Preparation and physicochemical properties of nanostarches produced by high speed jet

Wen Xia*, Ji-Hua Li, Fei Wang, Xiao-Yi Wei, and Yan-Yun Lin

Agricultural Product Processing Research Institute at Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, China
*Corresponding author

Abstract. After pretreatment of micronization for 60 mins, the nanostarches were obtained by high speed jet (HSJ) of one cycle at 240 Mpa. The nanostarches were also observed by morphological analysis. Moreover, the zeta potential of nanostarches (-17 mv) dramatically decreased compared with native (-4.90 mv), and the pasting properties of nanostarches significantly changed, indicating the disruption of the crystalline structures. The obtained nanostarches were related 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 it has been widely used in food industry such as gelling agent thickener and paper [3, 4]. Starch is also one of the most abundant natural resources, while, native starches have some limitations using in the food industry, and one of that is the relatively large particle size. Nanostarches have received much attention of public due to the unique surface area and reaction activity [5]. However, many reports have declared that the single treatment of micronization could affect the physicochemical properties of starches, but it is relatively difficult, and costly to obtain nanostarches [1, 2, 5, 8]. High speed jet (HSJ) is a novel device combination with ultra high speed, which may be useful in preparing nanostarches, and it is a model of liquid-solid impact which is different from that of liquid-liquid. The key part of it was shown in **Fig 1**. To the best of our knowledge, rare studies had focused on the preparation of nanostarches produced by high speed jet after pretreatment of micronization. Native starch was pretreated by micronization in order to increase the solubility of starch, which could improve the efficiency of HSJ. The objective of this research was to prepare nanostarches using tapioca starch and the physicochemical properties were also investigated.

2. Experimental

2.1 Materials.
Tapioca starch (Thai World Import and Export, Bangkok, Thailand) was purchased from a food factory in Thailand, and the purity degree and moisture content of it were 99.70% and 14.80% (w/w). All chemicals used were of analytical grade.

2.2 Preparation of nanostarches
Tapioca starch was pretreated by a vibrating superfine mill (**WZJ6, China**) for 60 mins (MT60), and then it was subjected to HSJ treatment in a TS Series Benchtop Cell Disruptor (**Constant Systems TS**

1.1kw, UK) at 240 Mpa for one cycle (HSJ1). The samples were vacuum filtered, and dried in an oven at 40 °C for 24 h and ground for analysis.

3. Methods

3.1 Morphological analysis
Microstructural images of native and MT60 were obtained from scanning electron microscope (S-4800, Hitachi Limited, Tokyo,Japan) operated at 3.0 kV and 1000 magnification. The nanostarches (HSJ1) were observed directly with TEM (JEM-100, JEOL, Tokyo, Japan) operated at an accelerating voltage of 100 kV.
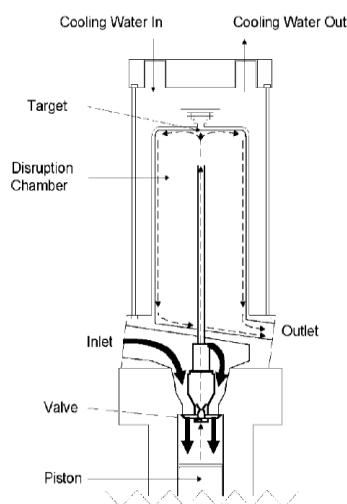

Figure. 1. The key components of high speed jet (HSJ) [6]

3.2 Zeta potential measurement
The method was carried out according to Wongsagonsup et al. [9] with some modifications. Eight milligrams of samples (pass 200 mesh sifter) were added to 40 mL de-ionized water (DI-water). The tapioca starch-water suspension was completely dispersed through a stirring rod and the supernatant was injected directly into the capillary cell of a Nano-ZS MPT (Malvern Instrument Inc., London, UK). Every sample was replicated thrice and the value of zeta potential was obtained directly by the instrument software.

3.3 Differential scanning calorimetry (DSC) analysis.
Samples were analyzed by the DSC using Q2000-DSC (TA Corp., New Castle, USA) according the method of Xia et al. [10] with some modifications. The samples were heated from 20°C to 100 °C at a heating rate of 10 °C/min. The onset temperature T_o, peak temperature T_p, conclusion temperature T_c and gelatinization enthalpy (ΔH_g) were calculated by a Universal Analysis Program, version 4.7A (TA Instruments).

3.4 Statistical analysis.
All of the experiments were done in triplicate. The data were analyzed using the SPSS (SPSS Inc., 1998, Chicago, IL, USA) version 9.0 for Windows (Duncan's test). The results were expressed as means ± standard deviations. Significance differences were used at $P<0.05$.

4. Results and discussion

4.1 Morphological analysis

The morphology of all samples were investigated by SEM (**Fig.2 A, B**) and TEM (**Fig.2 C**). It can be seen that the native tapioca starch granules were smooth surfaces with spherical. However for MT60 (**Fig.2 B**), the structure of tapioca starch was dramatically destroyed, and it became rough and loose with cracks at granule surface. As shown in **Fig.2 C**, after HSJ treatment for one cycle, nanostarches were obtained. we can observed that nanostarches displayed a circular shape and aggregated with each other. The nanostarches were obtained may be due to the breakdown of starch molecules.
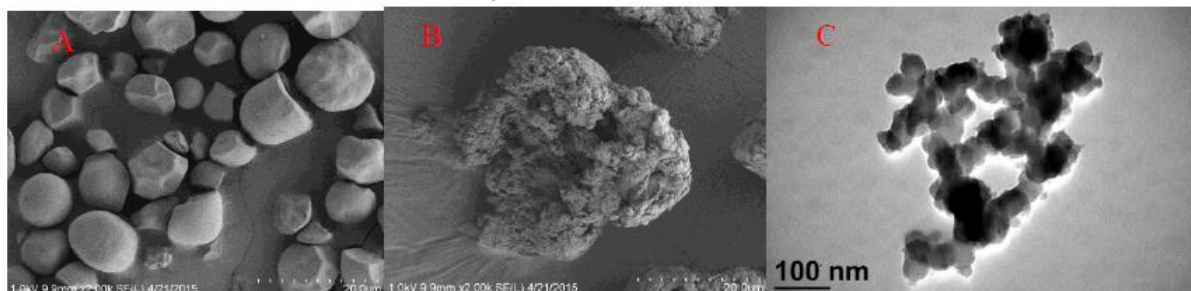

