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High efficiency and low cost preparation of size controlled starch nanoparticles through ultrasonic treatment and precipitation

Yanjiao Chang, Xiaoxia Yan, Qian Wang, Lili Ren, Jin Tong, Jiang Zhou *

Key Laboratory of Bionic Engineering (Ministry of Education), College of Biological and Agricultural Engineering, Jilin University, Changchun 130022, China

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ABSTRACT

The purpose of this work was to develop an approach to produce size controlled starch nanoparticles (SNPs), via precipitation with high efficiency and low cost. High concentration starch aqueous pastes (up to 5 wt.%) were treated by ultrasound. Viscosity measurements and size exclusion chromatography characterization revealed that, after 30 min ultrasonic treatment, viscosity of the starch pastes decreased two orders of magnitude and the weight average molecular weight of the starch decreased from 8.4×10^7 to 2.7×10^6 g/mol. Dynamic light scattering measurements and scanning electron microscopy observations showed that the SNPs prepared from the starch pastes with ultrasonic treatments were smaller (~75 nm) and more uniform. Moreover, SNPs could be obtained using less non-solvents. X-ray diffraction results indicated that effect of the ultrasonic treatment on crystalline structure of the SNPs was negligible. Ultrasound can be utilized to prepare smaller SNPs through nanoprecipitation with higher efficiency and lower cost.

1. Introduction

Starch nanoparticles (SNPs) have attracted considerable attention in recent years because of their great potential for applications in the food industry (Kim, Park, & Lim, 2015). Since starch-based nanoparticles could act as stabilizers for oil-water emulsions (Li, Sun, & Yang, 2012; Tan et al., 2014), the edibility and biodegradability of SNPs enable them to be used as particulate emulsifier in food and pharmaceuticals. SNPs could also be used as nanocapsules of food ingredients (Fathi, Martin, & McClements, 2014). It was reported that the nanoparticles of starch-β-carotene composites improved the dispersibility of β-carotene in water and enhanced the stability of β-carotene against chemical oxidation (Kim & Huber, 2016). At the nano-scale, which is frequently defined as the range of 10–1000 nm (Mohanraj & Chen, 2007; Rao & Geckeler, 2011), properties of particles can be significantly different from the original bulk material (Hoover, Hughes, Chung, & Liu, 2010; Le Corre, Bras, & Dufresne, 2010). Size and size distribution of SNPs are of paramount importance for the applications mentioned above, and preparation of size controlled SNPs with high efficiency and low cost is the basis of their applications.

Various methods have been attempted to prepare starch or starch derivative nanoparticles (Kim et al., 2015). Among the numerous manufacturing methods, nanoprecipitation is a very simple and convenient method for production of nanoparticles with desired sizes (Perevyazko et al., 2012). The precipitation process involves a successive addition of a dilute starch solution into a non-solvent or inversely. Previous works showed that concentration of starch solution, volume ratio of solvent to non-solvent and types of solvent and non-solvent influenced the size of precipitated SNPs (Chin, Pang, & Tay, 2011; Dong, Chang, Wang, Tong, & Zhou, 2015; Tan et al., 2009; Wu et al., 2015). In order to synthesize smaller SNPs through precipitation, highly diluted starch solution and larger volume of non-solvents have to be used because high starch concentration leads to the formation of viscous solution. High viscosity of starch solution hampers diffusion of starch solution toward non-solvent which results in larger particles. However, using highly diluted starch solutions and larger volume of non-solvents to prepare SNPs will inevitably decrease production efficiency and increase cost.

Ultrasonic treatment is a method which can be used to physically modify polymers, such as starch. Some advantages of this method are that it is simple, effective and environmentally friendly. It was demonstrated that ultrasonic treatment of chitosan and starch aqueous solutions is an efficient procedure to reduce the molecular weight of these polysaccharides due to the intense mechanical effect associated with cavitation (Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Rosiak, 2005). Cavitation is the collapse of microbubbles that burst and propagate as a sound wave passes

* Corresponding author.
E-mail address: jiang.zhou@jlu.edu.cn (J. Zhou).

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through a solution (Langton, 1969; Price & Smith, 1993). The shear forces created due to the collapse of the bubbles may break covalent bonds in polymeric materials (Farzi, Saffari, Emam-Djomeh, & Mohammadifar, 2011; Zhang et al., 2013). It was reported that viscosity of starch solution and molecular weight of starch were reduced after ultrasonic treatment (Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008).

