

Swelling Behaviors of a Three-Component Copolymer (Starch Graft Sodium Acrylate and 2-Acrylamido-2-methyl-propanosulfonic Acid) Synthesized by Microwave Polymerization

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ABSTRACT: A superabsorbent of starch, 2-acrylamido-2-methyl-propanosulfonic acid (AMPS), and sodium acrylate was synthesized by microwave irradiation, and the effect of AMPS on the performance of the polymer was investigated. The best mass fraction of the three components was determined (starch/acrylic acid/AMPS = 2 : 5 : 3). The structure of the polymer was characterized by Fourier transform infrared, ^{13}C cross-polarization/magic-angle spinning NMR, and scanning electron microscopy, and the morphology of the surface of the sample was studied. The results showed that the morphology of the polymer was changed to some extent under microwave irradiation, and the swelling rate of

the polymer synthesized by microwave polymerization was faster than the swelling rate of a polymer synthesized by a traditional method. The best absorbent capacities of the product in distilled water and a 0.9% sodium chloride solution were 450 and 53 g/g, respectively. Meanwhile, the introduction of AMPS to a superabsorbent resin was an effective method for improving the performance of the polymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1050–1054, 2005

Key words: graft copolymers; irradiation; morphology; structure-property relations

INTRODUCTION

Superabsorbent polymers (SAPs) are materials that are capable of absorbing and holding large amounts of water, and they have been applied in many fields such as pharmaceuticals, agriculture, and other industries.^{1,2} With various traditional polymerization methods, including solution polymerization,³ inverse suspension polymerization,⁴ and inverse emulsion polymerization,⁵ the synthesis of SAPs has been studied for several decades. However, these traditional methods for synthesizing SAPs have many disadvantages, such as longer reaction times and complicated procedures. Recently, microwave irradiation has been widely applied to enhance chemical reactions because of its main benefits of significant rate enhancements and higher yields.⁶ Meanwhile, microwave irradiation has been used as a method of polymerization to synthesize SAPs in our previous work and that of other research groups.⁷ The absorbent capacity of a resin in water was higher, but it was lower in a sodium chloride solution; because the equilibrium of swelling of SAPs could be broken by an electrolytic solution, the vol-

ume of the gel seriously shrank in the salt solution. From a practical viewpoint, improving the tolerance toward salt solutions of a resin has become very important in the development of SAPs.

2-Acrylamido-2-methyl-propanosulfonic acid (AMPS) is an anionic monomer with high solubility (150 g/100 g of water at 25°C). Because it contains a hydrophilic sulfonic acid (SO_2) functional group and a nonionic amide group in its molecular structure,⁸ AMPS has often been used as the monomer of polymerization to improve the performance of synthesized resins.⁹ In recent years, considerable work has been done on it. However, the effects of the AMPS content and microwave irradiation on the system of polymerization and the swelling rate of resins have not yet been reported. In this study, AMPS was used as the third monomer of graft polymerization to enhance the performance of a resin; meanwhile, the swelling rate of the resin was improved. Through experimentation, we have improved the process of traditional solution polymerization by microwave irradiation. The results show, for samples of the same composition synthesized by different methods, the swelling rate of the resin synthesized by the microwave irradiation method was much faster than that of the resin synthesized by the traditional method. The effect of microwave irradiation on the swelling rate of the resin was also examined in this work.

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EXPERIMENTAL

Materials

Acrylic acid (AAc) and AMPS, as monomers, were purchased from the YiLi Chemical Group (Beijing, China). *N,N'*-Methylenebisacrylamide and ammonium persulfate were the crosslinking agent and initiator, respectively; corn starch (St), containing 27% amylase, was purchased from the DaCheng Group (Jilin, China). All reactants were analytical-grade and were used without further purification.

