Carbohydrate Polymers 106 (2014) 359–364

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and characterization of starch nanoparticles through ultrasonic-assisted oxidation methods

Qingjie Sun*, Haoran Fan, Liu Xiong

School of Food Science and Engineering, Qingdao Agricultural University, Qingdao, Shandong Province 266109, China

ARTICLE INFO

Article history:
Received 29 November 2013
Received in revised form 21 January 2014
Accepted 20 February 2014
Available online 28 February 2014

Keywords:
Starch
Nanoparticles
Ultrasonication
Oxidation

ABSTRACT

In this work, starch nanoparticles (SNPs) were prepared from waxy corn starch (WCS) through ultrasonic-assisted oxidation. Three SNPs samples were produced by one time oxidation followed by ultrasonic treatment (O1U1-SNPs), twice oxidation and twice ultrasonic treatment (O2U2-SNPs) and TEMPO-mediated oxidation with ultrasonic treatment (TEMPO-SNPs), respectively. Differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were used to characterize the thermal properties, morphology, and structure of the ensuing nanoparticles. The results revealed that the size of the O1U1-SNPs, O2U2-SNPs, and TEMPO-SNPs particles reached 30–50 nm, 20–50 nm and 20–60 nm, respectively. Compared to WCS, the crystallinity of the O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs samples decreased from 36.32% to 11.35%, 1.64% and 1.72%, respectively. The O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs exhibited smaller or no endotherms. The SNPs had higher carboxyl and carbonyl content.

1. Introduction

Starch is a primary source of stored energy, and reserves carbohydrates synthesized in many parts of plants. Starch is the second most abundant biomass material on Earth, next to the organic compound cellulose (Eliasson, 2004). The starch molecule is composed of an amorphous region (amylose) and a crystalline region (amylopectin). The shortcomings of native starch, such as poor tolerance to a broad range of processing conditions and poor functional properties, can be overcome through physical, chemical or enzyme modification, and this property has made starch a useful polymer. A common chemical modification of starch is oxidation. Oxidized starch is commonly produced by reacting starch with a specified amount of oxidizing agent under controlled temperature and pH (Wurzburg, 1986). Several oxidizing agents have been applied to starch oxidation, including sodium hypochlorite (NaOCl), bromine, periodate and the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system.

Ultrasonic technology has been widely applied in chemical processes. Application of ultrasonic irradiation in food processing has been increasing over the past few years because it shortens the processing times required and lowers energy consumption, creating an effective process (Jambrak, Lelas, Mason, Krešić, & Badanjak, 2009; Mason, Paniwnyk, & Lorimer, 1996). Ultrasonic treatment is a physical method for modifying starch (Azhar & Hamdy, 1979; Chung, Moon, Kim, & Chun, 2002; Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008; Zuo, Knoerzer, Mawson, Kentish, & Ashokkumar, 2009). Ultrasonication generates ultrasonic cavitation in the solution and causes micro-bubbles. When micro-bubbles collapse, high energy is released and converted to high pressure and high temperature. The process causes degradation of polymers and/or catalytic acceleration of reactions (Kawasaki, Takeda, & Arakawa, 2007).

In recent years, nanoparticles originated from biopolymers have received considerable attention as novel and biofunctional materials in diverse industries. For example, in drug delivery systems, polysaccharide nanoparticles may exhibit prominent sustained release profiles, with assured safety (Lin, Huang, Chang, Feng, & Yu, 2011). Furthermore, increasing interest in nanoparticles of natural origin and their unique properties has led to intensive research in nano-sized particles from natural polysaccharide polymers such as starch (LeCorre, Bras, & Dufresne, 2010). Starch nanoparticles (SNPs) can be readily obtained with mechanical treatment such as ultrasonication (Bel Haaj, Magnin, Pétrier, & Boufi, 2013; Chong, Uthormporn, Karim, & Cheng, 2013), extrusion (Giezen, Jongboom, Gotlieb, & Boersma, 2000), high-pressure homogenization (Liu, Wu, Chen, & Chang, 2009), enzymatic treatment (Kim, Park, and Lim, 2008) and acid hydrolysis (Kim, Lee, Kim, Lim, & Lim, 2012; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003, Angellier, Choisnard,

---

* Corresponding author at: School of Food Science and Engineering, Qingdao Agricultural University, 266109, 700 Changcheng Road, Chengyang District, Qingdao, China. Tel.: +86 532 88030448; fax: +86 532 88030449.
E-mail address: phdsun@163.com (Q. Sun).

http://dx.doi.org/10.1016/j.carbpol.2014.02.067
0144-8617/© 2014 Elsevier Ltd. All rights reserved.