In this paper, a facile approach to prepare size-controlled SNPs using high concentration starch aqueous pastes and less non-solvent via nanoprecipitation was presented. In order to develop a high efficiency and low cost manufacturing method of SNPs, the starch aqueous pastes with higher concentration were treated by ultrasound, aiming to reduce viscosity of the starch pastes without decreasing concentration, so that the high concentration starch aqueous pastes could be used for nanoprecipitation with less non-solvent. Through examining the size, morphology and structure of the SNPs obtained by using ultrasonic treated starch aqueous pastes, effects of ultrasonic treatment of starch aqueous pastes on the morphological and structural characteristics of SNPs were investigated.

2. Materials and methods

2.1. Materials

The native potato starch (containing about 20% amylose) was purchased from HuahaiShunda Grain & Oil Seasoning Co. Ltd. (Cangzhou, China). Absolute ethanol was purchased from Beijing Chemical Works (Beijing, China). Isoamylase from *Pseudomonas sp.* (E-ISAMY) was from Sigma–Aldrich (Castle Hill, NSW, Australia). Dimethyl sulfoxide (DMSO, GR grade for analysis) was purchased from Merck Co. Inc. (Kilsyth, VIC, Australia). All other chemicals were reagent grade and used as received.

2.2. Ultrasonic treatment of starch paste

Starch aqueous paste with a certain concentration (3 wt.% or 5 wt.%) was prepared by dispersing starch granules in distilled water, and heating in a water bath at 100 °C for 60 min under continuous stirring of 160 rpm to completely gelatinize starch granules. After the temperature of the obtained starch paste was cooled to 20 °C, 60*g* of the starch paste, held in a plastic container with height of 68 mm and diameter of 54 mm, was treated by ultrasound for a certain time using a 22 kHz ultrasound generator (HN-1000Y, Shanghai Hanno Instrument Corp., Shanghai, China) equipped with a tapered horn tip (10 mm end diameter). The power output of 100 W and 2/4 s on/off pulses were applied.

2.3. Viscosity measurement

Apparent viscosity of the starch aqueous pastes after the ultrasonic treatments was measured at 20 °C using a viscometer (RVDV-III, Brookfield Engineering Laboratories, Middleboro, USA) at the spindle rotation of 90 rpm.

2.4. Preparation of SNPs

SNPs were prepared by adding the starch aqueous paste dropwise into absolute ethanol which was continually agitated with ultrasound. The volume ratio of starch paste to non-solvent (absolute ethanol), S/NS, was 1/2, 1/5, and 1/10, respectively. The resulting mixture was then centrifuged at 4000*g* for 5 min. The precipitated SNPs were obtained by removing the supernatant and rinsed 1 time by centrifugation with absolute ethanol. The final product was freeze dried.

2.5. Size-exclusion chromatography

Size-exclusion chromatography (SEC) was used to analyze molecular size distribution of the potato starch before and after the ultrasonic treatments. Freeze dried SNPs obtained from the starch aqueous pastes with different ultrasonic treating times were dissolved in DMSO containing 0.5 % (w/w) LiBr at a concentration of 2 g/l in thermomixer at 80 °C for 24 h during which the thermomixer was inverted by hand occasionally. The prepared solutions were centrifuged at 4000*g* for 10 min and the supernatants were transferred to SEC vials for analysis. Starch molecules were eluted using DMSO/LiBr solution as the mobile phase and were separated using porous chromatogram column as the stationary phase.

Freeze dried SNPs obtained from the starch aqueous pastes with different ultrasonic treating times were de-branched using isoamylase, following the method described by Hasjim, Lavau, Gidley, and Gilbert (2010) with modifications. Starch precipitate (~4 mg, dry weight) was dissolved in 0.9 ml water and then mixed with 2.5 μl isoamylase, 0.1 ml acetate buffer solution (0.1 M, pH 3.5), and 5 μl sodium azide solution (0.04 g/ml). The mixture was incubated at 37 °C for 3 h. The de-branched starch suspension was then heated in a water bath at 80 °C for 2 h after being neutralized with 0.1 M NaOH, and then freeze-dried. The obtained freeze dried samples after de-branched were dissolved in DMSO containing 0.5 % (w/w) LiBr at a concentration of 4 g/l for subsequent analysis by SEC.