Microwave polymerization

A 0.375 mol/L sodium hydroxide solution (6.7 mL) was added to 4 g of a starch solution (50 wt %) to get a gelatinous starch. A 2 mol/L sodium hydroxide solution was added to pure AAc and an AMPS water solution (50 wt %) to obtain a neutralized solution; the degrees of neutralization were 85 and 95%, respectively. The aforementioned solutions, including certain weights of the initiator (0.0438 mol/L) and crosslinking agent (0.0324 mol/L), were mixed to get a well-dispersed reactant. All operations were carried out with stirring. The mixture was put into the microwave reactor under 540 W for 3 min. The dried resin was obtained without further operation. The product was smashed to gain the powder of the resin. The microwave frequency was 2450 Hz, and the highest power was 900 W. The system had five work modes (20, 40, 60, 80, and 100%).

Purification of the sample

The sample powder of the dried polymer was immersed in 400 mL of a 0.5 mol/L sodium hydroxide solution for 1 h with magnetic stirring at 50°C to remove unreacted starch. The gel was isolated by centrifugation at 4000 rpm and immersed in 400 mL of distilled water again with magnetic stirring to remove the homopolymer. The procedure was repeated several times. The solid was isolated with a large amount of acetone. The solid isolated was dried *in vacuo* at 50°C for more than 24 h.

Swelling measurements

To measure the absorbent capacity, a 0.1-g sample of the resin powder (60–80 mesh) was immersed in 200 mL of distilled water for approximately 3 h and was allowed to reach the equilibrium of swelling. Each dispersion was filtered through a 100-mesh wire, and the excess water was removed carefully from the retained gel. The absorbent capacity of the resin (Q) in distilled water or in 0.9 wt% NaCl solution was determined as follows:

$$Q = (M - M_0) / M_0$$

where M is the mass of the gel and M_0 is the mass of the dried resin.

To measure the swelling rate of the resin, a 0.1-g sample of the resin powder (60–80 mesh) was immersed in 200 mL of distilled water under mild magnetic stirring. The absorbent capacity of the resin was measured as before at definite intervals to draw a profile of the swelling percentage versus the time for individual samples.¹⁰

Analysis

A Nicolet NEXUS 360 Fourier transform infrared (FTIR) instrument was used to analyze the spectrum. The resolution for the infrared spectra was 4 cm^{-1} , and there were 32 scans for each spectrum.

¹³C cross-polarization/magic-angle spinning (CP-MAS) NMR measurements were carried out on a Bruker AM 400M NMR spectrometer (Bruker, Germany) operating at 100.56 MHz. The magic-angle spinning rate was 5 kHz, and the contact time for cross-polarization was 1 ms. 2 k free induction decays were accumulated for the sample to obtain a satisfactory signal-to-noise ratio.

The morphology of the porous structure of the resin was studied with scanning electron microscopy (SEM). The dried resin powder was coated with a thin layer of gold and imaged in a Cambridge S-360 SEM instrument (Cambridge, UK).

RESULTS AND DISCUSSION

Characterization of the structure of the polymer

To detect whether the graft polymerization existed under the condition of microwave irradiation, the FTIR spectra were measured, and the spectra of the starch, the homopolymer of AMPS, and the graft co-

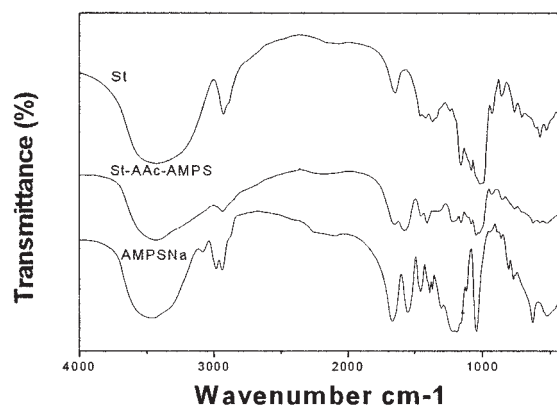


Figure 1 FTIR spectra for starch, AMPS, and starch graft sodium acrylate and AMPS.

