ORIGINAL RESEARCH PAPER

PREPARATION AND PROPERTIES OF OXIDIZED STARCH NANOPARTICLES

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Abstract: Starch nanoparticles (SNP) were prepared by traditional sulfuric acid hydrolysis using corn starch as raw material, and SNP was oxidized by potassium bromate ($KBrO_3$) to prepare oxidized starch nanoparticles (OSNP). The structure and properties of SNP and OSNP were characterized by Fourier transform infrared spectrometer, X-ray powder diffractometer, laser particle size analyzer and dispersion test experiment. The results showed that native starch was transformed from micro grade (6 - 10 μm) to nano grade with the formation of SNP (240 nm) and OSNP (180 nm). Compared with native starch, OSNP has good dispersibility due to its small particle size and negative charges, which will expand its application areas by combing the advantages of oxidized starches and nanoparticles.

Key words: *oxidized starch nanoparticles, preparation, characterization*

INTRODUCTION

Starch is a kind of native polymer material and a natural green reagents material. It has been widely used in food, papermaking, textile and cosmetics industry due to its characteristics of biocompatibility, biodegradability and bioadhesion. In addition, starch is cheap, renewable and widely available; it can come from the roots, stems, seeds and fruits of wheat, corn, potato and other plants [1 – 4]. However, the poor water-solubility, dispersibility and fluidity limits its application scope. Therefore, starch needs to be modified to improve its applicability. Up to now, multiple modification methods (chemical, physical and biological) have been utilized to widen its application. It is still attractive to explore new starch derivatives with new functions and features.

Starch nanoparticles (SNP) are nano-sized particles obtained by physical, chemical or biological treatment of native starch. SNP has become a research hotspot due to its advantages of small particle size, large specific surface area, surface effect, high strength, etc. Starch nanoparticles can be applied in various aspects of food, medicine, packaging and processing [5, 6]. However, SNP is easy to agglomerate in water which limits its application. There is a need to modify SNP to improve its dispersibility.

On the other hand, the hydroxyl groups in SNP can be selectively oxidized into carboxyl groups to form oxidized starch nanoparticles (OSNP). OSNP is easy to be deprotonated and the formed negative charges can hinder the aggregation of starch particles and increase its dispersibility. Up to now, oxidized starch has been widely used in food, paper making, textile, packaging, construction industry and medical fields [7 – 10] because of its low viscosity, high stability, film-forming property and binding property. Therefore, OSNP combining the merits of SNP and oxidized starch will enhance its properties and expand its application. Specifically, OSNP have large specific surface area, large negative charge and greatly improved adsorption capacity, which can endow it with new functions used as a good adsorbent to adsorb heavy metal ions or dyeing auxiliaries in wastewater. Muhammad [11] reported the preparation of OSNP by chemical dissolution and non-solvent precipitation method. In this paper, SNP was prepared through traditional sulfuric acid hydrolysis and it was further oxidized by bromate oxidation ($KBrO_3$). The structure and properties of native starch, SNP and OSNP were characterized by Fourier infrared spectrometer, X-ray powder diffractometer, laser particle size analyzer and the dispersibilty of OSNP was examined.

MATERIALS AND METHODS

Materials and characterization methods

Corn starch, Changchun Dacheng Corn Starch Co. LTD; $KBrO_3$, Tianjin Deen Chemical Reagent Co. LTD; H_2SO_4, Tianjin Fuyu Fine Chemical Co. LTD; Absolute ethanol, Luoyang Haohua Chemical Reagent Co. LTD.

High-speed centrifuge, LG 10-2.4 A, Changsha Yingtai Instrument Co. LTD; Fourier infrared spectrometer, Spectrum One, American PE Instrument Company; X-ray powder diffractometer, D8ADVANCE, Brock Instruments Germany; Malvern laser particle size analyzer, MS3000, UK Malvern Instruments Limited.

Preparation of starch nanoparticles (SNP)

SNP was prepared according to Angellier H [12] with some modifications. A starch suspension (14.7 %, w/v) was prepared by putting 10 g corn starch in 56.6 mL dilute sulfuric acid solution (3.16 M), stirred and hydrolyzed for 5 days at 35 $^{\circ}$C and 500 r·min^{-1}. The reaction was stopped by adjusting the pH value to neutral with 1 M NaOH. The sample was precipitated, washed by anhydrous ethanol, dried naturally in air and then grounded to powder.

Preparation of oxidized starch nanoparticles (OSNP)

OSNP was prepared with SNP as raw material and with $KBrO_3$ as oxidant. 5.0 g SNP, 5.41 g $KBrO_3$ and 20 mL deionized water were stirred in a 100 mL three-necked flask, and 9 mL H_2SO_4 (1.67 M) was added dropwise within 60 min. After reacting at room temperature for 24 h, the reaction was stopped by adjusting the pH value to neutral with 1 M NaOH. The slurry were precipitated with ethanol, washed with the mixture of distilled water and ethanol (1 : 10, v:v), and dried naturally in the air.