Molina-Boisseau, Ozil, & Dufresne, 2004). A combined process of acid hydrolysis for a short period (2 days at 40 °C) followed by facile ultrasonication (60% amplitude, 3 min) has been reported for nanocrystal formation (Kim, Han, Kweon, Park, & Lim, 2013; Kim, Han, Park, Kim, & Lim, 2013).

In this paper, the combined process of oxidation for a short period and ultrasonication produced SNPs. During ultrasonic-assisted oxidation waxy corn starch, carbonyl and carboxyl groups which produced by oxidation could be introduced to the surface of SNPs. The surface charges of SNPs caused by carbonyl and carboxyl groups generated electrostatic repulsive energy. The repulsive forces were strong enough to repulse SNPs away from each other and produced stable suspensions. Therefore, this influence might decide the dispersity and stability of SNPs suspension. To the best of our knowledge, no study has been reported on the different ultrasonic-assisted oxidation methods for preparing SNPs. This approach is easy and efficient.

2. Materials and methods

2.1. Materials

Waxy corn starch (WCS, 11.6% moisture) was obtained from Zhucheng Xingmao Corn Development Co., Ltd. (Shangdong, China). Sodium hypochlorite (Sinopharm Chemical Regent Co. Ltd., China) containing 10 g active chlorine/100 g was used in this experiment. All other chemicals used were of analytical grade.

2.2. Preparation of O1U1-SNPs and O2U2-SNPs

The oxidized starch was prepared by following Wang and Wang's (2003) method with some modifications. The WCS slurry (35 g/100 g solids) was prepared with distilled water and maintained at 35 °C in a heating mantle. The pH was adjusted to 9.5 with 2 M NaOH. Sodium hypochlorite (1 g/100 g active chlorine concentration) was slowly added into the starch slurry over 30 min while the pH was maintained at 9.5 with 1 M H_2SO_4. After NaOCl was added, the pH of the slurry was maintained at 9.5 with 1 M NaOH for an additional 6 h. The slurry was then adjusted to pH 7.0 with 1 M H_2SO_4, filtered by suction with a Buchner filter funnel (Whatman filter #4), washed with a two-fold volume of distilled water and dried in a convection oven at 40 °C for 48 h.

The oxidized starch slurry was prepared by dispersing 10 g of oxidized starch in 100 ml of distilled water in a glass beaker, immersed in a water bath at a constant temperature of 5 °C. Sonication was carried out in an ultrasonic bath (KQ-500TDE, Kunshan, China) with power ultrasound of 500 W with 100% amplitude at a frequency of 40 kHz. Sonication was continued for 180 min under continuous stirring to prevent the oxidized starch granules from settling to the bottom. The mixture was separated by centrifugation at 3000 rpm for 10 min, the precipitate was used for the second oxidation and the supernatant was centrifuged at 10,000 rpm for 10 min. Then the precipitate was freeze-dried to obtain O1U1-SNPs (the yield was about 40%). The precipitate of centrifugation at 3000 rpm was treated according to this method for oxidation followed by ultrasonication for the second time. The precipitate was then freeze-dried to obtain O2U2-SNPs (the yield was about 70%).

2.3. TEMPO oxidation with ultrasonic treatment

TEMPO oxidation with ultrasonic treatment was prepared by following Qian et al.'s (2010) method with some modifications. A slurry of 10% WCS (100 g) was put in a beaker and held at 5 °C. The TEMPO (0.048 g, 0.01 mol per anhydroglucose unit of starch) and sodium bromide (0.635 g, 0.2 mol per anhydroglucose unit of starch) were dissolved in 100 ml distilled water. After TEMPO was completely dissolved, the solution was added to the starch solution at 5 °C. The pH of the solution was adjusted to 9.5 with 0.5 M NaOH. Then, 20 g of sodium hypochlorite solution was slowly added to the starch solution, and the pH was maintained at 9.5 by continuous addition of 0.5 M NaOH. The beaker was then dipped into the ultrasonic bath (KQ-500TDE, Kunshan, China) with power ultrasound of 500 W with 100% amplitude at a frequency of 40 kHz. Sonication was continued for 180 min under continuous stirring at 5 °C. The mixture was separated by centrifugation at 3000 rpm for 10 min, and the supernatant was centrifuged at 10,000 rpm for 10 min. The precipitate was washed with water and centrifuged three times. Then the precipitate was freeze-dried to obtain TEMPO-SNPs (the yield was about 50%).

