Crosslinking of Corn Starch with Sodium Trimetaphosphate in Solid State by Microwave Irradiation

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ABSTRACT: Corn starch was crosslinked with sodium trimetaphosphate (STMP) in solid state under microwave irradiation to improve the degree of substitution (DS) and decrease the reaction time. The effects of modification factors on the crosslinking of starch were systematically studied. It was found that the microwave irradiation provided a convenient and efficient method to prepare crosslinked starch with sufficient DS. The DS value of crosslinked starches obtained by microwave irradiation was significantly improved and the reaction time was also dramatically decreased to achieve an appropriate DS value by microwave irradiation, when compared with using traditional method. The high microwave power provided faster reaction kinetics to obtain the desired DS value at an identical reaction condition. If the reaction temperature is lower than the decomposition temperature of crosslinked starch, the higher DS value can be achieved at the higher microwave power. It was detected that the DS data obtained by reacting intermittently was higher than those by reacting continuously. It was also noticed that DS data varied drastically with the increasing of the amount of STMP and sodium carbonate. The swelling ratio of crosslinked starch in water was lower than that of native starch because of the nongelatinization of highly crosslinked starch. SEM analysis indicated that the crosslinking of corn starch by microwave irradiation caused no significant changes in the microstructure of starch granules. Light microscope analysis also showed the uniformity of so-prepared crosslinked corn starch applying microwave irradiation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5854–5860, 2006

Key words: crosslinking; starch; sodium trimetaphosphate; solid state; microwave irradiation

INTRODUCTION

Crosslinked starches are resistant to high temperature, low pH, and high shear, and improve viscosity and textural properties of the native starch.[1–3] They are widely used as thickeners in food, animal feed, beverage, and pharmacy industry. Crosslinking is performed by treating granular starch with bifunctional or multifunctional reagents capable of forming ether or ester linkages with hydroxyl groups in starch. These bifunctional or multifunctional reagents include monosodium phosphate, sodium trimetaphosphate (STMP), sodium tripolyphosphate, epichlorohydrin, phosphoryl chloride, a mixture of adipic and acetic anhydrides, and a mixture of succinic anhydride and vinyl acetate. Among them, STMP is one of the most important food additives and a solid of low toxicity. The traditional methods to crosslink starches with STMP are usually carried out at warm temperature in an aqueous slurry.[3–5] However, it is difficult to reach high degree of crosslinking in short period applying the conventional approaches. Therefore, we employed the microwave irradiation for preparation of crosslinked starch to achieve high degree of substitution (DS) within a short period of reaction time.

Currently, a significant attention has been paid to the use of microwave irradiation in organic synthesis. Microwave dielectric heating not only raises the energy of the molecules rapidly, but also provides a different heating approach from traditional conductive heating. Consequently, more molecules become energized under microwave dielectric heating, which usually results in rapid reaction rates.[6]

Most experiments utilizing microwave irradiation are carried out in liquid phase.[7,8] Unfortunately, this method does not favor to fabricate the crosslink starch with STMP, because of the gelatinizing property of starch. Recently, some researches have been reported to modify starch by microwave irradiation in solid state.[9–12] However, few researches have been conducted to crosslink starch with STMP in solid state by microwave irradiation.

The main objective of this work is to study the effects of fabrication parameters on the crosslinking degree of corn starch with STMP in solid state by

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microwave irradiation. From our investigation, it is found that the method used to prepare crosslinked starch is cost-effective and ready to obtain the product with high degree of crosslinking with a fast kinetics. The originality of our investigation is attributed to the systematic study on crosslinking parameters.

EXPERIMENTAL

Materials and equipment

Corn starch was purchased from Jincheng Corn Development (Changchun, China). Sodium trimetaphosphate (STMP) was self-made according to the literature.[13] All other reagents were A.R. grade and were used as received. The irradiation was carried out in a WD900ESL23I-3 Galanz microwave oven emitting 2450 MHz microwave frequency, with microwave output power 900 W, cavity dimentions 215 mm $\times$ 350 mm $\times$ 330 mm, and valid area of rotating table 0.077 m^2.

Preparation of crosslinked corn starch

Preparation of mixed reactants

Distilled water (970.00 mL) containing STMP (1.25 $\times$ 10^{-1} mol) and sodium carbonate (3.33 $\times$ 10^{-1} mol) was added into corn starch (10.00 mol of anhydroglucose units). These reactants were mixed thoroughly and then dried at 40°C in a thermostatic oven for 24 h. The mixed reactants were grounded evenly before being used. The water content in the mixed reactants was determined to be 8.16 wt %, and this mixture of reactants was used for investigating the effects of microwave power, reaction time, and reaction patterns on the degree of substitution (DS).