Determination of carboxyl group content of OSNP

The carboxyl content of OSNP was determined according to the modified procedure of Komulainen [13]. 1 g dry OSNP were dispersed in 200 mL distilled water in a beaker, and its pH was adjust to 3.0 with 0.1 M HCl at room temperature. The mixture was stirred for 0.5 h, and titrated to pH 8.0 with 0.1 M NaOH standardized solution. Native corn starch was used as blank sample. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU) and calculated by the following Equation 1.

$$\frac{COOH}{100GU} = \frac{(V_1 - V_2) \times M \times 0.045 \times 100}{W}$$
(1)

Where V_1 is the volume of NaOH required for the OSNP (mL), V_2 is the volume of NaOH used to test the blank (mL), M is the molarity of NaOH and W is the sample weight.

FTIR analysis

An appropriate amount of samples were mixed with KBr and grinded under the irradiation of infrared lamp; the ground mixture powder was compressed into a transparent thin tablet. The IR spectra were measured with KBr tablet as a blank control within the wavelength range of 4000 ~ 400 cm^{-1}, and the average value was obtained after 45 scans.

X-ray diffractometer analysis

The X-ray diffraction pattern of the sample was obtained with an X-ray diffractometer (Bruker, Germany). The parameters were set as follows: starting Angle: 2 θ = 5°; Termination Angle: 2 θ = 40°; Scanning step length: 0.05°; Scanning speed: 5°·min^{-1}; Integration time 2 s; Pipe flow: 15 mA; Pipe pressure: 30 KV; Slit: DS, SS 1.0 mm, RS

0.1 mm [14]. The crystallinity was calculated according to the method provided by Amaya-Llano et al. (Equation 2) [15, 16].

$$Xc - \frac{Ac}{Ac + Aa}$$

(2)

where: Xc is relative crystallinity; Ac and Aa represent the crystalline area and the amorphous area in the diffraction pattern, respectively.

Particle size determination

The particle size distribution of native corn starch and the modified was measured by Malvern laser particle sizer. The measured samples were diluted by deionized water with a sample concentration of 0.01 % (m/V). The refractive indexes of dispersant and particles were set to 1.33 and 1.53 respectively. The average value was taken for the three measurements [17].

Dispersion test

The solution of 1 % native starch and oxidized starch nanoparticles were prepared and oscillated by ultrasonic for 20 minutes, and then 10 mL of each dispersion was put into a test tube. A photo of each sample was taken after a moment.

RESSULTS AND DISCUSSION

Carboxyl group contents of OSNP

The carboxyl group content of OSNP determined by conventional titration was 8.73 %. Compared with the oxidized starch prepared by Nathan Levien Vanier [18], the carboxyl content is higher, which is caused by different sources of starch, different reaction conditions, different types of oxidants and the dimension of oxidized starch [19].

FTIR analysis

The IR spectra of native starch, SNP and OSNP were shown in Figure 1. The absorption peak at 1645 cm^{-1} is a typical band of starch and its derivatives, which is caused by the bending vibration of H_2O [20]; The absorption peak at 3200-3600 cm^{-1} belongs to the O-H bond stretching vibration peak of the glucose unit, the C-H stretching vibration absorption peak of -CH_2 appears at 2931 cm^{-1}, and the stretching vibration absorption peak of C-O-C bond on the glucose ring is at 1158 cm^{-1}. Compared with native starch, the characteristic peak of SNP has almost no change, but the absorption peak of O-H at 3370 cm^{-1} is enhanced, indicating that the association effect of O-H in the molecular structure of SNP is weakened, and the bending vibration peak of O-H at 1645 cm^{-1} is weakened due to the removal of the bound water in starch particles [17]. Compared with the native starch, OSNP has a new strong peak at 1740 cm^{-1}, which is attributed to the stretching vibration peak of C=O, indicating the formation of carboxyl group [19].
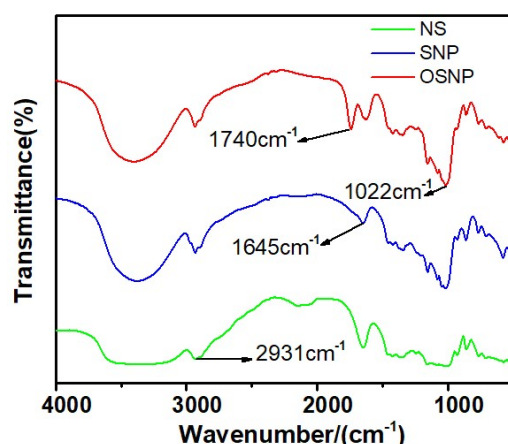
Figure 1. FT-IR spectra of native starch and modified starch

