsorbents, starch-based superabsorbents prepared by hydrolyzing starch-graft-polyacrylonitrile have been studied extensively and water absorbency from a few hundreds (Lu, Duan, & Lin, 2003) to greater than 1000 g/g has been reported(Lim, Whang, Yoon, & Ko, 2001). The reaction processes include graft copolymerization, saponification of graft copolymers, washing and drying of saponified products. The saponification time is about 3 h and the total synthesis time of superabsorbent is about 6 h (United States Department of Agriculture, 1961) (except drying time).

In this work, the effect of AMPS on the synthesis time of starch-based superabsorbents was reported. The incorporation of AMPS into starch-graft-polyacrylonitrile can decrease the saponification time of copolymers to 17 min, then decrease the total synthesis time of superabsorbents to 2.5 h (except drying time). The experiments were conducted to optimize the saponification conditions using response surface methodology (RSM) (Vazquez &and Martin, 1998).

---

* Corresponding author. Tel.: +86 510 5869281; fax: +86 510 5869541.
* Corresponding author. Tel.: +86 0713 8538643.
E-mail addresses: qytong@263.net, tqy@sytu.edu.cn (T. Qunyi), zhangganwei214036@126.com (Z. Ganwei).

0144-8617/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2005.07.016



Scheme 1. The rapid synthesis process of superabsorbent.

This technique generates contour plots from the linear, interaction and quadratic effects of two or more variables and fits the experimental data to calculate the optimal response of the system. In addition, Effect of starch gelatinization on water absorbency and saponification time was discussed also.

2. Experimental

2.1. Materials

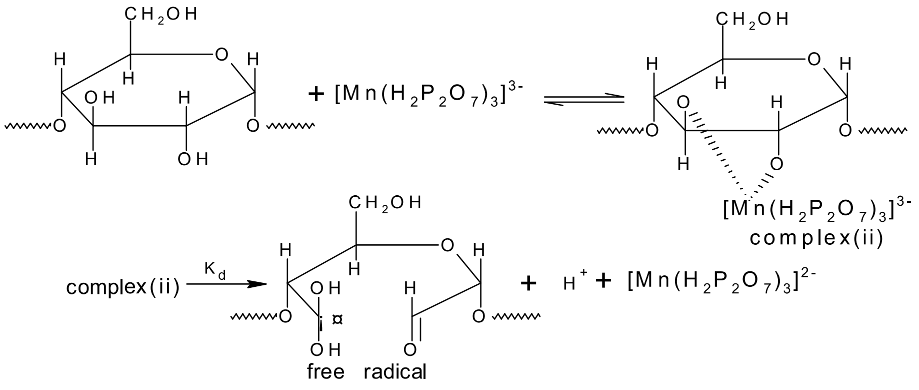
Most chemicals were analytical grade reagents from China Medicine (Group) Shanghai Chemical Reagent Corporation. Sweetpotato starch was produced by ourselves. AMPS was from Lubrizol Corp and used as received. Acrylonitrile was distilled under reduced pressure of N_2, and stored in the dark at 4 °C.

2.2. Preparation of the initiator (Fanta & Burr, 1969)

Three milliliters of a solution of Mn^{2+} ions prepared by dissolving 0.790 g $MnSO_4$ H_2O in 100 ml distilled water was added to 10 ml of 2.630 g sodium pyrophosphate ($Na_4P_2O_7$ $10H_2O$) in 100 ml distilled water. The pH of the resulting solution was adjusted to 3 by adding 2 mol/l H_2SO_4 using an accurate pH Meter. The Mn^{2+} ions were then oxidized to Mn^{3+} ions by titrating with Mn^{7+} ions (obtained by dissolving 0.180 g $KMnO_4$ in 100 ml distilled water) using a platinum electrode. About 3 ml of the permanganate solution was required.