2.4. Determination of carbonyl content

The carbonyl content was determined according to the titrimetric method as described by Smith (1967). A starch sample (2 g) was added to 100 ml of distilled water in a 500 ml flask. The suspension was gelatinized in a boiling water bath for 20 min, cooled to 40 °C and adjusted to a pH value of 3.2 with 0.1 M HCl. A hydroxylamine reagent (15 ml) was then added to the mixture. The flask was stoppered and placed in a 40 °C water bath for 4 h with slow stirring. The excess hydroxylamine was determined by rapidly titrating the reaction mixture to a pH value of 3.2 with standardized 0.1 M HCl. A blank determination with only the hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by first dissolving 25 g of hydroxylamine hydrochloride in 100 ml of 0.5 M NaOH, before the final volume was adjusted to 500 ml with distilled water. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (CO/100 GU), as calculated with Eq. (1):

$$\frac{\mathrm{CO}}{100\,\mathrm{GU}} = (Vb - Vs) \times M \times 0.028 \times \frac{100}{W} \tag{1}$$

where Vb is the volume of HCl used for the blank (ml), Vs is the volume of HCl required for the sample (ml), M is the molarity of HCl and W is the sample weight (db).

2.5. Carboxyl content

The carboxyl content of the oxidized starch was determined according to Chattopadhyay, Singhal, and Kulkarni's (1997) procedure with some modifications. Approximately 2 g of a starch sample was mixed with 25 ml 0.1 M HCl, and the slurry was stirred occasionally for 30 min with a magnetic stirrer. The slurry was then vacuum-filtered through a 150 ml medium porosity fritted glass funnel and washed with 400 ml distilled water. The starch cake was then carefully transferred into a 500 ml beaker, and the volume was adjusted to 300 ml with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch dispersion was then adjusted to 450 ml with distilled water and titrated to a pH value of 8.3 with standardized 0.01 M NaOH. A blank test was performed with unmodified starch. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU), as calculated with Eq. (2):

$$\frac{\mathrm{COOH}}{100\,\mathrm{GU}} = (Vs - Vb) \times M \times 0.045 \times \frac{100}{W} \tag{2}$$

where Vs is the volume of NaOH required for the sample (ml), Vb is the volume of NaOH used to test the blank (ml), M is the molarity of NaOH and W is the sample weight (db).

2.6. *Scanning electron microscopy*

The morphology of the SNPs was observed by using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 10 kV. Powdered SNPs were diluted and spread onto the copper grids coated with a carbon-supported film. The copper grids were left to stand for freeze-drying. The dry samples were observed with SEM.

2.7. *Thermal property*

The thermal transition properties of the WCS and SNPs were examined using a differential scanning calorimeter (DSC 1, Mettler-Toledo, Schwerzenbach, Switzerland). The instrument was calibrated with indium, and an empty pan was used as the reference. The samples (3.0 mg, dry basis) were weighed in an aluminum pan ME-00026763, Mettler-Toledo), and water (6.0 mg) was added. The pan was then hermetically sealed and equilibrated at 4 °C for 24 h before analysis. The scanning temperature range and heating rate were 40 °C to 120 °C and 10 °C/min, respectively. The transition temperatures reported were the onset temperature (To), peak temperature (Tp), conclusion temperature (Tc) and temperature range ($\Delta T = Tc - To$). In addition, the enthalpy change in gelatinization (ΔH) was estimated by integrating the area between the thermograms and a baseline under the peak, and was expressed in terms of J/g of dry starch.

2.8. *X-ray diffraction analysis*

The crystalline structure of the WCS and SNPs was analyzed with freeze-dried samples by using an X-ray diffractometer (Bruker D8 ADVANCE, Germany). The starch powder was packed tightly into small holders. The scanning range and rate were 5–40° (2θ) and 1.0°/min, respectively. The relative crystallinity (RC) of starch was quantitatively calculated with Nara and Komiya's (1983) method: RC = Ac/(Aa + Ac), where Ac was the crystalline area, and Aa was the amorphous area on the X-ray diffractogram.