In addition, mixed reactants with different content of water were prepared as follows: water (97.00 mL) containing STMP (1.25 $\times$ 10^{-2} mol) and sodium carbonate (3.33 $\times$ 10^{-2} mol) was added into the corn starch (1.00 mol of anhydroglucose units). The six blends were mixed thoroughly and then were dried at 40°C for different times. The six mixed reactants were grounded evenly before being used. The water content in each blend was determined to be 17.53, 15.34, 13.53, 10.22, 8.06, and 6.37 wt %, respectively. The six mixed reactants were used to investigate the effect of the content of water in mixed reactants on DS.

Microwave irradiation treatment

The mixture of reactants (20 g) was irradiated in a glass beaker (250 mL), sealed with a perforated polyethylene film, under a certain microwave power for various time period ranging from 20 to 360 s. Then, distilled water (30 mL) was added into the beaker. The mixture was stirred and was adjusted to the pH of 6.5 by adding 1 mol/L sulfuric acid.[14–17] The as-prepared crosslinked starch was filtered and washed with sufficient amount of water until no phosphorus was determined in the filtrate. The starch was dried at 40°C until the content of water in the starch was less than 20 wt %. At last, the crosslinked starch was dried at 105°C for 2 h before the determination of the content of bound phosphorus in it. One blank sample was prepared by washing the mixed reactants that had not been irradiated until no phosphorus was determined in the filtrate.

Determination of bound phosphorus in crosslinked starch and calculation of the degree of substitution

Phosphorus in crosslinked starch and filtrate was determined by ICP-AES (Mattson, spec-II). Bound phosphorus in crosslinked starch was calculated by subtracting the phosphorus in blank from the total phosphorus in crosslinked starch. The degree of substitution (DS) was calculated according to the equation shown:[5]

$$\mathrm{DS} = \frac{162P}{30.974(100 - 3.8734P)}$$

where P is the percent content of bound phosphorus and the reported values are the averages of three determinations of each sample.

Determination of the swelling ratio of starch

Distilled water (25 mL) was added into a beaker (100 mL) containing dry starch (0.5 g). After agitating evenly, the beaker was heated in water bath with constant temperature of 82–85°C for 2 min. The slurry was formed and kept stirring continuously. The slurry was cooled to the room temperature, and two small aliquots of 10 mL of the slurry were collected and placed into the centrifugal tubes, which had been weighed respectively. The two centrifugal tubes were symmetrically placed in the centrifugal machine and centrifugalized for 2 min at a speed of 4000 rpm. Then the water at upper strata was taken out, and then the centrifugal tubes containing wet sediments were weighed accurately. These centrifugal tubes containing wet sediments were dried in the thermostatic oven to obtain constant weights. The centrifugal tubes containing dry sediments were weighed, respectively, to calculate the swelling ratio of starch. This swelling ratio was calculated using the following equation:

$$\text{Swelling ratio } (\%) = \frac{m_1}{m_2} \times 100$$

where m_1 was the weight of wet sediment and m_2 was the weight of dry sediment, and the reported

values are the averages of three determinations of each sample.

Analysis of thermal stability and microstructure

Thermogravimetry (TG) analysis was carried out using PerkinElmer TGA7 thermogravimetric analyzer in an inert atmosphere at a heating rate of 10°C/min. The morphology of starches was characterized by KYKY-1000B scanning electron microscope. A lightly crosslinked starch prepared by microwave irradiation was heated in excess water at 95°C, and the swelled starch was examined under an Olympus BX51 light microscope with iodine staining to determine whether all granules were swelled uniformly.[8]

RESULTS AND DISCUSSION

Effects of microwave power and reaction time on DS

To investigate the effects of microwave power and reaction time on DS, the experiments were carried out under different microwave powers and different continuous reaction time. The results are shown in Figure 1.