The weight distributions of the whole (fully branched) and de-branched starch molecules were analyzed using the SEC system (Agilent 1260 series, Agilent Technologies, Waldbronn, Germany) which consisted of an isocratic pump, auto sampler without temperature regulation, an online degasser, a refractive index detector (Optilab T-Rex, Wyatt Technology Corp., America) and a multi-angle laser light scattering (MALLS) detector (Wyatt DAWN Heleos II, Wyatt Technology Corp., America). Astra 6 software was used for data processing. The samples were injected into a GRAM pre-column with a flow rate of 0.3 ml/min for starch solution and 0.6 ml/min for de-branched starch solution. The separation was carried out with GRAM columns (Polymer Standard Service (PPS), Mainz, Germany) placed in a column oven at 80 °C. The column dimension of pre-column was 8 × 50 mm (internal diameter × length). The dimension of column used for de-branched starch was 8 × 300 mm and the type was GRAM 100 and GRAM 1000. The dimension of column used for fully branched starch was 8 × 300 mm and the type was GRAM 30 and GRAM 3000. A series pullulan standards (PSS, Mainz, Germany) with molecular weights from 342 to 2.35×10^6 were used to generate a universal calibration curve and determine the hydrodynamic volume V_h or hydrodynamic radius R_h ($V_h = 4/3 \cdot \pi R_h^3$) (Vilaplana & Gilbert, 2010) from the elution volume. The Mark–Houwink parameters for pullulan in this eluent at 80 °C measured by PSS were $K = 2.424 \times 10^{-4}$ dL/g and $\alpha = 0.68$ (Cave, Seabrook, Gidley, & Gilbert, 2009; Wang et al., 2015). The specific RI (refractive index) increment value, d*n*/d*c*, measured by PSS was 0.071 ml/g.

2.6. Characterization of SNPs

The mean size of the obtained SNPs was measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano-ZS90 (Malvern Instruments Ltd., UK). The measurements were performed using the samples prepared by dispersing the SNPs in deionized water at a concentration of about 0.1 mg/ml. The mean size and polydispersity index (PDI) were reported.

The morphologies of the SNPs were observed using a scanning electron microscope (ZEISS, MERLIN Compact, Germany). Powder

samples were mounted on specimen stubs with carbon black tape and then sputtercoated with gold before observation.

The crystalline structure of the SNPs was analyzed by using a Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation (λ = 1.542 Å) at a target voltage of 40 kV and current of 250 mA. The scanning range and rate were 4.00–40.00° (2θ) and 2°/min, respectively.

2.7. Experimental design

Measurements were done in triplicate for viscosity measurement of the aqueous starch pastes with different ultrasonic treating times. The average values and standard deviations were reported. The measurement of mean size and PDI of SNPs consisted of two full replications, while individual replicate analyses of SNPs were conducted in triplicate. The average value and standard deviation of the six measurements were reported.

3. Results and discussion

3.1. Apparent viscosity of starch pastes

It is easy to imagine that the high viscosity of starch paste could hamper the diffusion of starch paste toward non-solvent during precipitation, which in turn resulted in formation of larger particles. Therefore, it is desirable to reduce the viscosity of starch paste to prepare smaller SNPs through nanoprecipitation.

The results of previous studies (Iida et al., 2008; Zhang et al., 2013; Zhu, Li, Chen, & Li, 2012) already showed that ultrasonic treatment reduced the molecular weight of starch and decreased the viscosity of starch solutions. Fig. 1 displays the change of apparent viscosity of the starch aqueous pastes against ultrasonic treating time. Compared with the starch paste without ultrasonic treatment, the viscosity of the starch paste decreased considerably with increasing ultrasonic treating time. For the starch paste with concentration of 3 wt.%, the viscosity declined from 244 mPa s to 3 mPa s after 30 min ultrasonic treatment while the viscosity of the 5 wt.% starch paste descended from 1628 mPa s to 16 mPa s. In other words, the 30 min ultrasonic treatment resulted in a decrease in viscosity of starch aqueous pastes by two orders of magnitude. The intense mechanical effect and heat induced by ultrasonic treatment could break the entanglements and intermolecular interactions of starch molecular chains and cause chain scission. Therefore, viscosity of starch aqueous pastes reduced after ultrasonic treatment. In addition, it was found that the viscosity of the starch pastes decreased rapidly within the initial 15 min ultrasonic treatment. Thereafter, the decrease in viscosity was slower. This phenomenon could be attributed to the characteristic of ultrasound-induced chain scission, i.e., there was a definite minimum chain length limiting the degradation process (Czechowska-Biskup et al., 2005). When the minimum chain length was reached, no further chain scission occurred. Therefore, the viscosity of starch paste hardly decreased any further.