2.3. Rapid synthesis of superabsorbent

Four gram sweetpotato starch (on a dry basis) was slurried in the required amount of distilled water in a 500 ml four-neck flask equipped with stirrer and immersed in a constant temperature bath. The stirred slurry was gelatinized by heating at 80 °C for 30 min and then the pasty mixture was cooled back to 25 °C. A brisk stream of oxygen-free nitrogen was bubbled at the same time. Then the system was heated to desired temperature. Acrylonitrile and the initiator were added first, followed after 1 min by AMPS. The pasty mixture was kept at different temperatures for 1.5 h. The desired KOH in 40 ml distilled water was added and then mixture was heated at 95 °C. It was kept for 30 min after the change in color from deep red to light yellow. The mixture was left to cool, and 80 ml ethanol was poured into. The precipitate was washed with ethanol to neutrality and



Scheme 2. The reaction scheme about graft copolymer of acrylonitrile and AMPS onto starch using a manganic pyrophosphate redox initiation system.

dried under vacuum at 60 °C for 3 h. The synthesis process was at Scheme 1.

The reaction mechanism of graft copolymer of acrylonitrile and AMPS onto starch using a manganic pyrophosphate redox initiation system was free radical polymerization (Mehrotra & Ranby, 1977). The reaction scheme was at Scheme 2.

2.4. Infrared spectral analysis

After the homopolymer was removed with DMF, the infrared spectra of starch and graft polymers were taken in KBr pellets using American Nicolet 5D×B FT-IR spectrometer.

2.5. Determination of water absorbency (Fanta & Burr, 1969)

The sample of dry copolymer (1–5 mg) was immersed in 50 ml distilled water for 30 min. The swollen copolymer was then separated from unabsorbed water by screening through a 280 mesh sieve. The weight of swollen copolymer was measured after draining for 20 min. The water absorbency was calculated according to the following equation:

$$\text{Absorbency}\left(\frac{\mathrm{g}}{\mathrm{g}}\right) = \frac{W_2 - W_1}{W_1}$$

where W_1 and W_2 are the weights of dry copolymer and swollen copolymer, respectively.

2.6. Response surface methodology (Inan et al., 1999)

Response surface methodology (RSM) is a group of techniques used to evaluate relationships between one or more measured responses and a number of quantitative independent variables that may have important effects on the measured responses. It requires fewer treatments than equivalent factorial designs to evaluate how the independent variables affect the measured response. This procedure was used to understand the overall effect of KOH volume, KOH concentration, saponification temperature during the saponification on the water absorbency of products. Since this study was limited to KOH volume, KOH concentration, saponification temperature, all other parameters influencing the water absorbency were fixed at constant values as described above.

Optimization of saponification conditions using response surface methodology was made according to a central composite statistical design for the study of three factors (Table 3), each at three levels and the other condition was constant. A central composite experiment design is used to acquire data that fit an empirical, full second order polynomial model. KOH Volume, KOH concentration, saponification temperature are independent variables or factors. The water absorbency of final products is dependent variable or response. Levels of factors used in the experimental design are presented in Table 1.

Table 1
Levels of factors used in the experimental design in response surface methodology (RSM)

Levels	KOH volume (ml) (X_1)	KOH concentration (mol/l) (X_2)	Saponification temperature (°C) (X_3)
−1.68	116	0.33	83.6
−1	150	0.4	87
0	200	0.5	92
1	250	0.6	97
1.68	284	0.67	100.0

In order to fit empiric second order polynomial model, a central composite design was performed. The quadratic model for predicting the optimal point was expressed according to following equation:

$$y = b_0 + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j \qquad (1)$$

Where y is the response variable, b is the regression coefficients, and x is the coded level of the independent variable.

A full second order polynomial model obtained by a multiple regression technique for two factors using the SAS Package (SAS Institute inc., Cary, NC, USA) was adopted to describe the response surface.

3. Results and discussion

3.1. Effect of gelatinization on water absorbency and saponification time

Because of the different secondary construction between granulated starch and gelatinized starch, the superabsorbents from these materials have different water absorbency and their synthesis time is also unlike. The water absorbency and saponification time of starch graft copolymer from gelatinized starch or granulated starch was shown in Table 2 under constant other conditions.