2.9. *Fourier transform infrared spectroscopy*

The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded in an FTIR spectrometer (470 FTIR, Nicolet, USA). The dried samples were mixed with KBr and grounded, and pressed into a pellet. FTIR spectra were obtained in the wave number range from 400 cm^{-1} to 4000 cm^{-1}.

2.10. *Statistical analysis*

The data are represented as the averages of three replications. The data were subjected to statistical analysis using SPSS 17.0 (SPSS Inc., Chicago, USA). The experiment data were analyzed using analysis of variance (ANOVA) using the Origin Pro 8.0 statistics program and expressed as mean values ± standard deviation. Differences were considered at a significant level of 95% ($p < 0.05$).

3. Results and discussion

3.1. *Determination of carbonyl and carboxyl group content*

The content of the carbonyl and carboxyl groups of the SNPs is presented in Table 1. As shown in Table 1, the carbonyl and carboxyl content of the SNPs were significantly higher than that of the native WCS. Furthermore, the carbonyl and carboxyl content of the oxidized WCS increased as the oxidation period increased. However, the carboxyl content increased at a much faster rate than the carbonyl content, which indicated that the hydroxyl groups in the starch molecules were initially oxidized to carbonyl groups and then to carboxyl groups as the primary final product. This could have occurred because as the oxidization times increased, more hydroxyl groups were converted to carbonyl groups and promptly oxidized to carboxyl groups. In addition, O2U2-SNPs and TEMPO-SNPs showed higher carbonyl and carboxyl content than that of O1U1-SNPs. Ultrasonic treatment of waxy maize starch granules resulted in the surface of the granules appears to be progressively broken down and eroded (Bel Haaj et al., 2013). Kardos and Luche (2001) revealed that many chemical reactions could be initiated by sonication because of the highly reactive conditions created during cavitation. Holes appeared in the starch granules after one-time oxidation followed ultrasonication (Daris Kuakpetoona & Ya-Jane Wang, 2008), thus accelerating the second oxidation treatment (Qin, Tong, Chin, & Zhou, 2011). At the same time, the degradation process would also be accelerated, as well as the hydrolyzation of the amorphous region. The ultrasound damaged the surface of the starch oxidized by TEMPO in the ultrasonic system, and the permeation of the reagents and oxidation were accelerated. Moreover, the starch became more and more hydrophilic when the hydroxyl groups were transformed to carboxyl groups gradually, and the process for starch oxidation became easier. Therefore, the carbonyl and carboxyl content of O2U2-SNPs and TEMPO-SNPs was higher than that of O1U1-SNPs and WCS. Thus, ultrasonic treatment may help in enhancing starch oxidation.

Table 1
Carbonyl and carboxyl contents of starch nanoparticles.

Sample	Carboxyl content (COOH/100 GU)	Carbonyl content (CO/100 GU)
O1U1-SNPs	0.4815 ± 0.08^b	0.1246 ± 0.04^b
O2U2-SNPs	0.7406 ± 0.02^a	0.1661 ± 0.01^a
TEMPO-SNPs	0.8400 ± 0.00^a	0.1602 ± 0.02^a

Values are means ± standard deviation of three replications.
Mean values in the same column with different letters are significantly different ($p < 0.05$).
O1U1-SNPs: the SNPs produced by one time ultrasonic treatment, O2U2-SNPs: the SNPs produced by oxidation performed twice and ultrasonic treatment performed twice, TEMPO-SNPs: the SNPs produced by TEMPO-mediated oxidation with ultrasonic treatment.

3.2. *Morphology of samples*

The SEM images of native WCS and O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs are shown in Fig. 1. The SEM revealed that the native WCS granules were ellipsoid with a mean size of about 5–15 μm. Under the microscope, the average size of the O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs particles was estimated to range from 30 to 50 nm, 20 to 50 nm and 20 to 60 nm, respectively. The particles were round, which might correspond to the starch blocklets (Gallant, Bouchet, & Baldwin, 1997). Nevertheless, the O1U1-SNPs starch particles seemed to be more uniform than those of O2U2-SNPs and TEMPO-SNPs. Some O2U2-SNPs particles were observed as aggregation rather than as singular bodies. The SNPs prepared with TEMPO-assisted oxidation seemed to be more inhomogeneous than others with different sizes. SEM revealed that no micro-sized particles were observed after treatment, confirming the complete disintegration of the starch granules into nano-sized particles. During treatment, the ultrasonication was suggested to play a significant role in a major change in the starch and the oxidation played an auxiliary function. Oxidation of starch granules resulted in surface erosion with notch and groove formation and some holes appeared in the starch granules after oxidation (Daris Kuakpetoona & Ya-Jane Wang, 2008). The ultrasonication which followed easily degrades the starch molecule into nanoparticles.