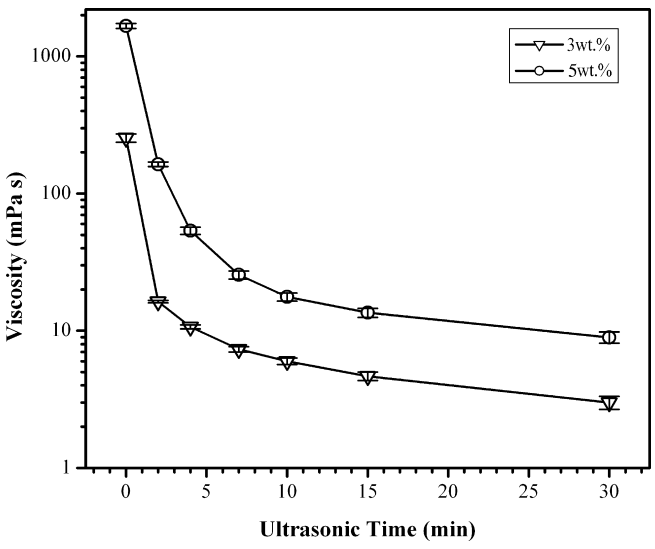

Fig. 1. Changes in viscosity of starch aqueous pastes with different concentrations against ultrasonic treating time.

3.2. Molecular size distributions of starch molecules

Fig. 2(a) shows SEC weight distributions, $w_{de}(\log V_h)$, of de-branched starches which were obtained from SNPs prepared by using starch aqueous pastes with different ultrasonic treating times. The chromatograms of the de-branched starch samples generally consisted of three peaks. Peak 3 mainly represents the amylose and/or extra-long amylopectin chains, Peak 2 represents the long amylopectin side chains (B chains) and Peak 1 represents the short amylopectin outer side chains (A chains) as stated in the amylopectin model of Robin et al. (Radosta, Kiessler, Vorwerg, & Brenner, 2016; Robin, Mercier, Duprat, Charbonnigre, & Guilbot, 1975). As shown in Fig. 2(a), Peaks 1 and 2 were nearly overlapping for all the samples and there were no obvious differences. These results suggested that the degradation of the amylopectin mainly took place by a scission of the α-1, 6-glycosidic linkages at the branching points and a scission of the α-1, 4-glycosidic linkages of the long inner amylopectin C chains. Kang, Zuo, Hilliou, Ashokkumar, and Hemar (2016) concluded from FT-IR measurement that molecular scission in high-power ultrasound depolymerized starch pastes mainly occurred at the C—O—C bond of the α-1, 6-glycosidic linkage. With an increase in ultrasonic treating time, intensity of the Peak 3 increased, suggesting an increase of amylose content. By determining the area under curve (AUC) of the amylose peak (Peak 3) and the total AUC, the ratio of amylose to amylopectin in the starch can be evaluated. The calculated ratio for the starch without ultrasonic treatment and the ones with 2 min, 10 min and 30 min ultrasonic treatments was 19.5%, 24.4%, 30.4% and 33.6%, respectively. Chan, Bhat, and Karim (2010) also reported that amylose content in corn and potato starches increased after ultrasonic treatment.

Fig. 2(b) shows the molar mass distribution of the starch samples with different ultrasonic treating times. The molar mass distribution curve moved down with increase of ultrasonic treating time, indicating that the molecular weight of the starch decreased gradually. The range of molar mass of the starch without ultrasonic treatment was 4.0×10^6–3.8×10^8 g/mol and its weight average molecular weight was 8.4×10^7 g/mol. After 30 min ultrasonic treatment, the range of molar mass was 1.1×10^5–1.8×10^7 g/mol and the weight average molecular weight was 2.7×10^6 g/mol. The decreasing extent of molecular weight after ultrasonic treatment was similar to that of the previous study (Iida et al., 2008).

3.3. Size and size distribution of SNPs

Fig. 3(a) shows mean sizes and PDIs of the SNPs prepared using the starch aqueous pastes with different ultrasonic treating times. For all cases, increase in concentration of starch aqueous paste resulted in an increase in particle size. While with the increase of ultrasonic treating time, the size of the SNPs decreased gradually. When the starch concentration was 5 wt.%, the mean size of the SNPs reduced from 221.6 nm to 95.0 nm after 30 min ultrasonic treatment. For the starch paste with the concentration of 3 wt.%, the particle size decreased from 216.0 nm to 77.0 nm. These results