The result in Table 1 showed that the superabsorbent from gelatinized starch has better water absorbency and shorter synthesis time than from granulated starch.

Table 2
The water absorbency and saponification time of starch graft copolymer from gelatinized starch or granulated starch

	Water absorbency (g/g)	Saponification time (min)
Granulated starch	875	60
Gelatinized starch[a]	1325	23

[a] Gelatinization for 30 min at 85°C.

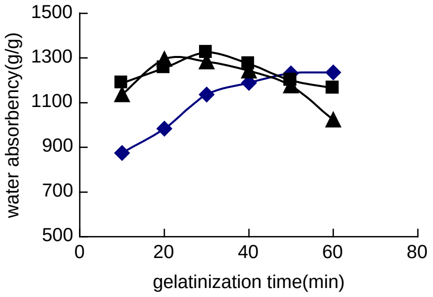


Fig. 1. The effect of gelatinization time on water absorbency ◆70°C■85°C▲100°C.

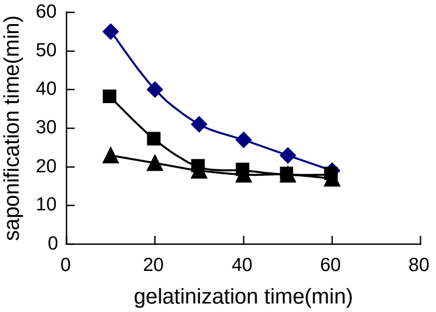


Fig. 2. The effect of gelatinization time on saponification time◆70°C■85°C▲100°C.

The effect of gelatinization time on water absorbency and saponification time at different temperatures was shown in Figs. 1 and 2, respectively.

It was observed from Figs. 1 and 2 that water absorbency of superabsorbent was increased and the saponification time was shorted as gelatinization time of starch increased when the gelatinization temperature was at 70 °C. But the different was not distinct when the gelatinization temperature was at 80 and 100 °C. In this work, the optimum gelatinization temperature was 80 °C and the optimum gelatinization time was 30 min.

3.2. The effect of AMPS% on saponification time

The starch-graft-polyacrylonitrile copolymers undergo some chemical and color changes during the saponification reaction. The color change can be used as the indicator of the endpoint of saponification reaction. When the color of reaction mixture turns from deep red to yellow, the graft copolymerization reaction is finished. The effect of AMPS% during graft copolymerization on saponification time of copolymerization products is presented in Table 3. Results show a gradual decrease in saponification time with the increase in the AMPS%. The hydrophile of AMPS enable alkali liquid to penetrate easily into the interior of graft copolymer, then the saponification of graft copolymer is more easiness. The shortest saponification time is 17 min when AMPS% is 6.68%. The graft copolymer will become soluble with further increase of AMPS%.

Table 3
The effect of AMPS% during graft copolymerization on saponification time of copolymerization products

AMPS%	0	3.32	4	5	6	6.68	8
Saponification time (min)	150	43	26	22	19	17	Soluble

Table 4
The result of experiments during saponification

Exp no.	Independent variables			Response
	KOH vol. (ml) (X_1)	KOH con. (mol/l) (X_2)	Sap. temp. (°C) (X_3)	Water abs. (g/g) (Y)
1	150	0.4	87	1031
2	150	0.4	97	1072
3	150	0.6	87	1191
4	150	0.6	97	1178
5	250	0.4	87	1165
6	250	0.4	97	1210
7	250	0.6	87	1130
8	250	0.6	97	1105
9	116	0.5	92	1095
10	284	0.5	92	1140
11	200	0.33	92	1087
12	200	0.67	92	1153
13	200	0.5	83.6	1205
14	200	0.5	100.0	1270
15	200	0.5	92	1354
16	200	0.5	92	1330
17	200	0.5	92	1345
18	200	0.5	92	1335
19	200	0.5	92	1350
20	200	0.5	92	1344

Exp no., experiment number; KOH vol., KOH volume; KOH con., KOH concentration; Sap. temp., saponification temperature; Water abs., water absorbency.