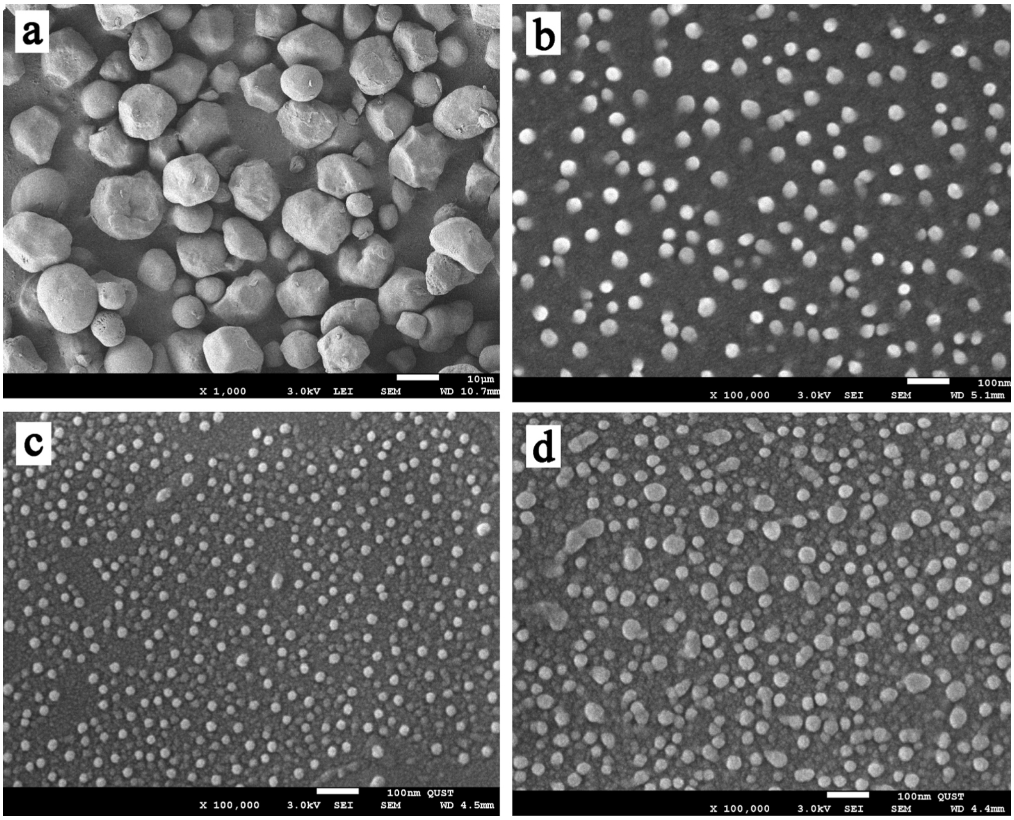

Fig. 1. SEM images of native waxy corn starch and starch nanoparticles: (a) native waxy corn starch (bar = 10 µm); (b) O1U1-SNPs; (c) O2U2-SNPs; (d) TEMPO-SNPs (b–d, bar = 100 nm).

3.3. Thermal properties and XRD analysis

The thermal transition behaviors of WCS, O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs are presented in Fig. 2, and the X-ray diffraction patterns of the WCS and freeze-dried SNPs were measured (Fig. 3). The samples prepared by ultrasonic-assisted oxidation exhibited smaller or no endotherms (Fig. 2), in accordance with the XRD data. The WCS exhibited peaks at Bragg angles (2θ) 15°, 17°, 18° and 23°, showing that it had the typical A-type diffraction pattern of cereal starch (Zobel, 1964). There was an important change in the XRD spectra of the starch nanoparticles by ultrasonic-assisted oxidation. All of the diffraction peaks of O1U1-SNPs decreased in intensity. Furthermore, O2U2-SNPs and TEMPO-SNPs nearly lost diffraction peaks at 15°, 17°, 18° and 23°, indicating a substantial disruption of the crystalline structure by the ultrasonic treatment. Compared to WCS, all the diffraction peaks of the SNPs exhibited a broad peak from 5° to 40° associated with an amorphous phase that was mainly observed on the diffraction spectra.