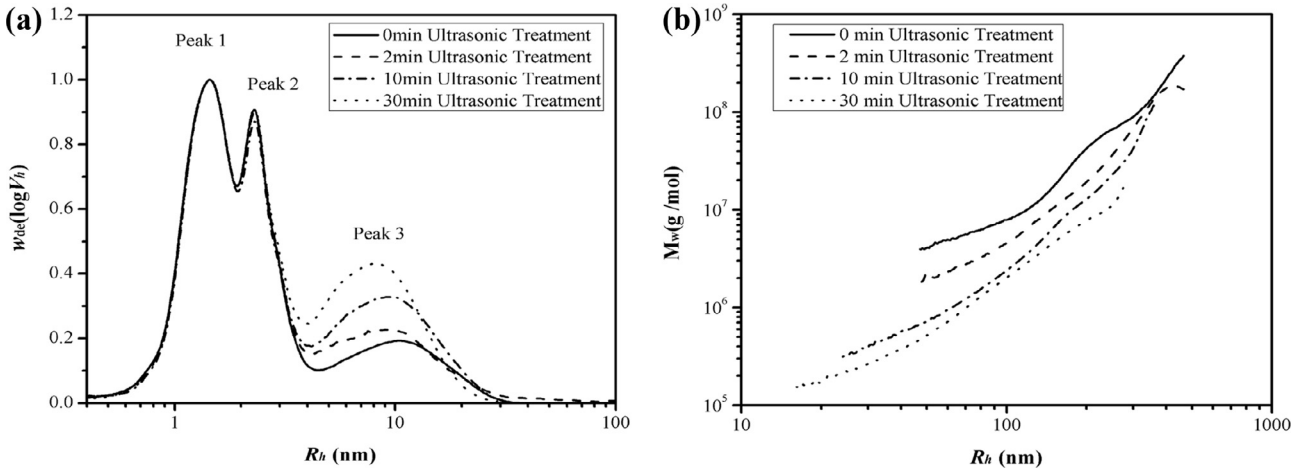

Fig. 2. SEC weight distributions, $w_{de}(\log V_h)$, of the de-branched starches (a) and molar masses of the starches with different ultrasonic treating times.

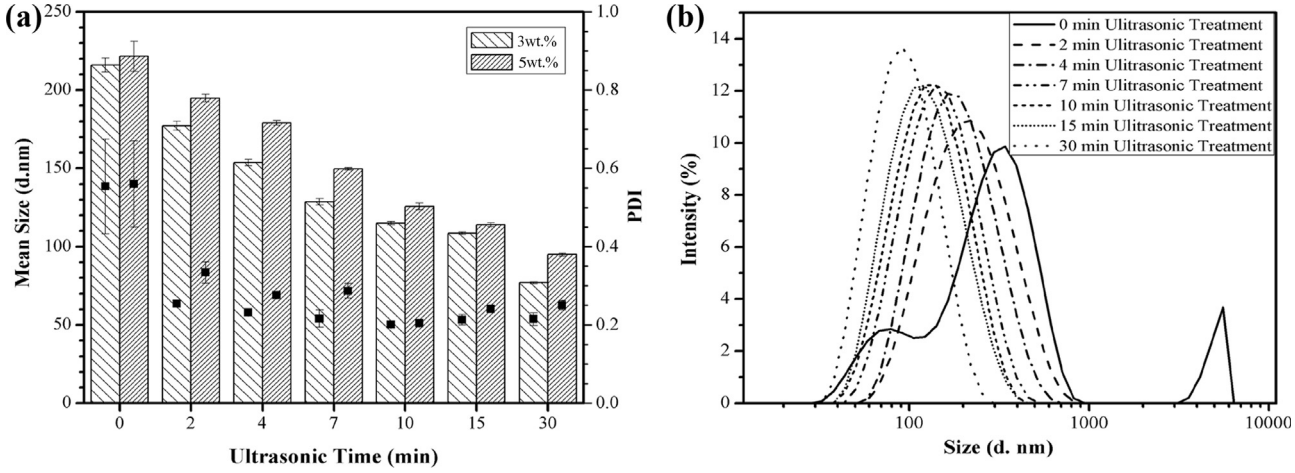

Fig. 3. Mean size (column) and PDI (solid square) of the SNPs prepared using ultrasound treated starch pastes (a) and typical size distribution patterns of the SNPs obtained by using 3 wt.% starch pastes with different ultrasonic treating times (b) (S/NS = 1/10).

indicated that, after ultrasonic treatment, high concentration starch pastes can be used to prepare smaller SNPs via nanoprecipitation and this will considerably increase production efficiency of SNPs. It was noted that the PDI values of the SNPs were around 0.6 and exhibited larger errors when the starch pastes without ultrasonic treatment were used, meaning that the products had a broad size distribution and contained large particles or aggregates. PDI, the dimensionless number extrapolated from the autocorrelation function, is a parameter defined nanoparticle size distribution obtained from DLS. PDI ranges from value 0.1–0.5 for suitable measurements and good quality of the colloidal suspensions to values close to 0.7 for poor quality samples which has a very broad size distribution and may contain large particles or aggregates (Zetasizer Software for the Nano. APS and mV, Version 7.01, Malvern Instruments). However, after the ultrasonic treatments, the values of PDI decreased, suggesting that the obtained SNPs were more uniform and less large particles existed.