As shown in Figure 1, in the three cases, 450, 270, and 90 W, the DS increased to a highest value when reaction time was 40 s, 3 min, and 4 min, respectively, and then decreased with the increasing of reaction time. The reasonable explanation is due to the chance of collision between reactants increased with the increasing of reaction time, and the DS thus increased correspondingly. On the other hand, the temperature of the system would increase, which will possibly result in the decomposition of the starch. When the temperature of the system was higher than the decomposition temperature of crosslinked starch, the crosslinked starch began to decompose gradually, and consequently the DS tended to decrease with the increasing temperature. It is noticed that the color of starch has changed when microwave radiation was executed at high power and long reaction time, such as 450 W and 3 min, respectively. From Figure 1, it is also detected that the higher the microwave power was, the more rapidly the DS varied with the reaction time. In short, if the operating temperature of reaction system is lower than the decomposition temperature of starch, the DS will increase with the increasing of reaction time. It is safe to conclude that the higher DS was attributed to a higher microwave power if the starch was thermally stable and no decomposition of starch studied occurred. To control the crosslinking reaction readily, the suitable microwave powers were 270 W and 90 W. With respect to the high DS of crosslinked starch preparation, 270 W was more favorable. We found that the DS ranging from 1.60×10^{-2} to 1.90×10^{-2} of crosslinked starch obtained by microwave irradiation was about one order higher than that of 0.70×10^{-2}, by traditional method at identical condition.

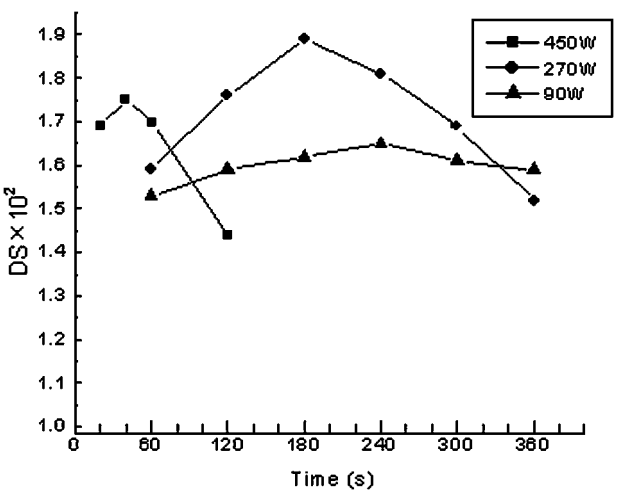

Figure 1 Effects of microwave power and reaction time on DS.

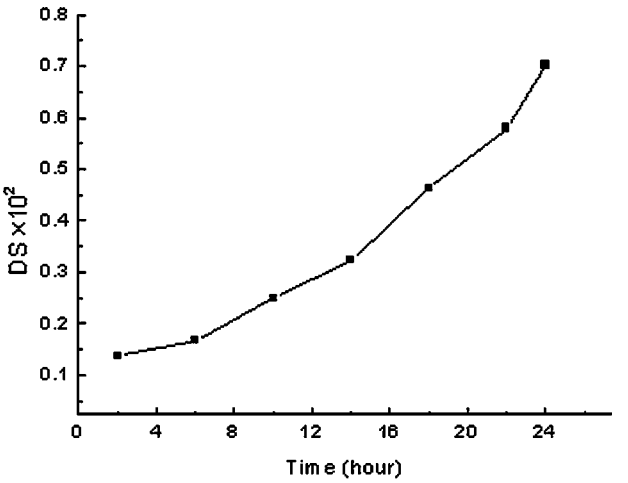

Figure 2 The DS under different reaction time by traditional method.

In addition, the reaction time was dramatically decreased to obtain a satisfactory DS by microwave irradiation when compared with the traditional method. To compare these two methods, the DS under different reaction time by the traditional method was also investigated.[5] The reaction time of traditional method were shown in Figure 2. At microwave power of 270 W, the reaction time is $\sim$ 3 min to achieve the average DS of 1.89×10^{-2}, while it will take 24 h by traditional method to obtain a DS of 0.70×10^{-2}. The results depicted that the reaction kinetics has been improved by one order in magnitude using microwave irradiation.

Furthermore, by microwave irradiation, 57.39% of the phosphorus in STMP mixed with starch became esterified to the starch when DS was 1.89×10^{-2}. But by traditional method, only 13.38% of the phosphorus in STMP became esterified to the starch when DS was 0.70×10^{-2}. So, microwave irradiation is an efficient method to prepare crosslinked starch.

Effect of reaction patterns on DS

When microwave power was 270 W, we also investigated the effect of reaction patterns on DS. The mixed reactants were heated by microwave irradiation intermittently, i.e., there was an interval of 10 min between every reaction time of 1 min. The results are shown in Figure 3, compared with that of 270 W under continuous pattern.

