



Ultrasonic effect on the octenyl succinate starch synthesis and substitution patterns in starch granules



Hai-ming Chen, Qiang Huang*, Xiong Fu*, Fa-xing Luo

College of Food Sciences, South China University of Technology, 381 Wushan Road, Guangzhou 510640, PR China

ARTICLE INFO

Article history:

Received 7 May 2013

Accepted 8 August 2013

Keywords:

Ultrasonic

Octenyl succinate starch

Synthesis

Substitution patterns

ABSTRACT

Octenyl succinate starch (OS-starch) was prepared with ultrasonic-assisted treatment. The substitution patterns in starch granule was estimated by acid hydrolysis, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction, confocal laser scanning microscopy and chemical surface gelatinization. The pasting properties of starch derivatives were studied by Brabender pasting analyzer. Results showed that ultrasound could reduce reaction time and improve the reaction efficiency over the control by 15–20%. Substitution pattern with the OS-groups located predominantly in the amorphous domains and on the granule surface with a surface effect that is more pronounced than in acetylation reactions. Ultrasonic treatment during octenyl-succinylation results in a somewhat less pronounced surface effect. Compared with OS-starch made by traditional method (OSS), OS-starch prepared under ultrasonic condition (UOSS) has slightly higher pasting temperature, break down and setback values, lower peak viscosity, hot paste viscosity and final viscosity.

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1. Introduction

OS-starch is an important chemically modified starch, which was first synthesized with water phase method by Caldwell and Wurzburg (1953). Because both hydrophilic and hydrophobic groups are present, OS-starch is widely used as emulsifier in food and industrial areas. During recent years, preparation methods and functional properties of OS-starch have been studied extensively (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005; Bao, Xing, Phillips, & Corke, 2003; Huang, Fu, et al., 2010; Song, He, Ruan, & Chen, 2006). Normally, the reaction between octenyl succinic anhydride (OSA) and starch granules is retarded due to poor penetration of the big oily droplets of OSA into the starch granules in an aqueous suspension, and the site of reaction is limited to the surface of starch granules. As a consequence, the OS groups are not evenly distributed throughout the starch granule (Huang, Fu, et al., 2010; Shogren, Viswanathan, Felker, & Gross, 2000).

Abbreviations: OSA, octenyl succinic anhydride; OSS, octenyl succinic anhydride modified starch; UOSS, OSS prepared under ultrasonic conditions; CLSM, confocal laser scanning microscopy; DS, degree of substitution; FTIR, Fourier transform Infrared spectroscopy; XRD, X-ray diffraction; T_p , pasting temperature; BD, back down value; SB, setback value; PV, peak viscosity; FV, final viscosity; HPV, hot paste viscosity; PMT, photomultiplier; MB⁺, methylene blue; RE, reaction efficiency; RT, reaction time; BU, Brabender units.

* Corresponding authors. Tel.: +86 20 8711 3845; fax: +86 20 8711 3848.

E-mail addresses: fechoh@scut.edu.cn (Q. Huang), lfxfu@scut.edu.cn (X. Fu).

Ultrasonic treatments have been reported to accelerate chemical reaction, such as saccharification (Montalbo-Lomboy et al., 2010), acetylation (Zhang, Zuo, Wu, Wang, & Gao, 2012), oxidation (Orozco, Sousa, Domini, Araujo, & Band, 2013), transesterification (Gharat & Rathod, 2013) and degradation (Xu, Chu, Graham, & Nigel, 2013). When ultrasound passes through a liquid medium, the interaction among ultrasonic waves, liquid and dissolved gas leads to acoustic cavitation that may affect morphology and structure of the starch granules. Previous reports have studied the ultrasound effects on the supramolecular structure of potato and maize starches, suggesting that notch and groove were formed on the starch granule surface (Huang, Li, & Fu, 2007; Zhu, Li, Chen, & Li, 2012). As a result, the surface area of starch particles is increased, which may improve reaction efficiency (RE). Besides, starch degradation could happen, possibly due to the breakage of α -1,6 glycosidic bond (Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008; Isono, Kumagal, & Watanabe, 1994). Furthermore, ultrasonic processor also can be used in the generation of nano-size dispersions of the reagent in water, because of the de-agglomeration effect and the reduction of droplet size. Kentish et al. (2008) reported that low frequency ultrasound (20 kHz) was employed to efficiently reduce the size of oil droplet in an aqueous suspension. However, shear forces generated at high frequency are relatively weaker than that generated at lower frequency, and not suitable for emulsification applications (Chemat, Zill-e-Huma, & Khan, 2011; Hielscher, 2005; Chandrapala, Oliyier, Kentish, & Ashokkumar, 2012).