Fig. 3(b) shows the typical size distribution patterns of the SNPs prepared by precipitating 3 wt.% starch aqueous pastes with different ultrasound treating in absolute alcohol (S/NS = 1/10). When the starch paste without ultrasonic treatment was used, there were three peaks in the size distribution pattern of the obtained SNPs. The main peak located at about 400 nm and the peak in the range of 3 μm–6 μm suggested existence of large particles or aggregates. However, when the starch pastes with the ultrasonic treatment were used, the obtained size distribution curves only had a single peak. Moreover, with increase of ultrasonic treating time, this peak gradually shifted to small size and the width of the peak became narrower, meaning the SNPs were smaller and more uniform.

The decrease in mean size of the precipitated SNPs with the increase of ultrasonic treating time might be explained by considering three factors: the viscosity of starch paste, the molecular weight of starch and the amylose content in starch. It is known that high starch concentration leads to high viscosity of starch paste and the viscosity of starch paste is related to the entanglements and intermolecular interactions of starch molecular chains. When viscous starch paste with high concentration was used for precipitating SNPs, more starch molecular chains would remain associated during the diffusion process, which could lead to formation of larger SNPs. After the ultrasonic treatments and with increase of ultrasonic treating time, the entanglements and intermolecular interactions of starch molecular chains were broken, which would be beneficial to diffusion of starch molecular chains toward the non-solvent. Thus, SNPs with small size and narrow distribution could be obtained even using high concentration starch paste. Besides viscosity of starch paste, decrease in molecular weight of starch might also be responsible to the size reduction of the SNPs. The ultrasonic treatment cut starch molecular chains and caused

decrease in starch molecular weight. As a result, the shorter starch molecular chains diffused into the non-solvent easily, aggregated and formed smaller particles. A previous study showed that the mean hydrodynamic diameter of polylactide nanoparticles increased with increase of molar mass (Legrand et al., 2007), which is consistent with the results of this work. In addition, amylose content in starch might also influence the size and size distribution of SNPs. Qin, Liu, Jiang, Xiong, and Sun (2016) reported the differential structural and morphological properties of SNPs through the nanoprecipitation method using seven native starches with low, medium and high amylose content. Their results showed that the starches with medium content of amylose (18.9–26.5%) were more suitable for SNPs through nanoprecipitation because the prepared SNPs were more uniform in size. As calculated in Section 3.2, the amylose content in the starch of this study increased from 19.5% to 33.6% after 30 min ultrasonic treatment. Combining the data of amylose content with the size distribution patterns of the SNPs in Fig. 3(b), it could be concluded that, in the investigated range, the higher the amylose content in starch, the smaller and the more uniform the SNPs. How the amylose content in starch influences the size and size distribution of precipitated SNPs needs further exploration and study.

Table 1 presents the mean sizes and PDIs of the SNPs prepared through nanoprecipitation by using 3 wt.% starch aqueous paste with different ultrasonic treating times at various S/NS volume ratios (1/2, 1/5, 1/10). It was noted that, when the starch paste without ultrasonic treatment was used, mean size of SNPs increased with decrease of S/NS volume ratio. This result was different from the previous ones which showed the size of SNPs prepared by nanoprecipitation decreased with decreasing of S/NS volume ratio (Chin et al., 2011; Dong et al., 2015). It should be mentioned that the concentration of starch pastes in those previous works was 1 wt.%. Since the starch concentration was low, the interactions of starch molecular chains were weak and the viscosity of the starch paste was low. Herein, the concentration of the starch paste was 3 wt.% which is much higher than the one previously used. Consequently, starch molecular chains could entangle by overlapping and interpenetrate into each other, which significantly increased viscosity of the paste. The high viscosity of starch paste and strong interactions of starch molecular chains could hamper an appropriate diffusion of starch molecular chains toward non-solvent during precipitation. When S/NS volume ratio was high, i.e., less non-solvent was used, only a part of starch molecular chains, probably those having less interactions with others, diffused into non-solvent, aggregated and formed nanoparticles. Thus, the mean size of SNPs was smaller. As S/NS volume ratio decreased, i.e., large amount of non-solvent was used, more starch molecular chains, including those having strong interactions with others, had an opportunity to diffuse into non-solvent and aggregated to form larger particles. Therefore, the mean size of precipitated SNPs increased with decrease of S/NS volume ratio when high concentration starch pastes were used. It was reported that, if the solvent had a polymer concentration that was too high, it prevented nanoprecipitation and the higher the polymer concentration in the solvent, the higher the loss of polymer (Bilati, Allémann, & Doelker, 2005). A previous study showed that the yield of polylactide nanoparticles by nanoprecipitation decreased with increase of polymer concentration in the solvents (Legrand

Table 1
Mean sizes and PDIs of the SNPs prepared by precipitating 3 wt.% starch pastes with different ultrasonic treating times into absolute ethanol at various S/NS volume ratios.