We can see from Figure 3 that the DS of reacting intermittently is higher than that of reacting continuously. This is possibly because the time that the starch was under the temperature of undecomposition was longer when reacting intermittently than reacting continuously. This indicates that reacting intermittently is preferable than reacting continuously to obtain the high DS.

Effect of the amount of STMP in mixed reactants on DS

The amount of STMP apparently affects the DS in crosslinking starch by traditional method.[4] The effect of the amount of STMP in mixed reactants on DS was also investigated by microwave irradiation in this article. The method of preparation of mixed reactants and microwave irradiation treatment was essentially the same as the preparation of crosslinked corn starch. Seven mixed reactants were prepared and all were irradiated by microwave under 270 W for 2 min. The

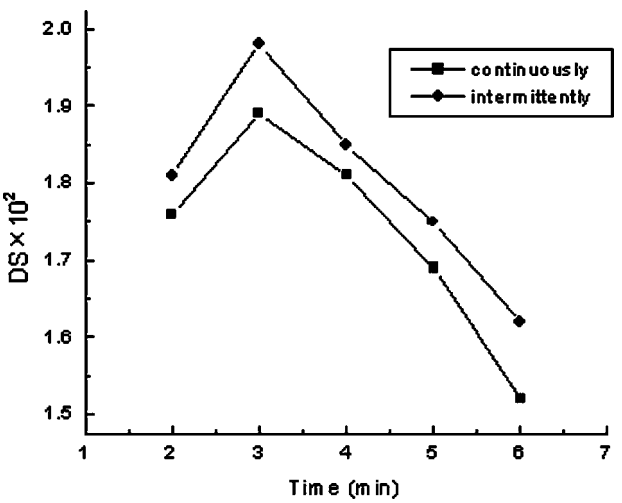

Figure 3 Effect of reaction patterns on DS.

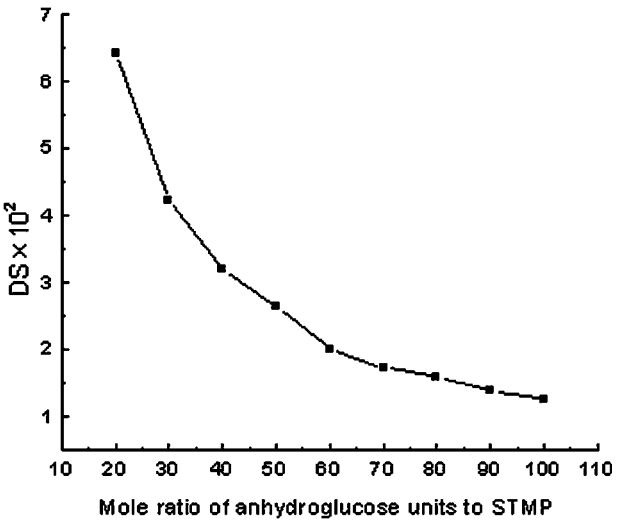

Figure 4 Effect of the amount of STMP in mixed reactants on DS.

mole ratio of anhydroglucose units to sodium carbonate was 20:1 in every mixed reactant. The mole ratio of anhydroglucose units to STMP were 100 : 1, 90 : 1, 80 : 1, 70 : 1, 60 : 1, 50 : 1, 40 : 1, 30 : 1, and 20 : 1, respectively. The results are shown in Figure 4.

As can be seen from Figure 4, the DS increased markedly with the decreasing of the molar ratio of anhydroglucose units to STMP, i.e., with the increasing of STMP in mixed reactants. The reason is that the effective collision between STMP and starch increased with the increasing of the amount of STMP, when microwave irradiation was carried out, and the DS thus increased correspondingly. If the ratio of anhydroglucose units to STMP was less than 20 : 1, it is difficult to dissolve the STMP in corresponding volume of water. This makes it impossible to increase DS further by increasing the amount of STMP.

Effect of the amount of sodium carbonate in mixed reactants on DS

When crosslinking starch was prepared by traditional method, the pH of the slurry influenced the DS markedly.[5,9] So, the effect of the amount of sodium carbonate in mixed reactants on DS was investigated by microwave irradiation. Six mixed reactants were prepared and irradiated by microwave under 270 W for 2 min. The mole ratio of anhydroglucose units to STMP was fixed at 60 : 1 in every mixed reactant. The mole ratio of anhydroglucose units to sodium carbonate were 60 : 1, 50 : 1, 40 : 1, 30 : 1, 20 : 1, and 10 : 1, respectively. The results are shown in Figure 5.