The XRD results revealed that when WCS were oxidized and treated with ultrasonication, the inherent crystalline structure of the starch was disrupted. Bel Haaj et al. (2013) demonstrated that ultrasonication of starch granules at a temperature of 8 °C for 75 min resulted in a serious disruption of the crystalline structure of clustered amylopectin, apparently leading to nanoparticles with low crystallinity or an amorphous character. It was assumed that the ultrasonic treatment exerted effects on the cluster structure inside the starch granules, especially the crystalline region (Zhu, Li, Chen, & Li, 2012). Furthermore, as the particle size decreased to 20–60 nm (Fig. 1), the crystallite size decreased, and the diffraction peak became broader, since the width at the half height of a peak

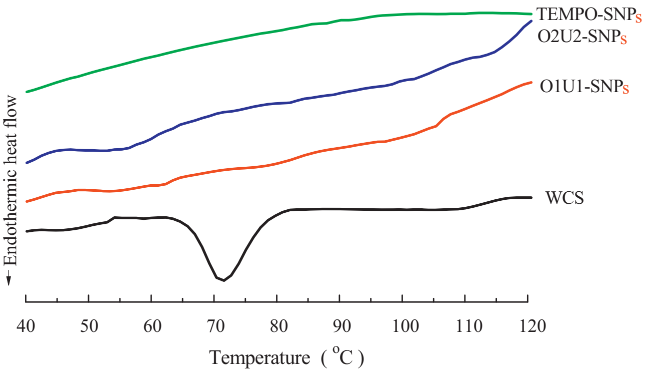

Fig. 2. DSC images of WCS, O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs.

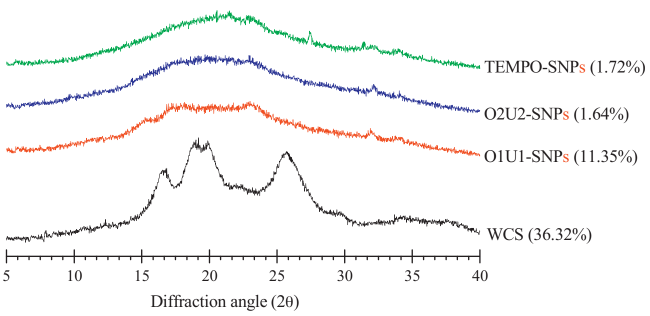

Fig. 3. XRD profiles of WCS, O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs.

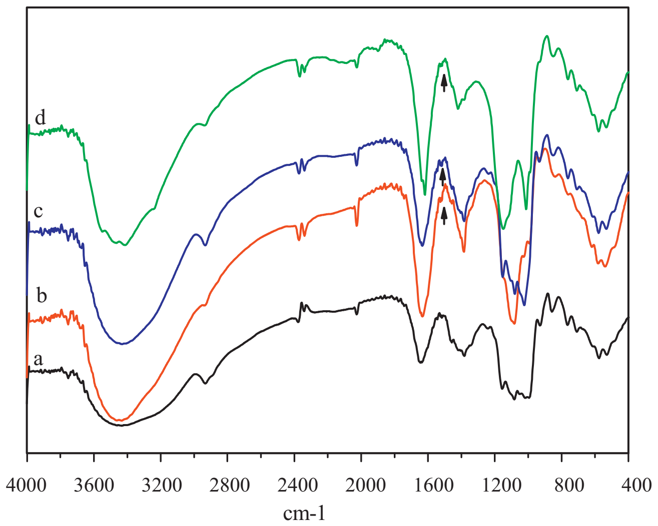

Fig. 4. FTIR spectrums for native waxy corn starch and starch nanoparticles: (a) waxy corn starch; (b) O1U1-SNPs; (c) O2U2-SNPs; (d) TEMPO-SNPs. Arrows are the peak at 1570 cm^{-1}.

was inversely proportional to the crystallite size (Bel Haaj et al., 2013).