Mean size (d, nm)/PDI							
S/NS	0 min	2 min	4 min	7 min	10 min	15 min	30 min
1/2	192.1 ± 3.0/0.536	154.5 ± 3.2/0.250	151.3 ± 2.3/0.253	130.0 ± 2.0/0.226	115.1 ± 1.0/0.201	109.5 ± 1.0/0.219	77.0 ± 0.7/0.256
1/5	198.4 ± 9.6/0.436	169.1 ± 1.9/0.254	149.8 ± 0.7/0.238	132.8 ± 0.9/0.225	114.8 ± 1.3/0.204	108.1 ± 0.3/0.191	75.0 ± 0.9/0.232
1/10	212.0 ± 8.3/0.613	171.7 ± 0.8/0.254	152.3 ± 0.5/0.234	127.5 ± 1.3/0.207	115.3 ± 0.9/0.198	109.6 ± 0.9/0.20	74.8 ± 0.8/0.228

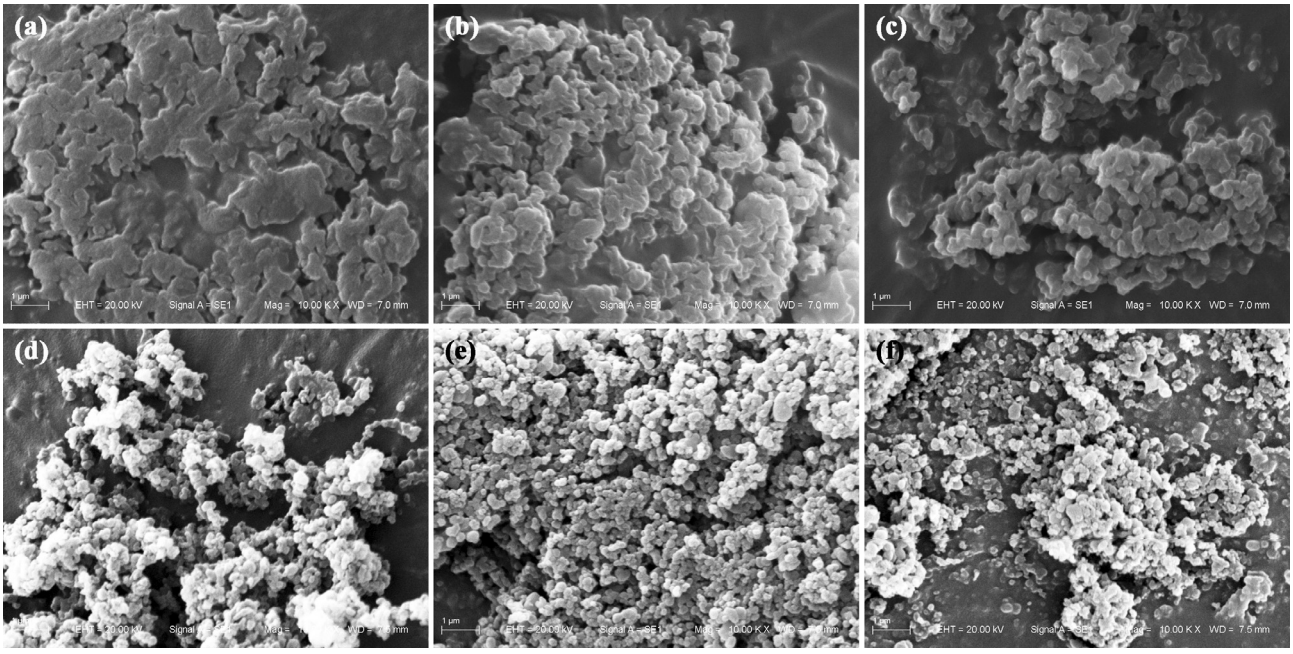

Fig. 4. SEM micrographs of the SNPs obtained by using 3 wt.% starch paste without ultrasonic treatment: (a) S/NS = 1/2, (b) S/NS = 1/5, and (c) S/NS = 1/10; and using the one with 30 min ultrasonic treatment: (d) S/NS = 1/2, (e) S/NS = 1/5, and (f) S/NS = 1/10.

et al., 2007). These results suggested that, when high concentration solutions were used, only a part of polymer molecules aggregated and formed nanoparticles during precipitation.