From Figure 5, we can see that the amount of sodium carbonate in mixed reactants affects the DS, just as traditional method did. First, the DS increased with the increasing of the amount of sodium carbonate. When the mole ratio of anhydroglucose units to so-

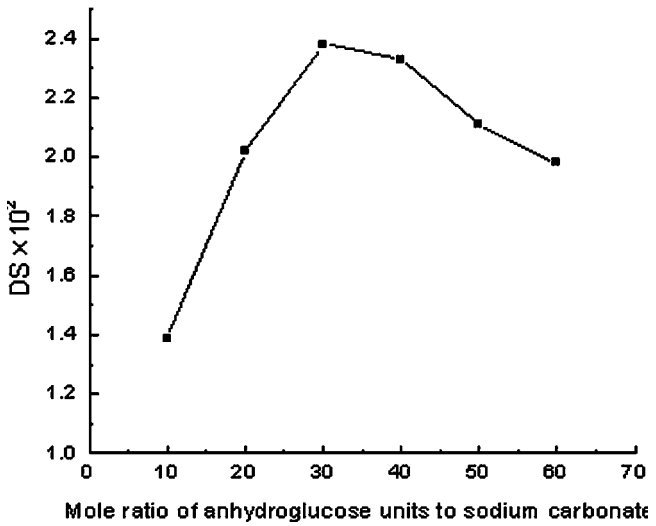

Figure 5 Effect of the amount of sodium carbonate in mixed reactants on DS.

dium carbonate was 30 : 1, the DS reached the highest value of 2.38 $\times$ 10^{-2}, and then the DS decreased with the addition of sodium carbonate. It is known that sodium carbonate functioning as a catalyst can weaken the hydrogen bond between molecules of starch, and make the molecules of starch swell, so as to activate the hydroxyls of starch. This is the reasonable assumption that the DS increases with the increasing of the amount of sodium carbonate.

On the other hand, Figure 5 depicted that the DS decreased when the mole ratio of anhydroglucose units to sodium carbonate was lower than 30 : 1. To understand the mechanism, thermogravimetric analysis of native starch and four mixed reactants with different amounts of sodium carbonate were carried out. The results are shown in Figure 6 and Table I.

Figure 6 indicates that with the increasing of sodium carbonate, the decomposition temperature of starch decreased gradually. When the temperature of reaction system was lower than the decomposition temperature of starch, the starch did not decompose.

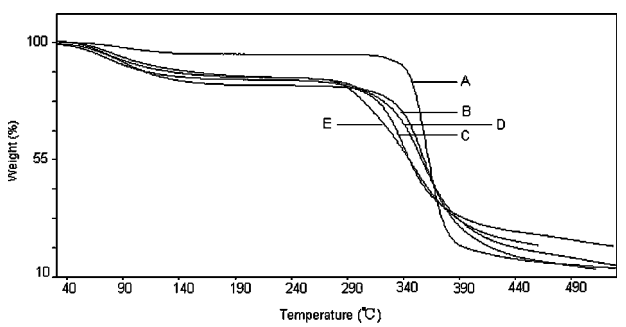

Figure 6 Thermogravimetric analysis of native starch and mixed reactants with different mole ratio of anhydroglucose units to sodium carbonate: (A) native starch; (B) 40 : 1; (C) 30 : 1; (D) 20 : 1; (E) 10 : 1.

TABLE I
Decomposition Temperature of Starch

Mole ratio of anhydroglucose units to Na_2CO_3	Decomposition temperature (°C)
Native starch	344.5
40 : 1	315.71
30 : 1	314.14
20 : 1	306.43
10 : 1	282.62

In this condition, more sodium carbonate can activate more hydroxyls of starch. So, the DS increased with the increasing of the amount of sodium carbonate first. But, Figure 6 shows that more sodium carbonate can lower the decomposition temperature of starch. When sodium carbonate reached a certain amount, the decomposition temperature of starch could be lower than the temperature of reaction system, and the starch had been decomposed at that temperature. The decomposition temperature decreased with the increasing of sodium carbonate, and this caused the decreasing of DS. Why sodium carbonate can lower the decomposition temperature of starch needs to be studied in-depth.