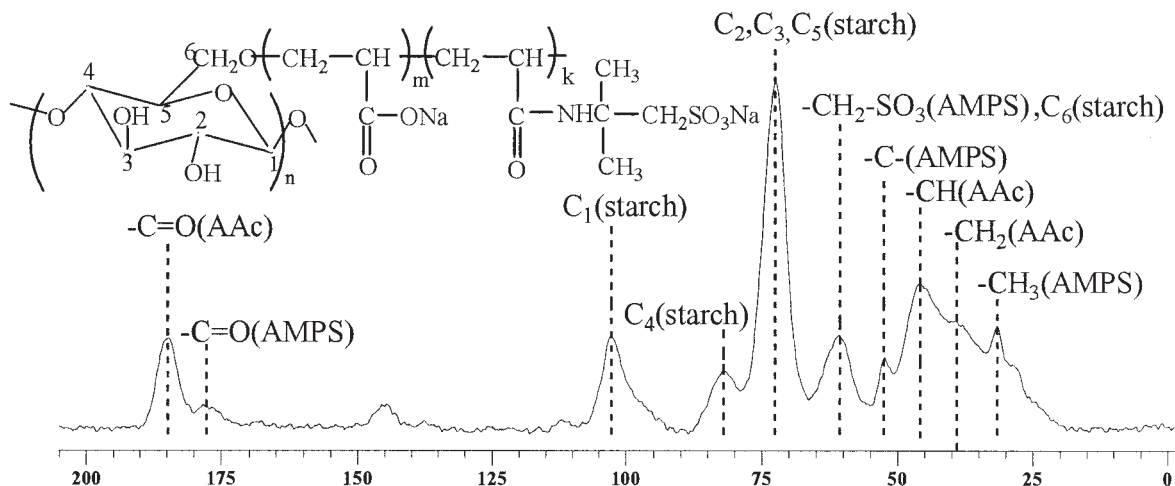


Figure 2 ^{13}C CP-MAS NMR spectrum for starch graft sodium acrylate and AMPS.

polymer of starch, sodium acrylate, and AMPS are shown as Figure 1.

In the FTIR spectra of AMPS and the purified sample, the typical asymmetric and symmetric stretch frequencies of SO_2 appear at 1219 and 1045 cm^{-1} , respectively; this confirms the graft polymerization of AMPS in the starch molecule. For AAc, the presence of the carboxylic group can be identified with the bands at 1410 and 1578 cm^{-1} . In the FTIR spectrum, the stretch frequency of free hydroxide and hydroxide banding of the C_6 atom of starch appear at 3400 and 1020 cm^{-1} , respectively.¹¹ Changes in them can provide lots of important information about the graft reaction. Compared with the curves of starch and St-AAc-AMPS, the typical stretch frequency of hydroxide, which appears at 3430 cm^{-1} , declines. The stretch frequency of hydroxide banding of the C_6 atom of starch appears at 1016 cm^{-1} . The band obviously is reduced in intensity in the spectrum of the graft copolymer. All these confirm that AAc and AMPS were grafted onto the starch backbone. On the other hand, we used ^{13}C CP-MAS NMR spectrum to detect the structure of graft copolymer of starch, AAc and AMPS (Figure 2), and the assignments of spectrum peak are given in Table 1.¹²

TABLE I
Chemical Shifts and Assignments for the Sample

| Chemical shifts (ppm) | Assignment |
|-----------------------|--|
| 31.60 | $-\text{CH}_3$ (AMPS) |
| 39.86 | $-\text{CH}_2$ (AAc) |
| 45.75 | $-\text{CH}$ (AAc) |
| 52.38 | $-\text{C}-$ (AMPS) |
| 60.73 | $-\text{CH}_2-\text{SO}_3^-$ (AMPS) |
| 62.31–102.86 | $-\text{CH}-$; $-\text{CH}_2-$ (starch) |
| 178.24 | $-\text{C}=\text{O}$ (AMPS) |
| 184.72 | $-\text{C}=\text{O}$ (AAc) |

The results also indicated that the purified sample was the graft copolymer of starch, AAc and AMPS.

Effect of the AMPS content on the absorbency of the resin

In our previous work, the graft polymerization onto starch of AAc was investigated. The results showed that the best mass ratio of starch to AAc was $40 : 100$. Thus, for this study, the same ratio was chosen. The content of AMPS was changed to investigate the effect of the AMPS content on the absorbent capacity of the resin.