The patterns of substitution starches are distributed non-uniformly throughout the starch granules. It was found that amylose is higher substituted than amylopectin (Steeneken & Smith, 1991; Van der Burgt et al., 1998; Van der Burgt et al., 2000). The crystalline regions are less accessible for substitution than amorphous ones (Hood & Mercier, 1978; Steeneken & Smith, 1991; Van der Burgt et al., 2000). In the crystalline domains, branching zones are favored over linear regions (Van der Burgt et al., 1998; Van der Burgt et al., 1999).

Although many studies on the synthesis and physicochemical characteristics of OS-starch have been conducted (Bhosale & Singhal, 2007; Franco, Cabral, & Tavares, 2002; Huang, Fu, et al., 2010; Jyothi, Raiasekharan, Moorthy, & Sreekumar, 2005; Park, Chung, & Yoo, 2004; Song et al., 2006), little work has been reported about ultrasonic effect on the OS-starch synthesis and OS group substitution in starch granules. The use of chemical gelatinization for revealing surface effects in starch modification has been described in rapid esterifications (Chen, Schols, & Voragen, 2004; Steeneken & Woortman, 2008), but not in slow etherification reactions. Steeneken and Woortman (2008) have obtained depth profiles of acetate groups in granular starch acetate by chemical gelatinization. In this study, OS-starch preparation was assisted by ultrasonic power (UOSS) and the products were compared to reference starches prepared without ultrasonic treatment (OSS). OS group substitution in amorphous/crystalline and surface/inner region of starch granules were further investigated by acid hydrolysis, chemical surface gelatinization, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and confocal laser scanning microscopy (CLSM) techniques.

2. Materials and methods

2.1. Materials

Maize starch was purchased from Dacheng Company (Changchun, China). The original moisture content was 13.44%. High purity 2-Octen-1-ylsuccinic anhydride (OSA) was obtained from Sigma–Aldrich Chemical Co. (Milwaukee, WI) and all other chemicals were commercial products of analytical reagent grade.

2.2. Preparation of OS-starch

The preparation of OS-starch was conducted in an ultrasonic dispersion instrument NP 8000 (Newpower Ultrasonic Equipment Co., Ltd, Guangzhou, China). Fig. 1 shows the schematic diagram of this apparatus. Pliers type ultrasonic transducers (single frequency factor at 20 kHz) are not contact with the samples, in order to avoid metal ion pollution. Transducers are powered by a generator which maximum output power 1000 W. The combined use of jacketed heat exchanger and a radiator fan ensure the temperature being controlled in an appropriate range. The probes of pH monitor and thermometer are installed in the storage tank (6 L). A pneumatic pump fitted with an air compressor was utilized in the samples circulation at a rate between 1 and 6 L/min. After the experiment is finished, the slurry was sucked out with the aid of vacuum pump.