Figure.2 morphology of samples：A (native), B (MT60) and C (HSJ1)

4.2 Zeta potential analysis
The zeta potential of all samples are presented in **Table 1**. The zeta potential of native TS was -4.90 mv, indicating that native TS particle is accounted for the agglomeration [9], and decreased to -13.7 mv for MT60. When the sample of MT60 treated by HSJ for one cycle at 240 Mpa, the zeta potential of -17 mv was obtained. This suggested that nanostarches could dispersed better in water than native TS, since the magnitude of zeta potential as an indicator of the potential stability of the colloidal system. The greater the absolute value of zeta potential, the more stable it is. Similar result was also found by Wongsagonsup et al. [9].

Table 1. Pasting properties and zeta potential of samlpes

Sample name	T_o(°C)	T_p(°C)	T_c(°C)	ΔH_g(J/g)	Zeta potential (mw)
native	63.83±0.11a	68.27±0.21a	77.70±0.10a	2.07±0.07a	-4.90±0.08a
MT60	57.07±0.10b	64.21±0.10b	72.40±0.10b	1.39±0.03b	-13.7±0.03b
HSJ1	---	---	---	---	-17±0.07c

    Data are presented as means ± standard deviations of triplicate measurements. Significant differences in each column are expressed as different letters (p<0.05).
    T_o, Onset temperature; T_p, Peak temperature; T_c, Conclusion temperature; ΔH_g,

4.3 DSC analysis
Differential scanning calorimetry (DSC) was used to investigate the gelatinization properties of samples . The gelatinization properties of samples are listed in **Table 1**. The gelatinization temperatures (T_o, T_p, T_c) and gelatinization enthalpy (ΔH_g) were shifted to lower values in MT60 compared with control. The finding implied that the thermal properties of MT60 was changed. The reason may be that pregelatinization of starch during micronization process, leading to the decrease in ΔH_g and gelatinization temperatures (T_o, T_p, T_c). The reduction in ΔH_g confirmed the disruption of the crystalline structures [7], which was also in accordance with the results obtained from SEM. However, no gelatinization temperatures (T_o, T_p, T_c) and gelatinization enthalpy (ΔH_g) were detected in HSJ1, indicating that the sample were fully gelatinization after treated by HSJ for one cycle.

5. Conclusions
Nanostarches were obtained by HSJ after pretreatment of micronization which was confirmed by morphological analysis. The zeta potential of nanostarches were dramatically decreased from -4.9 (native)

to -17 mw, and the gelatinization temperatures and gelatinization enthalpy were not detected, indicting the nanostarches were fully gelatinization after HSJ. This work may supply knowledge of a new way to produce nanostarches, which could expand its applications in food processing.

Acknowledgements

References

[1] Chan, W., He, X. W., Qiang, H., Xiong, F., & Sha, L. (2013). Physicochemical properties and application of micronized cornstarch in low fat cream. J*ournal of Food Engineering*, *116*, 881-888.

[2] Devi, A. F., Fibrianto, K., Torley, P. J., & Bhandari, B. (2009). Physical properties of cryomilled rice starch. *Journal of Cereal Science*, *49*, 278-284.

[3] Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: a review. *Carbohydrate Polymers*. *45*, 253-267.

[4] Liu, P. L., & Zhang, B. S. (2006). Non-crystal starch granule. Journal of the Chinese Cereals and Oils Association. 21, 18-22.

[5] Ren, G. Y., Dong, L., Wang, L. J., Özkan, N., & Mao, Z. H. (2010). Morphological properties and thermoanalysis of micronized cassava starch. *Carbohydrate Polymers*, *79*, 101-105.

[6] Soon, S. Y., Harbidge, J., Titchener-Hooker, N. J., & Shamlou, P. A. (2001). Prediction of drop breakage in an ultra high velocity jet homogenizer. *Journal of Chemical Engineering of Japan*, *34*, 640-646.

[7] Sandhu, K. S., Singh, N., & Lim, S. T. (2007). A comparison of native and acid thinned normal and waxy corn starches: physicochemical, thermal, morphological and pasting properties. *LWT-Food Science and Technology*, *40*, 1527-1536.

[8] Wu, Q., & Miao, Y. (2008). Mechanochemical effects of micronization on enzymatic hydrolysis of corn flour. *Carbohydrate Polymers*, *72*, 398-402.

[9] Wongsagonsup, R., Shobsngob, S., Oonkhanond, B., & Varavinit, S. (2005). Zeta potential and pasting properties of phosphorylated or crosslinked rice starches. *Starch-Starke*, *57*, 32-37.

[10] Xia, W., Wang, F., Li, J., Wei, X., Fu, T., & Cui, L., et al. (2015). Effect of high speed jet on the physical properties of tapioca starch. *Food Hydrocolloids*, *49*, 35-41.