The resin was immersed in distilled water and a 0.9% sodium chloride solution to measure its absorbent capacity. The water absorbency of the resin as a function of the AMPS content in the resin is shown in Figures 3 and 4. The results show that the absorbent capacity of the resin increased with increasing AMPS content. After a peak was reached, it decreased with

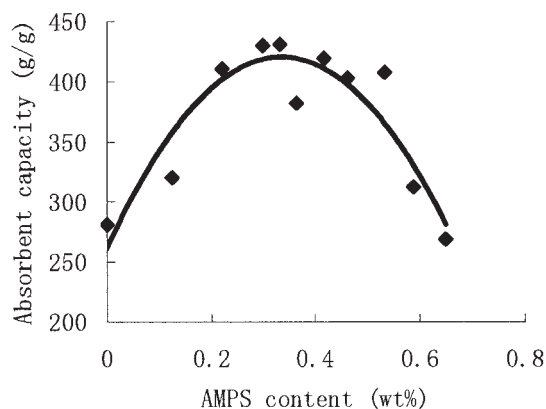


Figure 3 Effect of AMPS on the absorbent capacity of the resin in distilled water.

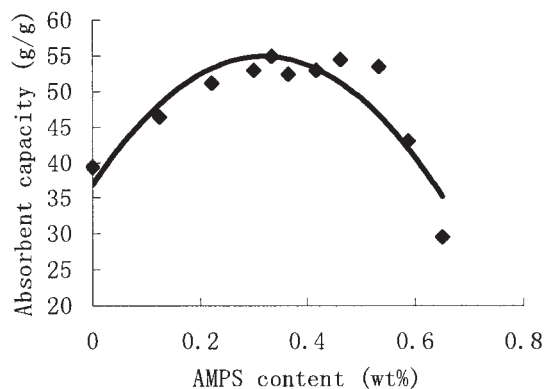


Figure 4 Effect of AMPS on the absorbent capacity of the resin in a 0.9% sodium chloride solution.

the AMPS content. The best absorbent capacities of the resin in distilled water and a 0.9% sodium chloride solution were 450 and 53 g/g, respectively.

The trend of the curves was attributed to the change in the volume of polymer networks. As far as the molecular structure of the polymer was concerned, there were SO_2 and carboxyl groups. The major factor that led to the change in the absorbent capacity of the polymer was a repulsive interaction between the charges in the chain of the polymer.¹³ The density of the charge in the chain of the polymer increased with increasing AMPS content. At a low AMPS content, there were few charges in the chain of the polymer. The repulsive interaction between the charges was weak because the distance of the charges was far. The chain of the polymer grafted into starch was relaxed. Thus, the absorbent capacity of the polymer was poor. However, at a high AMPS content, more charges were introduced into the chain of the polymer. The repulsive interaction between the charges led to the crimping of the chain of the polymer. Thus, the absorbent capacity of the polymer decreased. In summary, if the

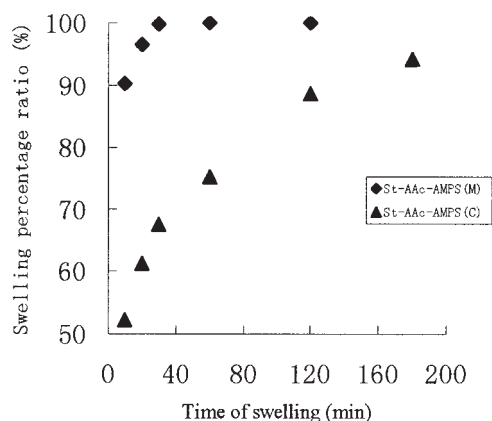
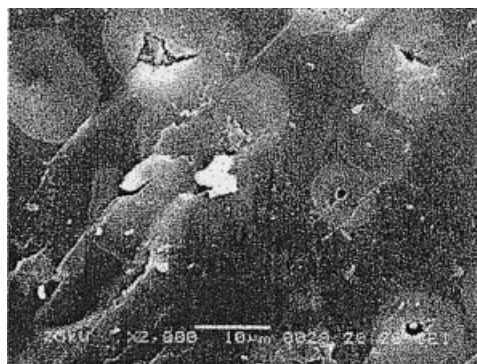


