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Research paper

Advanced technology for nanostarches preparation by high speed jet and its mechanism analysis



Wen Xia^a, Dong-ning He^b, Yun-fei Fu^c, Xiao-yi Wei^a, Hong-chao Liu^a, Jiang-ping Ye^d, Yun-fei Liu^d, Ji-hua Li^{a,*}

- ^a Key Laboratory of Tropical Crop Products Processing of Ministry of Agriculture, Agricultural Products Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang, 524001, China
- ^b Centre for Future Materials, University of Southern Queensland, Toowoomba, 4350, Australia
- ^c Deakin University, School of Engineering, Warn Ponds, Pigdons Road, Geelong, Vic, 3216, Australia
- ^d State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang, Jiangxi, 330047, China

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ABSTRACT

Nanostarches were successfully prepared by high speed jet (HSJ) after pretreatment of micronization. The nanostarches were obtained at the conditions of micronization treatment for 60 min, and then one cycle at 240 MPa of HSJ (188.1 nm). Moreover, after HSJ treated for three cycles, the particle size could reach the level of nanometer materials (66.94 nm). The physicochemical properties of nanostarches had been characterized. Rapid Visco-Analysis (RVA) showed that the viscosity of nanostarches significantly decreased compared with native tapioca starch and slightly decreased with increasing processing cycles of HSJ. Steady shear analysis indicated that all samples displayed pseudoplastic, shear-thinning behavior, while the flow curves of nanostarches were little impact by the processing cycles of HSJ. X-ray diffraction analysis showed that the complete destruction of tapioca starch crystalline structure was obtained after HSJ treatment. Molecular characteristics determination suggested that the degradation of amylopectin chains occurred after the treatment of micronization and HSJ, which was proved by the decrease of weight-average molar mass. The results demonstrated that nanostarches were obtained due to the breakdown of starch molecules. This study will provide useful information of the nanostarches for its potential industrial application.

1. Introduction

Starch is an important biopolymer and also one of the most abundant natural resources which has been widely applied in food industry such as thickener, paper and gelling agent (Hoover, 2001; Liu & Zhang, 2006). However, native starches using in the food industry have some limitations and one of that is due to the relatively large particle size. For example, wheat starch has a bimodal size distribution of 20–35 μm and 2–10 μm , corn starch has an average diameter of about 15 μm , rice starch has an average size of 5 μm , potato starch has an average size of 40 μm and tapioca starch has an average size of 5–35 μm . At present, various treatments (physical, chemical and enzymatic) have been used to modify starch structure, and its particle size. However, the regulation of chemically and enzymatically modified starch for food, especially baby food is very strict. There are environmental concerns on wastewater (Galliard, 1987), the demand of physical treatments for starch modification is increasing.

Micronized starch made by a vibrating superfine mill belongs to

physically modified starch. During the micronization process, starch granules peel off layer by layer from their surface edge to the interior, finally break into irregularity, small granules through the forces between iron rods and starch granules which combination with extrusion, collision, and friction. As the shape of starch granules change, the distribution of particle size of starch granules also alter (Edwards, Osborne, & Henry, 2008; Park, Wilson, Chung, & Seib, 2004; Shinji, Makoto, Katsunori, Takuo, & Tetsuya, 1998). Recently, nanostarches (the particle size is in the range of 1-1000 nm) have driven a wide range of study and received much attention of public because of its unique surface area and reaction activity (Ren, Dong, Wang, Özkan, & Mao, 2010). However, many reports have suggested that the single treatment of micronization could destroy the crystalline structure (Devi, Fibrianto, Torley, & Bhandari, 2009; Wu & Miao, 2008), increase the solubility (Zoran et al., 2010) and decrease the particle size of starches (Ren et al., 2010), but it is practically impossible to obtain nanostarches.

High speed jet (HSJ) is a novel device combination with ultra high

E-mail address: foodpaper@126.com (J.-h. Li).

^{*} Corresponding author.

velocity (Soon, Harbidge, Titchener-Hooker, & Shamlou, 2001), and it is a model of liquid-solid impact which is different from that of liquid-liquid. The operating pressure of HSJ ranges from 0 to 270 MPa which is higher than various treatments of high pressure technology such as dynamic high pressure microfluidization. HSJ is only needs high pressure which is different from jet cooking or spray cooking those requires temperature. In addition, the fixed orifice and the hydraulic system of HSJ controlled by electronically which ensure the disruption environment is repeatable, and finished in a short time. Our previous research (Xia et al., 2015) has suggested that HSJ is an intense mechanical treatment which is capable of affecting the size and gelatinization properties of TS polymer. However, native starch with poor solubility is resistant to breaking, and the process is time-consuming, powerwasting. Therefore, it is necessary to increase the solubility of starch before HSJ treatment, which could improve the efficiency of HSJ.