3.4. FTIR spectroscopy

The FTIR spectra of the native WCS and SNPs are shown in Fig. 4. Compared to the WCS, the band at around 3430 cm^{-1} of the SNPs was sharper, which suggests the interactions among the hydroxyl groups weakened, which was probably due to the disruption of the starch crystalline structure. In the fingerprint region of the FTIR spectra of the samples, three characteristic peaks appeared between 1000 and 1200 cm^{-1}, attributed to the C—O bond stretching of the starch (Ma, Yu, & Wang, 2007). Compared with WCS (Fig. 4a), the strong absorption bands at 1611 cm^{-1} and 1400 cm^{-1} can be seen in the spectra of O1U1-SNPs (Fig. 4b), O2U2-SNPs (Fig. 4c) and TEMPO-SNPs (Fig. 4d), which were assigned to the carboxyl group (Williams & Fleming, 1987). With the increased aldehyde content, the peak at 1150 cm^{-1} weakened, which was attributed to the C—O bond stretching of the C—OH group in the anhydroglucose ring. Compared with the WCS, the spectra of the SNPs showed a new peak at 1570 cm^{-1}, which indicated that carbonyl groups replaced hydroxyl groups in the starch molecules (Fang, Fowler, Sayers, & Williams, 2004). The differential FTIR spectra indicated that oxidation could change the hydroxyl groups of WCS into carbonyl and carboxyl groups of the SNPs.

4. Conclusions

Overall, the results suggested a process for preparing SNPs with ultrasonic-assisted oxidation methods at a low temperature. Complete conversion of the starch granules from the micronic to the nanometric scale after ultrasonic-assisted oxidation was confirmed with SEM, with the particle size of the SNPs ranging from 20 to 60 nm. DSC showed that the samples prepared by ultrasonic-assisted oxidation exhibited smaller or no endotherms. XRD analysis indicated that ultrasonication destroyed the crystalline structure of the WCS and decreased the crystallinity of the SNPs. A combination of ultrasonic treatment and oxidation is an effective process for producing SNPs.

Acknowledgement

Financial support from the China Postdoctoral Science Foundation (Grant 2013M540552) is gratefully acknowledged.

References

Angellier, H., Choisnard, L., Molina-Boisseau, S., Ozil, P., & Dufresne, A. (2004). Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. *Biomacromolecules*, *5*, 1545–1551.

Azhar, A., & Hamdy, K. (1979). Sonication effect on potato starch and sweet potato powder. *Journal of Food Science*, *44*, 801–804.

Bel Haaj, S., Magnin, A., Pétrier, C., & Boufi, S. (2013). Starch nanoparticles formation via high power ultrasonication. *Carbohydrate Polymers*, *92*, 1625–1632.

Chattopadhyay, S., Singhal, R. S., & Kulkarni, P. R. (1997). Optimization of conditions of synthesis of oxidized starch from corn and amaranth for use in film-forming applications. *Carbohydrate polymers*, *34*, 203–212.

Chong, W. T., Uthornporn, U., Karim, A. A., & Cheng, L. H. (2013). The influence of ultrasound on the degree of oxidation of hypochlorite-oxidized corn starch. *LWT-Food Science and Technology*, *50*, 439–443.

Chung, K. M., Moon, T. W., Kim, H., & Chun, J. K. (2002). Physicochemical properties of sonicated mung bean, potato and rice starches. *Cereal Chemistry*, *79*, 631–633.

Kuakpetoona, D., & Wang, Y.-J. (2008). Location of hypochlorite oxidation in corn starches varying in amylose content. *Carbohydrate Research*, *343*, 90–100.

Eliasson, A. C. (2004). *Starch in food*. England: CRC Press LLC.

Fang, J. M., Fowler, P. A., Sayers, C., & Williams, P. A. (2004). The chemical modification of a range of starches under aqueous reaction conditions. *Carbohydrate Polymers*, *55*(3), 283–289.

Gallant, D. J., Bouchet, B., & Baldwin, P. M. (1997). Microscopy of starch: Evidence of a new level of granule organization. *Carbohydrate Polymers*, *32*, 177–191.

Giezen, F., Jongboom, R., Gotlieb, K., & Boersma, A. (2000) Wo 00/69916.

Iida, Y., Tuziuti, T., Yasui, K., Towata, A., & Kozuka, T. (2008). Control of viscosity in starch and polysaccharide solutions with ultrasound after gelatinization. *Innovative Food Science and Emerging Technologies*, *9*, 140–146.

Jambrak, A. R., Lelas, V., Mason, T. J., Krešić, G., & Badanjak, M. (2009). Physical properties of ultrasound treated soy proteins. *Journal of Food Engineering*, *93*(4), 386–393.

Kardos, N., & Luche, J. L. (2001). Sonochemistry of carbohydrate compounds. *Carbohydrate Research*, *332*, 115–131.