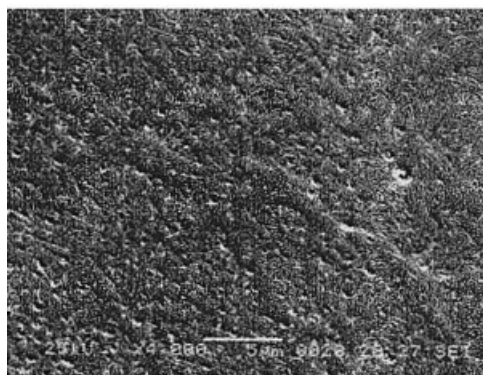
Figure 5 Relation between the swelling rate and time (M represents microwave polymerization, and C represents traditional polymerization).



(a)



(b)



(c)

Figure 6 SEM micrographs of the synthesized samples: (a) the surface of the sample synthesized by the traditional method (enlarged 2000 \times), (b) the surface of the sample synthesized by microwave polymerization (enlarged 2000 \times), and (c) the surface of the sample synthesized by microwave polymerization (enlarged 4000 \times).

density of the charge was excessively high or low, the absorbent capacity of the polymer decreased; when the density of the charge was appropriate, the repulsive interaction made the chain of the polymer stretch

more. Therefore, more water molecules could be accommodated in the networks of the polymer. With respect to the difference in the maximal value of the absorbent capacity of the polymer in water and a sodium chloride solution, it is well known that an ionic gel is deswollen in an electrolyte solution through the shielding of the repulsive interaction between chains. The results of the experiments showed that the best monomer mass fraction (starch/AAC/AMPS) was 2:5:3.

Effect of the microwave irradiation on the swelling rate of the resin

The swelling rate of a resin is closely related to the molecular structure of the polymer.¹⁴ It is well known that the conditions of synthesis seriously influence the molecular structure of the polymer. However, what change occurs in the molecular structure of the polymer by microwave irradiation? How does it influence the swelling rate of the product? To research these problems, we investigated the relation of the swelling rate and time. The samples were synthesized by different methods of synthesis.

The curves of Figure 5 show the results of experiments for polymer samples with the same composition (St/AAC/AMPS = 2 : 5 : 3): the percentage of water absorbency of the sample synthesized by microwave polymerization in 10 min with respect to that of equilibrium was 90%, but the percentage of the polymer synthesized by traditional solution polymerization was only 50% under the same conditions. The times at which they reached the equilibrium of swelling were 30 min and 2.5 h, respectively.

To further study the causes of the different swelling rates of the resin, the morphology of the surfaces of the samples was investigated with SEM. The results of SEM showed obvious differences existing between the surface of the resin prepared by microwave irradiation and by the traditional method. Enlarging the image of the sample synthesized by the traditional method by

2000 \times [Fig. 6(a)], we found several pores with unregulated shapes in the micrograph. However, under the same conditions, there were many well-dispersed pores in the surface of the sample synthesized by microwave polymerization, and the pore size was also even [Fig. 6(b)]. When the image of the sample synthesized by microwave polymerization was enlarged by 4000 \times [Fig. 6(c)], well-dispersed even pores could be seen more clearly. Through an analysis of the results of Figures 5 and 6, it can be concluded that the different swelling rates for the two kinds of resins were due to the different morphologies of the surfaces of the samples. The resin was synthesized and dried in one step under microwave irradiation. After the water on the surface and inside the resin quickly evaporated, steam bubbles left pores in the resin. Therefore, a large number of pores with an even size were produced on the surface. In comparison with microwave polymerization, the temperature of the reaction was too low to create bubbles by the traditional method, and the gelatinous product was dried by the common method, so there were fewer pores in the product.

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