Maize starch (1400 g, dry basis) was suspended in 2600 mL distilled water (35%, w/w) with agitation in a 5000 mL beaker. After the slurry was poured into the storage container, the air compressor was started to activate circulating pump. The pH of the suspension was adjusted to 8.5 with 3% (w/v) NaOH solution, and the temperature was controlled at 35 ± 3 °C and then ultrasonic power (0–1000 W) was switched on. Various doses of OSA (1–5%, based on the starch dry basis) was added slowly over 1 h. The reactions were carried out under ultrasonic condition. After completion of the reaction when pH in a constant state (all samples in Table 1) or

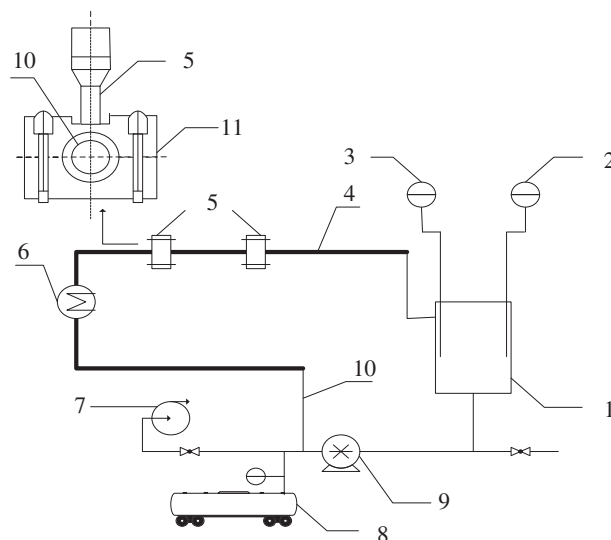


Fig. 1. Schematic diagram of the equipment for ultrasonic 1, Storage Tank; 2, pH Monitor; 3, Thermometer; 4, Jacketed Heat Exchanger; 5, Pliers Type Ultrasonic Transducers; 6, Radiator Fan; 7, Centrifugal Pump; 8, Air Compressor; 9, Pneumatic Pump; 10, Pipeline; 11, Pipe Clamp.

breaking reaction to obtain specific degree of substitution values (some samples in Table 2), the suspension was neutralized to pH 6.5 with 3% HCl and vacuum-filtered through filter paper, then the resulted modified starch was washed three times with distilled water and once with 95% alcohol to remove the residual reagents, and the solid was oven dried at 40 °C for 24 h. After drying, the samples were passed through a 100-mesh standard sieve.

2.3. Determination of the degree of substitution

The degree of substitution (DS) is the average number of hydroxyl groups substituted per glucose unit. The DS of OS-starch was determined by titration as previously reported (Song et al., 2006). OS-starch sample (5 g, dry weight) was accurately weighed and suspended by stirring for 30 min in 2.5 M HCl in isopropanol (25 mL). 100 mL 90% (v/v) aqueous isopropyl alcohol solution was added and the slurry stirred for an additional 10 min. The suspension was filtered through a glass filter and the residue was washed with 90% isopropyl alcohol solution until no Cl^- could be detected any longer (using 0.1 M AgNO_3 solution). The starch was re-dispersed in 300 mL distilled water, and then the dispersion was heated in a boiling water-bath for 20 min with stirring. The starch solution was titrated with 0.1 M standard NaOH solution, using phenolphthalein as an indicator. A blank was simultaneously

Table 1

^aEffect of ultrasonic on the DS^b and RE of OS-starch.

No.	UP/W	OSA/%	RT/h	DS($\times 10^{-3}$)	RE/%
1	0	3	6.5	17.58 \pm 0.10 ^a	75.78 \pm 0.43 ^a
2	200	3	1.5	17.95 \pm 0.06 ^b	77.37 \pm 0.30 ^b
3	400	3	1.5	19.87 \pm 0.09 ^c	85.65 \pm 0.23 ^c
4	600	3	1.5	20.33 \pm 0.05 ^d	87.63 \pm 0.16 ^d
5	800	3	1.5	20.32 \pm 0.04 ^d	87.59 \pm 0.16 ^d
6	1000	3	1.5	18.02 \pm 0.08 ^b	77.67 \pm 0.22 ^b

^a The data are averages of two measurements with standard deviation. Means in a column with different superscript letters (a–d) are significantly different ($p < 0.05$) by Duncan's least significant test.

^b DS, degree of substitution, RE, reaction efficiency, UP, ultrasonic power, RT, reaction time. All the experimental conditions were controlled pH 8.5, temperature 35 °C and starch concentration 35% (w/w).

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