3.3. Optimization of saponification conditions using response surface methodology

The water absorbency of superabsorbent was influenced during the saponification by many factors such as KOH volume, KOH concentration, saponification temperature and so on. Twenty experiments were arranged according to a central composite statistical design for the study of three factors (Table 1), each at three levels and the other condition was constant.

Table 5
Analysis of variance for the regression model of water absorbency obtained from the response surface

Source	DF	SS	F	Prominence
Linear	3	9164.18	31.70	**
Quadratic	3	185323	641.05	**
Cross-product	3	22534	77.95	**
Lack of fit	5	555.65	1.36	
Total error	5	408		
Sum	19	963.65		

DF, degree of freedom; SS, sum of squares.

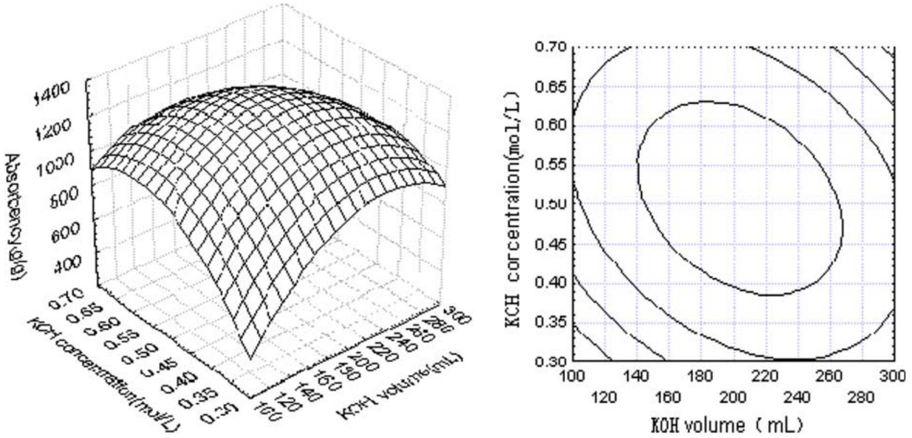


Fig. 3. The three-dimensional response surfaces and the two-dimensional contour plots for water absorbency at varying KOH volume, KOH concentration.

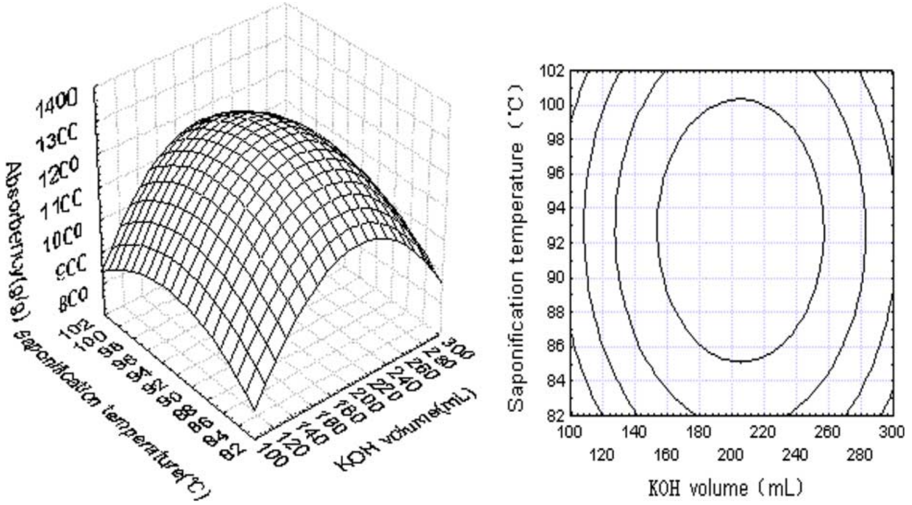


Fig. 4. The three-dimensional response surfaces and the two-dimensional contour plots for water absorbency at varying KOH volume, saponification temperature.