The data in Table 1 showed that, when the ultrasound treated starch pastes were used, the influence of S/NS volume ratio on size of the SNPs decreased. After 4 min ultrasonic treatment, the effect of S/NS volume ratio on the size of SNPs was not obvious. This is because ultrasonic treatment broke the entanglements and intermolecular interactions of starch molecular chains, which was beneficial to diffusion of starch chains toward the non-solvent. The results in Table 1 suggested that, after ultrasonic treatment of starch paste, SNPs could be prepared by nanoprecipitation with less amount of non-solvent, meaning production cost could be reduced.

3.4. Morphology of SNPs

Fig. 4 shows scanning electron microscopy (SEM) micrographs of the SNPs obtained by precipitating the 3 wt.% starch aqueous paste without ultrasonic treatment and the one with 30 min ultrasonic treatment into different amounts of absolute ethanol. The effect of ultrasonic treatment on morphological characteristics of the SNPs was significant. As shown in the SEM micrographs, the size of the SNPs obtained from the starch paste with 30 min ultrasonic treatment was smaller than those prepared with the one without ultrasonic treatment. It was also observed that when the starch paste without ultrasonic treatment was used, the morphology of SNPs changed from large agglomerates, moderate aggregates, and eventually well-defined nanoparticulate aggregates as S/NS volume ratio changed from 1/2 to 1/5 and 1/10. However, when the starch paste with 30 min ultrasonic treatment was used, all of the obtained SNPs were spherical in shape and showed a uniform distribution, indicating the effect of S/NS volume ratio on formation of SNPs was not significant. These observations were consistent with the measurements of DLS.

3.5. X-ray diffraction (XRD) analysis

Fig. 5 shows the XRD patterns of the SNPs obtained from starch aqueous pastes with different concentrations and ultrasonic treating times. Examining the XRD patterns in Fig. 5, there were weak diffraction peaks at 13.8°, 18.9° and 23.7° for all the SNPs, suggesting that the precipitated SNPs possess the V-type crystalline structure. Since there was no obvious difference in peak position and intensity of the XRD patterns for the SNPs obtained from the starch aqueous pastes with and without ultrasonic treatment, it could be concluded that effect of the ultrasonic treatments on structure and crystallinity of the precipitated SNPs was negligible.

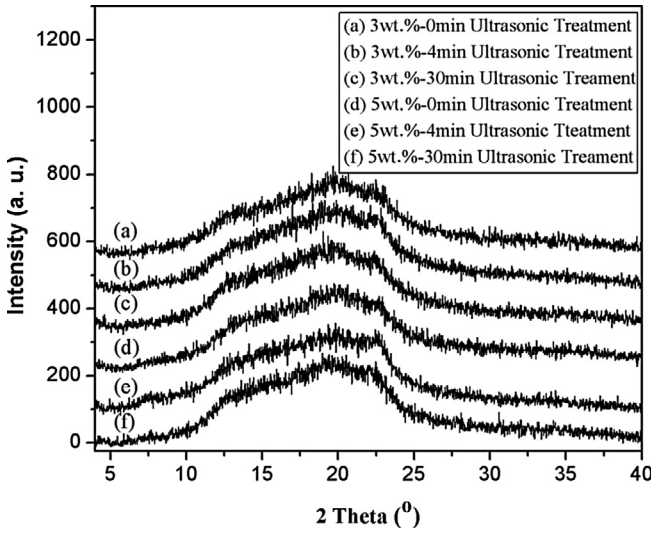

Fig. 5. X-ray diffraction patterns of the SNPs obtained from starch pastes with different concentrations and ultrasonic treating times.

4. Conclusions

SNPs were prepared using ultrasonic treated starch aqueous pastes via nanoprecipitation. The ultrasonic treatment led to decrease in viscosity of starch aqueous paste and caused starch chain scission. After ultrasonic treatment, high concentration starch aqueous paste (up to 5 wt.%) could be used to prepare SNPs, and the obtained SNPs were smaller and more uniform. Moreover, the ultrasonic treatment of starch pastes eliminated the influence of S/NS (starch paste/non-solvent) volume ratio on size of SNPs, making it possible to prepare SNPs with less non-solvent. In addition, effect of ultrasonic treatment on crystalline structure of the precipitated SNPs was not obvious. This study not only offers a convenient and easily controllable methodology to prepare SNPs with small size and narrow distribution through precipitation, but also provides an approach to produce SNPs with high efficiency and low cost.

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