Effect of the content of water in mixed reactants on DS

Six mixed reactants with different content of water prepared earlier (refer Preparation of mixed reactants section) were used to investigate the effect of the content of water in mixed reactants on DS. The method of microwave irradiation treatment was the same as mentioned earlier. The blends were all irradiated under 270 W for 2 min. The results are shown in Figure 7.

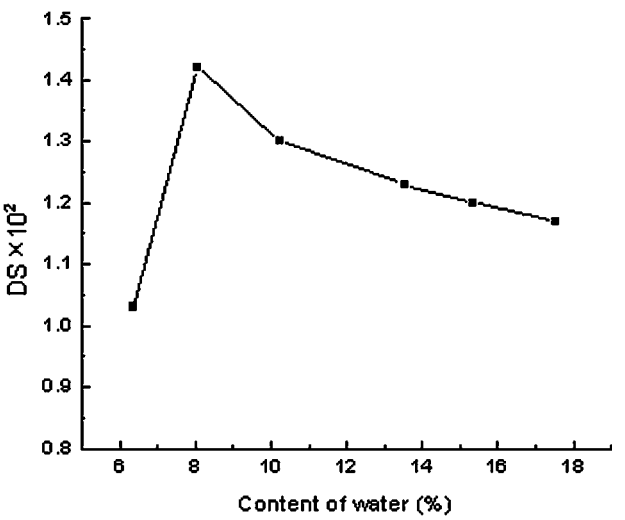

Figure 7 Effect of the content of water in mixed reactants on DS.

From Figure 7, we can see that with the decreasing of the content of water in mixed reactants, the DS increased until it reached a maximum. When the content of water was 8.06 wt %, the DS was the highest of 1.42×10^{-2}. With increasing the water component, the DS value tended to decrease accordingly. The reason is corresponding to the time-temperature profiles published in Grazyna's paper,[14] in which it is reported that with the samples of low moisture content, a rapid rise in temperature was observed, while for those with a higher moisture content the rise was much less pronounced. It is noticed that the temperature of reaction system increased rapidly with the decreasing of the content of water. Once the temperature was higher than the decomposition temperature of starch, the starch began to decompose, which results in the decrease in DS correspondingly. The temperature of reaction system is found to be higher than the decomposition temperature of starch with a water content of 6.37 wt %. Consequently, the DS decreased accordingly. Meanwhile, we can conclude that provided the temperature of reaction system is lower than the decomposition temperature of starch, the higher the temperature of reaction system is, the higher the DS is.

Comparison of the swelling ratio between native starch and crosslinked starches

Swelling ratio of native starch and crosslinked starches are shown in Figure 8. We can see from Figure 7 that the swelling ratio of native starch in which the DS was zero was much higher than that of crosslinked starches and the swelling ratio of those crosslinked starches were close to each other. This is because the crosslinking of starch restrains the gelatinization of starch granule. The crosslinked starches remain their granule states in hot water with limited swelling. The swelling ratio of crosslinked starch has correlation with the DS of it. The higher the DS is, the lower the swelling ratio is.

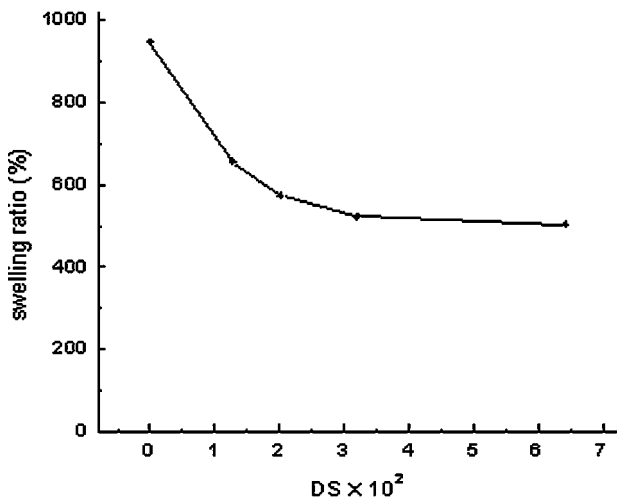

Figure 8 Compare of swelling ratio between native starch and crosslinked starches.