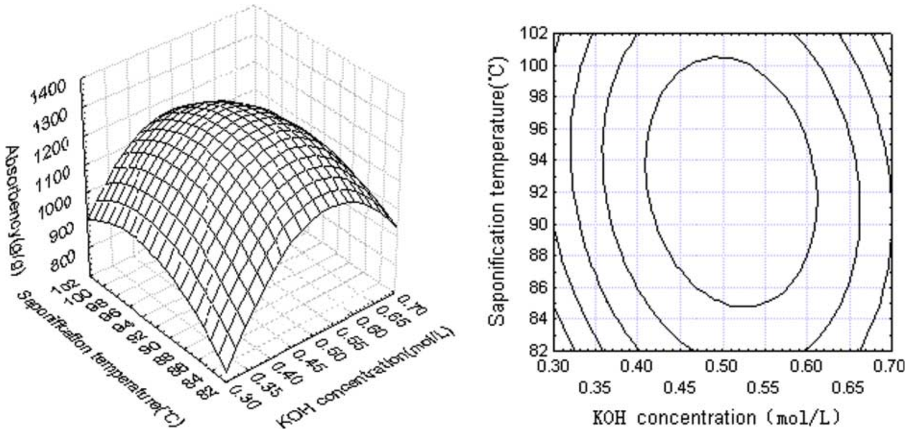


Fig. 5. The three-dimensional response surfaces and the two-dimensional contour plots for water absorbency at varying KOH concentration, saponification temperature.

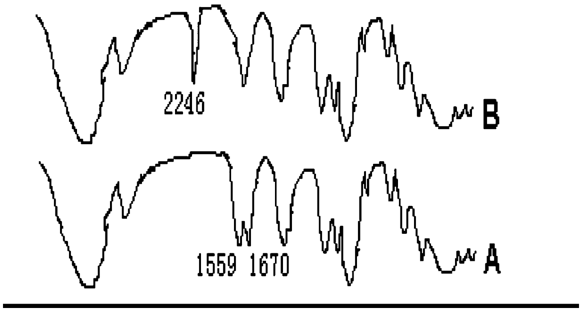


Fig. 6. IR spectra of graft polymers (B) and saponified graft polymers (A).

The experiments results on water absorbency of graft copolymers obtained at different saponification conditions are shown in Table 4.

The second order polynomial equation was used to fit these experimental data:

$$Y1 = 1342.89 + 26.37X_1 + 29.48X_2 + 22.07X_3 - 227.80X_1^2 - 138.12X_1X_2 - 2.76X_1X_3 - 225.45X_2^2 - 41.18X_2X_3 - 107.93X_3^2$$

The regression models were tested for adequacy by the analysis of variance and the data showed in Table 5.

The results from Table 5 suggested that water absorbency was determined by the all terms of the models. The results showed that the effect of every factor on response was not simple linear relationship. The lack of a fit test did not result in a significant *F* value. Figs. 3–5 present the three-dimensional response surfaces and the two-dimensional contour plots of water absorbency on factors, based on the explanatory equation given in.

It can be observed in Figs. 3–5 that the maximum response can be obtained. Canonical analysis allows the prediction of water absorbency, 1345 g/g, using the following operational conditions: KOH volume 203.7 ml, KOH concentration 0.51 mol/l, saponification temperature 92.6 °C. The shortest saponification time was 17 min. The results from three independent experiments were coincident with the estimated value. Thus the model was proven to be adequate.