To the best of our knowledge, rare studies had focused on the preparation of nanostarches produced by high speed jet after pretreatment of micronization. Tapioca (obtained from cassava root- Manihot esculenta) starch (TS) was used in this research since it is one of the most important crops used in several industries (Piyachomkwan, Chotineeranat, Kijkhunasatian, & Tonwitowat, 2002). The objective of this study was to prepare nanostarches and also the mechanism analysis for this novel technology. The TS was firstly pretreatment by a vibrating superfine mill in order to destroy the crystalline structure and increase the solubility of TS, and then treated by HSJ at 240 MPa for several cycles to obtain nanostarches. The physicochemical properties of nanostarches were also investigated by particle size, steady flow behavior measurements, microstructure, Rapid Visco-Analysis (RVA), X-ray diffraction (XRD) and molecular characteristics determination.

2. Materials and methods

2.1. Materials

The moisture content of tapioca starch (Thai World Import and Export, Bangkok, Thailand) was 14.80% (w/w), and it was purchased from a food factory in Thailand. All other chemicals used were of analytical grade (Chemical Company, Xi'an, China).

2.2. Pretreatment of tapioca starch

The solubility of micronized starch prepared by a vibrating superfine mill (WZJ6, China) with a micronization time of 10, 20, 30, 40, 50, 60, 70, 80 and 90 min are shown in Fig. 1A. The solubility (according to the method of Fu, Luo, Bemiller, Liu, & Liu, 2015a; Fu, Luo, Bemiller, Liu, & Liu, 2015b) of TS increased with increasing processing time of micronization. When the processing time was beyond 60mins, the enhancement was not obvious (Fig. 1A). Moreover, the longer the processing time, the more easily the gelatinization of starch happened. It

might cause a lot of loss, since gelatinized TS could stick on the device. Therefore, considering the energy consumption of the device, and the solubility of TS, the optimum condition of pretreatment was micronization for 60 min (MT60).

2.3. Preparation of nanostarches

The experiment was carried out according to the method of Xia et al. (2015) with some modifications. Briefly, pretreated tapioca starch (100 g) was added to 1000 mL distilled water, stirring with stirring rod at room temperature until pretreated tapioca starch completely dispersed, obtained the tapioca starch-water slurry. The slurry was subjected to HSJ treatment in a TS Series Benchtop Cell Disruptor (Constant Systems TS 1.1 kw, UK) for one, two and three cycles at 240 MPa. After HSJ treatment, samples were vacuum filtered, and then dried in an oven at 40 °C for 24 h and ground for analysis.

2.4. Particle size analysis

The particle size analysis of native and MT60 were investigated by the particle size analyzer (MS2000, UK) and carried out according to the method of (Muramatsu, Tagawa, & Kasai, 2005). The particle size of nanostarches were measured by a pho-ton correlation spectroscopy with a Nano-ZS (Malvern Instruments, UK). Eight milligrams of samples (pass 200 mesh sifter) were added to 40 mL de-ionized water (DIwater). The measurements were carried out in triplicate and the data were calculated by the instrument software.

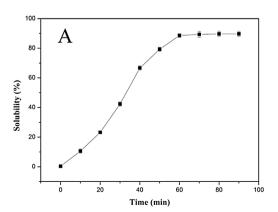
2.5. Morphological analysis

Samples of native and MT60 were mounted on aluminum nails and coated with platinum using an Ion Sputter E-100 coating system (Hitachi High-Technologies, Tokyo, Japan). Microstructural images were obtained from scanning electron microscope (S-4800, Hitachi Limited, Tokyo, Japan) operated at 3.0 kV and 1000 magnification.

The nanostarches (HSJ1, HSJ2 and HSJ3) were deposited from an aqueous dilute dispersion and cast one drop onto copper grid with carbon film support, and then dried at 20 $^{\circ}$ C. Samples were observed directly with TEM (JEM-100, JEOL, Tokyo, Japan) operated at an accelerating voltage of 100 kV.

2.6. RVA

According to the method of Li et al. (2015) with some modifications. Pasting properties of starches were obtained by RVA (Newport Scientific, Warriewood, NSW, Australia). Starch sample (3.0 g, db) was weighed using an RVA canister and 25 mL of distilled water was added into it. The suspension was then manually dispersed through a stirring rod to avoid lump formation before the RVA testing. Temperature was



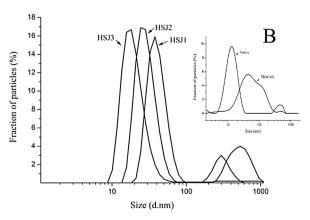


Fig. 1. Pretreatment of tapioca starch (A); Particle size distributions of tapioca starch (B).

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