Kawasaki, H., Takeda, Y., & Arakawa, R. (2007). Mass spectrometric analysis for high molecular weight synthetic polymers using ultrasonic degradation and the mechanism of degradation. *Analytical Chemistry*, *11*, 4182–4187.

Kim, J.-Y., Park, D.-J., & Lim, S.-T. (2008). Fragmentation of waxy rice starch granules by enzymatic hydrolysis. *Cereal Chemistry*, *85*, 182–187.

Kim, H.-Y., Lee, J. H., Kim, J.-Y., Lim, W.-J., & Lim, S.-T. (2012). Characterization of nanoparticles prepared by acid hydrolysis of various starches. *Starch/Stäke*, *64*, 367–373.

Kim, H.-Y., Han, J.-A., Kweon, D.-K., Park, J.-D., & Lim, S.-T. (2013). Effect of ultrasonic treatments on nanoparticle preparation of acid-hydrolyzed waxy maize starch. *Carbohydrate Polymers*, *93*, 582–588.

Kim, H.-Y., Han, J.-A., Park, J.-D., Kim, T.-S., & Lim, S.-T. (2013). Preparation of crystalline starch nanoparticles using cold acid hydrolysis and ultrasonication. *Carbohydrate Polymers*, *98*, 295–301.

LeCorre, D., Bras, J., & Dufresne, A. (2010). Starch nanoparticles: A review. *Biomacromolecules*, *11*, 1139–1153.

Liu, D., Wu, Q., Chen, H., & Chang, P. R. (2009). Transitional properties of starch colloid with particle size reduction from micro to nanometer. *Journal of Colloid and Interface Science*, *339*(1), 117–124.

Lin, N., Huang, J., Chang, P. R., Feng, L., & Yu, J. (2011). Effect of polysaccharide nanocrystals on structure, properties, and drug release kinetics of alginate-based icrospheres. *Colloids and Surfaces B: Biointerfaces*, *85*, 270–279.

Mason, T. J., Paniwnyk, L., & Lorimer, J. P. (1996). The uses of ultrasound in food technology. *Ultrasonics Sonochemistry*, *3*(3), S253–S260.

Ma, X. F., Yu, J. G., & Wang, N. (2007). Production of thermoplastic starch/MMT-sorbitol nanocomposites by dual-melt extrusion processing. *Macromolecular Materials and Engineering*, *29*, 2723–2728.

Nara, S., & Komiya, T. T. (1983). Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. *Starch*, *35*, 407–410.

Putaux, J.-L., Molina-Boisseau, S., Momaur, T., & Dufresne, A. (2003). Platelet nanocrystals resulting from the disruption of waxy maize starch granules by acid hydrolysis. *Biomacromolecules*, *4*, 1198–1202.

Qian, Y., Qin, Z., Vu, N.-M., Tong, G., & Frank Chin, Y. C. (2010). Comparison of nanocrystals from TEMPO oxidation of bamboo, softwood, and cotton linter fibers with ultrasonic-assisted process. *Bioresources*, *7*(4), 4952–4964.

Qin, Z., Tong, G., Chin, Y. C. F., & Zhou, J. (2011). Preparation of ultrasonic-assisted high carboxylate content cellulose nanocrystals by TEMPO oxidation. *Bioresources*, *6*(2), 1136–1146.

Smith, R. J. (1967). Production and used of hypochlorite oxidized starches. In R. L. Whistler, & E. F. Paschall (Eds.), *Starch chemistry and technology* (pp. 620–625). New York: Academic Press.

Wang, Y.-J., & Wang, L. (2003). Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers*, *52*, 207–217.

Williams, D. H., & Fleming, I. (1987). *Spectroscopic methods in organic chemistry*. London: McGrawhill Book Company.

Wurzburg, O. B. (1986). Converted Starches. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses*. Boca Raton, FL: CRC Press.

Zhu, J., Li, L., Chen, L., & Li, X. (2012). Study on supramolecular structural changes of ultrasonic treated potato starch granules. *Food Hydrocolloids*, *29*, 116–122.

Zobel, H. F. (1964). X-ray analysis of starch granules. In L. R. Whistler, & R. J. Smith (Eds.), *Methods in carbohydrate chemistry* (pp. 109–113). Academic press: New York.

Zuo, J. Y., Knoerzer, K., Mawson, R., Kentish, S., & Ashokkumar, M. (2009). The pasting properties of sonicated waxy rice starch suspensions. *Ultrasonics Sonochemistry*, *16*, 462–468.