3.4. Infrared spectroscopy

The IR spectra of graft polymers (B) and saponified graft polymer (A) were showed in Fig. 6. The IR spectra of graft polymers (B) showed that an obvious peak at about 2246 cm^{-1}, the characteristic absorption peak of –C≡N, was presented. The peak at about 2246 cm^{-1} was disappeared for the IR spectra of saponified graft polymer (A), but two new peaks at 1559 and 1670 cm^{-1} for –COOH and –$\mathrm{CONH_2}$ was appeared. This was showed that '–C≡N' of the graft polymers (B) was saponified into –COOH and –$\mathrm{CONH_2}$ (Fig. 6).

4. Conclusion

Rapid synthesis method of a superabsorbent from a saponified starch and acrylonitrile/AMPS graft copolymers was carried out. The addition of AMPS results in a gradual saponification time decrease for the graft polymer, then the total synthesis time decrease of superabsorbents. The hydrophile of AMPS enable alkali liquid to penetrate easily into the interior of graft copolymer, then the saponification of graft copolymer is more easiness. The maximum response at the optimal saponification conditions can be obtained using response surface methodology (RSM). The water absorbency was 1345 g/g dry superabsorbent and the shortest saponification time is 17 min, then the total synthesis time of superabsorbents is 2.5 h.

Acknowledgements

The authors appreciate the supports from the key project of Chinese Ministry of Education (01090).

References

Fanta, G. F., & Burr, R. C. (1969). *Journal of Polymer Science* , 1675–1678.

Hebeish, A., Beliakova, M. K., & Bayazeed, A. (1993). *Journal of Applied Polymer Science*, *68*, 1709.

Hebeish, A., El-Rafie, M. H., Higazy, A., et al. (1996). Synthesis, characterization and properties of polyacylamide–starch composites. *Starch/stärke*, *48*, 175–179.

Inan, M., Chiruvolu, V., Eskridge, K. M., Vlasuk, G. P., Dickerson, K., Brown, S., et al. (1999). Optimization of temperature-glycerol-pH conditions for fed-batch fermentation process for recombinant hookworm(Ancylostoma caninum) anticoagulant peptide(AcAP-5) production by Pichia pastoris. *Enzyme and Microbial Technology*, *24*, 438–445.

Lim, D. W., Whang, H. S., Yoon, K. J., & Ko, S. W. (2001). Synthesis and absorbency of a superabsorbent from sodium starch sulfate-g-polyacrylonitrile. *Journal of Applied Polymer Science*, *79*, 1423–1430.

Lu, S. J., Duan, M. L., & Lin, S. B. (2003). Synthesis of superabsorbent starch-graft-poly(potassium acrylate-co-acrylamide) and its properties. *Journal of Applied Polymer Science*, *88*, 1536–1542.

Mehrotra, R., & Ranby, B. (1977). Graft copolymerization onto starch. i. Complexes of Mn^{3+} as initiators. *Journal of Applied Polymer Science*, *21*, 3407–3415.

Pourjavadi, A., & Zohuriaanmehr, M. J. (2002). Modification of carbohydrate polymers via grafting in air. 1. ceric-induced synthesis of starch-g-polyacrylonitrile in presence and absence of oxygen. *Starch/stärke*, *54*, 140–147.

Sakiyama, T., Chu, C. H., Fujii, T., & Yano, T. (1993). *Journal of Applied Polymer Science*, *50*, 2021.

Shiga, T., Hirose, Y., Okada, A., & Kurauchi, T. (1992). *Journal of Applied Polymer Science*, *44*, 249.

United States Department of Agriculture, (1961) UA Patent 3981 100.

Vazquez, M., & Martin, A. M. (1998). Optimization of phaffia rhodoma continuous culture through response surface methodology. *Biotechnology and Bioengineering*, *57*, 314–320.

Wu, J. H., Wei, Y. L., Lin, J. M., & Lin, S. B. (2003). Preparation of a starch-graft-acrylamide/kaolinite superabsorbent composite and the influence of the hydrophilic group on its water absorbency. *Polymer International*, *52*, 1909–1912.

Yoshida, M., Asano, M., & Kumakura, M. (1989). *Eurupean Polymer Journal*, *25*, 1197.