Effect of micronization on the solubility, viscosity and structural properties of tapioca starch

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Abstract. Tapioca starch (TS) was treated by vibrating superfine mill with different micronization time (15, 30, 45, and 60 mins) and the solubility, viscosity and structural properties were also studied. The solubilities of treated samples were dramatically increased after micronization treatment. The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of samples did not display any new peaks compared to native TS but had different intensity in some peaks. Rapid visco analyzer (RVA) determination suggested that micronization process altered pasting features, resulting in a decrease in viscosity and pasting temperature.

1. Introduction
Micronization techniques belongs to physical modification, and ball milling is the most commonly micronization techniques, which used to modify starch granules when smaller fragments are required. Some researchers had been reported that ball milling could damage the crystalline structure [2], increase the solubility and decrease the granule size of starches [6].

Vibrating superfine mill (VSM) was also a machine of micronization technique. Through the forces between iron rods and starch granules, it keeps a linear contact with material, which was different from the mechanism of ball milling. So, vibrating superfine mill might be more efficiency and uniform than ball milling. The main parts of VSM are shown in Fig. 1. At present, the effect of VSM on the properties of starches were rare studies. Therefore, the objective of this study was to investigate the effect of VSM on the solubility, viscosity and structural characteristics of tapioca starch (TS) by Rapid visco analyzer (RVA), solubility and Fourier Transform Infrared Spectroscopy (FTIR).

Figure. 1. The equipment diagram of vibrating superfine mill
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 samples
Tapioca starch was treated by a vibrating superfine mill (WZJ6, China) for 15, 30, 45, and 60 mins. Then, the samples were put into package for using.

3. Methods

3.1 Determination of solubility
The solubility (S) was determined according to the method of Fu et al. [3].

3.2 Rapid visco analyzer (RVA)
RVA was used to investigated the pasting properties of starch, and the experiment was carried out according to the method of Xia et al. [7].

3.3 Fourier Transform Infrared Spectroscopy (FTIR)
According to the method of Xia et al. [7], samples were investigated by a Nicolet Nexus 470 spectrometer (Thermo Electron Corporation, Waltham, MA, USA). The dried samples were measured in the frequency range of 4000-400 cm^{-1} and the data were analyzed with Ominic 7.2 software.

4. Results and discussion

4.1 Solubility
The solubilities of native and micronized TS are depicted in Fig. 2. It can be seen that the solubility of native TS is poor and, it increased dramatically with increasing treating time from 15 to 60 mins, with highest value obtained at 60 mins. The solubility of starch was influenced by starch size distribution, crystalline structure and degree of gelatinization [1]. In our study, the increased of solubilities may be due to micronization process combination with extrusion and shear stress, leading the destruction of the crystalline structures and the partial gelatinization of micronized TS. The loose structure would make it became more accessible for water, resulting the increase in solubilities.

![Figure 2. The Solubility of native and micronized TS](image)

4.2 RVA
Pasting properties of all samples were investigated using a Rapid Visco Analyzer (RVA), which is an effective method to illustrate the pasting properties of starch during heating and cooling process. The
curves of all samples are shown in Fig. 3. Native TS displayed typical RVA pasting viscosity profiles, while completely different patterns in pasting viscosity profiles were observed for micronized starches. The curves of micronized starches were fluctuated (15 mins, 30 mins and 45 mins) which might be due to the partial gelatinization of TS granules after micronization and few ungelatinized TS granules embedded within the gelatinized matrix. Moreover, when the micronization time was 60 mins (MT60), the curve became almost a straight line. The note phenomenon implying that MT60 was almost fully gelatinization and the sensitivity of RVA appeared to be too low to detect viscosity of MT60.

Considering the dramatically decrease in viscosity of TS after treated by micronization, it might be expanded its application in food processing. Since being composed of high amylopectin content, TS often shows high viscosity, which limits its application in the food industry.

Figure. 3. The RVA of native and micronized TS

4.3. FTIR analysis

As shown in Fig. 4, the FTIR spectral pattern of all samples showed similarity in the shape, while with different intensity in some peaks. In the functional group region of the spectrum, a stronger and broader band between 3200 cm\(^{-1}\) and 3550 cm\(^{-1}\) was obtained after micronization treatment compared with the native TS. The result suggested that after pressure treatment induced by micronization, more hydroxyl groups of TS were exposed. Since the wave number at 3550-3200 cm\(^{-1}\), which was associated with the O-H stretching absorption. [9]. In addition, the peak associated with hydrogen bonds was 3320 cm\(^{-1}\) for native TS, while the micronized samples moved to the red shift were 3375 cm\(^{-1}\), 3393 cm\(^{-1}\), 3430 cm\(^{-1}\) and 3450 cm\(^{-1}\), respectively. These results showed that the intrachain and interchain hydrogen bonds between TS chains became weaker during micronization process. The intensity of band at about 1640 cm\(^{-1}\) was assigned to the deformation vibrations of hydroxyl groups in water [4], and the intensity of this band increased after micronization treatment, indicating that pressure cause the destruction of TS structure, resulting more deformation vibrations of the hydroxyl groups in water. Similar report was also found by Xia et al. [8].

Some characteristic peaks in the fingerprint region of the spectrum can also be observed that the wave number at 995 cm\(^{-1}\) and 926 cm\(^{-1}\) regions of treated samples became much broader compared to native. The finding implied that the structure of TS was destroyed, which became more accessible for water, since the band at about 926 cm\(^{-1}\) was attributed to the characteristic index of hydrophilicity of starches, and the wave number at 995 cm\(^{-1}\) was assigned to the interaction between water and starch [5]. The bands at 1020 cm\(^{-1}\) and 1047 cm\(^{-1}\) were assigned to the amorphous fractions and crystalline structures, respectively. The peak around 1047 cm\(^{-1}\) became less intense after micronization treatment. This may be ascribed to the crystalline region was destroyed by the treatment of micronization, resulting in an increase of amorphous fraction.
5. Conclusions
In this study, the effect of micronization on the solubility, viscosity and structural properties of tapioca starch was investigated. Results showed that the solubilities were significantly increased after micronization treatment, and the viscosity was dramatically decreased. The physical properties change may be due to the destruction of crystalline structures, which was also confirmed by FTIR analysis. The findings may provide some theoretical basis of modifying starch in food processing.

Acknowledgements
The authors gratefully acknowledged the Financial Support by Hainan Natural Science Foundation (Project no. 20163113 and 20163114) and National Natural Science Foundation of China (No. 31601397).

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