X-ray diffraction analysis

The X-ray diffraction pattern of native starch, SNP and OSNP are shown in Figure 2. The native starch and modified starch are all typical type A structure indicating by the presence of the strong and intense peaks at 5°, 17°, 18° and 23°. Compared with the native starch, the diffraction peak of SNP is sharper, and the crystallinity of SNP (57 %) is more than that of native starch (29 %). The reason is that the amorphous structure of the native starch is destroyed in some degree during the hydrolysis process, while the crystallized area is difficult to be hydrolyzed because of its dense structure. Therefore, the crystallinity of SNP increases, forming a good crystal structure [23]. However, the crystallinity of OSNP decreased to 25 %, indicating that the starch crystallization area was destroyed in the process of oxidation.
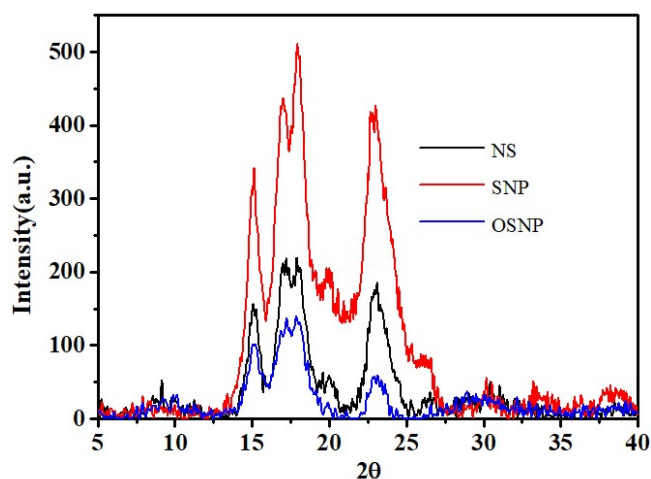

Figure 2. X-ray diffraction pattern of native starch and modified starch

Analysis of particle size distribution

Malvern laser particle size analyzer was used to determine the particle size of the sample, and the results are shown in Figure 3. The size of native starch granules ranged from 6 to 10 μm, and the size of SNP was mainly around 240 nm, which indicated that corn starch was successfully prepared into nanoparticles. The average particle size of OSNP is decreased to 180 nm, which may be due to the increase of negative charge.
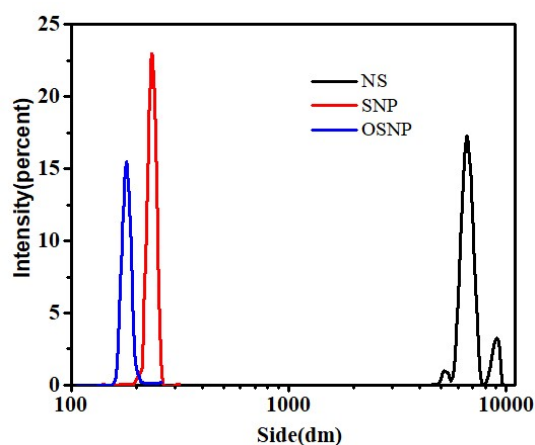

Figure 3. The size distribution of starch granules

Dispersion test

Figure 4 shows the dispersion state of native starch and OSNP before and after standing in the test tube. Both the native starch and OSNP are evenly dispersed in the solvent before standing. After standing for a period of time, the native starch precipitates and the solution becomes clear, while the OSNP can float in the water. The different delamination result is caused by their different particle size. Therefore, OSNP can disperse in water for a long time due to its small particle size, which further indicates that OSNP has good dispersion.
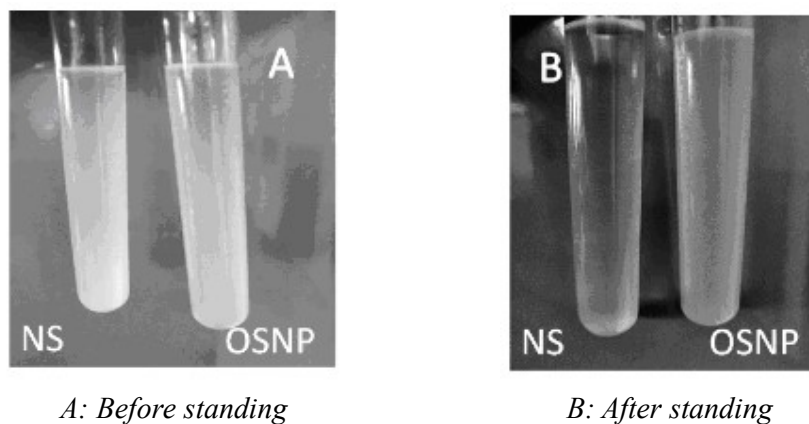

A: Before standing   B: After standing

Figure 4. Dispersion of native starch and oxidized starch nanoparticles

CONCLUSION

Native starch was transformed to starch nanoparticles (SNP) by traditional sulfuric acid hydrolysis method, and SNP was oxidized by potassium bromate (KBrO$_3$) to oxidized starch nanoparticles (OSNP), which is a relatively mature method. In this study, SNP has an average particle size of 240 nm, and the crystallinity was 96 % higher than that of native starch. Compared with SNP and native starch, OSNP has smaller average particle size (180 nm). Due to the small particle size and negative charge, OSNP can be used as a good adsorbent and has good application prospects in water pollution.

ACKNOWLEDGMENTS

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