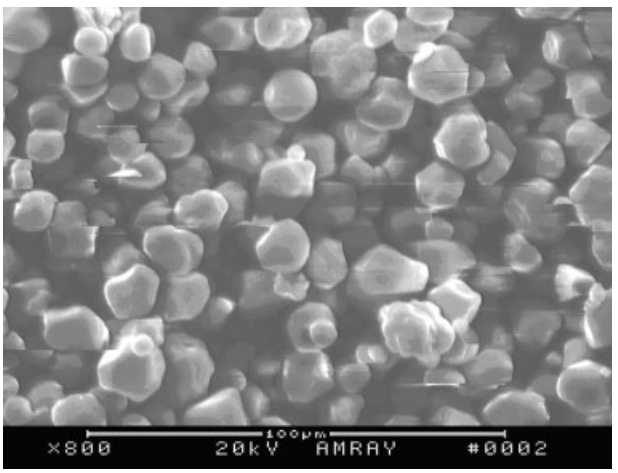

Figure 9 SEM of native starch.

SEM analysis

Figures 9 and 10 show the top-view morphology of native starch and crosslinked starch, respectively. From these two images, it is readily visible that there is no significant change in microstructure of native starch and crosslinked starch, which indicated that the crosslinking by microwave irradiation had no negative effect on the morphology of starch.

Light microscope analysis

It is generally accepted that microwave heating is known to be nonuniform. To determine the uniformity of the crosslinked corn starch formed applying

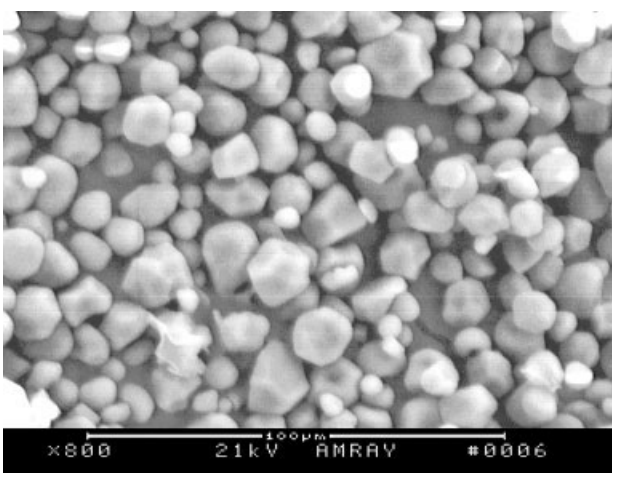

Figure 10 SEM of crosslinked starch.

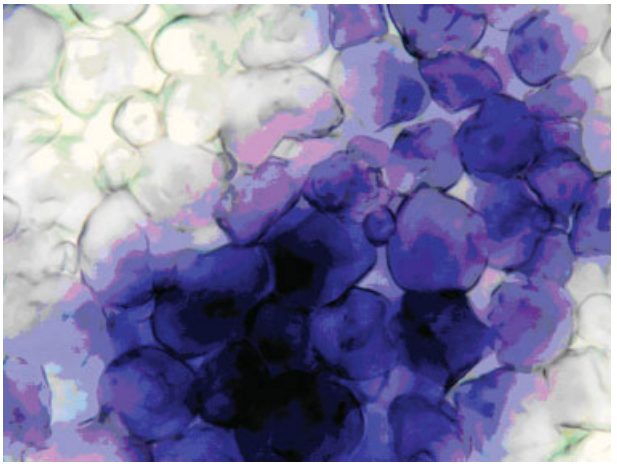

Figure 11 Light microscope of crosslinked corn starch prepared by microwave irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

microwave irradiation, light microscope analysis was carried out. It can be seen from Figure 11 that almost all granules swelled uniformly. This indicates that the crosslinking of corn starch by this method is uniformly proceeded.

CONCLUSIONS

- Microwave irradiation is an efficient method to prepare crosslinked starch. The higher the microwave power is, the more rapidly the DS varies with the reaction time. In the case of undecomposition of starch, the higher the microwave power is, the higher the DS is. To control the reaction easily, the suitable microwave powers are 270 W and 90 W. Meanwhile, reacting intermittently is more preferable than reacting continuously to obtain a higher DS.
- The amount of STMP and sodium carbonate in mixed reactant affect the DS markedly. The content of water in mixed reactants also affects the DS because it affects the temperature of reaction system.
- Swelling ratio of crosslinked starch is much lower than that of native starch because of the nongelatinization property of highly crosslinked starch.
- SEM analysis indicated that the crosslinking of corn starch by microwave irradiation caused no significant changes in the structure of starch granules. Light microscope analysis showed that the crosslinking of corn starch by this method is uniform.

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