

Effect of Ultrasonic Treatment on Physical Properties of Tapioca Starch

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Abstract. A new processing method for the production of modified starch, high power ultrasonic treatment (400 W), was applied to native tapioca starch. The effect of processing parameters such as ultrasound amplitude (50 and 100%) and sonication time (10, 20 and 30 minutes) on the properties of the modified starches was investigated. Starch granule morphology observed by scanning electron microscopy (SEM), swelling power, solubility and powder x-ray diffractometry (PXRD) of the obtained ultrasonically treated tapioca starch were determined and compared with native as well as heat-treated tapioca starches. The results from SEM and PXRD showed that the ultrasonic treatment of tapioca starch distorted the crystalline region in starch granules, especially at higher amplitude or sonication time. The swelling power of the tapioca starch increased after treatment with both heat and ultrasound, in which the swelling power of ultrasonically treated starch was higher than that of heat-treated starch. It was found that tapioca starch treated by ultrasound for a certain period of time has an increase in solubility. The increase in the swelling power is associated with water absorption capacity and starch granules solubility.

Introduction

Starch is a semi-crystalline biopolymer that is composed of a large number of glucose units. Starch granules contain two types of glucose polymers, amylose and amylopectin. Amylose molecules are linear, resulting from D-glucopyranosyl units connected by α 1,4 linkage. Amylopectins include a large number of short chains linked together at their reducing end side by α 1,6 linkage, which give rise to branching (1). The proportion of both molecules depends on the botanical sources of starch. Starch, in its native form, is insoluble in water and resistant to most chemical and enzymatic attacks. Consequently, modification of starch is carried out to overcome defect of native starches and increase the usefulness of starch for industrial applications. A physical modification causes substantial changes in chemical and the physical nature of granular starch due to the rearrangement of intra- and intermolecular hydrogen bonding between the water and starch molecules, resulting in the collapse or disruption of molecular orders within the starch granules (2). This results in irreversible changes in the starch properties (3). New methods for the physical modification of starches have been investigated in the last decade, including ultrasonic treatment.

Ultrasonic is attributed to the cavitation process composed of formation, growth, and rapid collapse of microbubbles (4). The rapid collapse can produce localized high pressure and temperature estimated to be approximately 5000 K (5). As a result, the polymer chains near the collapsing microbubbles are caught in a high gradient shear field, which leads to the breakage of macromolecular C–C bonds, and formation of long chain radicals (6). The aim of this study was to investigate the effect of a high power ultrasonic treatment (400 W) on physical properties of native tapioca starches. Various processing parameters were used, i.e., ultrasound amplitude (50 and 100%) and treatment time (10, 20 and 30 min). The modified tapioca starches were characterized and compared with native and heat-treated tapioca starches.

Experimentals

Ultrasonically treated sample was prepared by high intensity probe (model UP400S, Hielscher, Germany). Aqueous starch slurry (3% w/w) was treated for 10, 15 and 30 min with different amplitudes (i.e., 50 and 100%) of ultrasound power (400 W, 24 KHz). For heat-treated starch, the aqueous starch slurry was heated at 80°C in an oil bath with stirring for 30 min to completely solubilize. The modified starches were dried by freeze dryer (model Freezone 2.5, Labconco, USA) and then powdered using a laboratory mill before further characterization.

The surface morphology of native and modified tapioca starches was observed using a scanning electron microscope (SEM; model Maxim-2000, Camscan Analytical, England), under accelerating voltage of 15 keV. Starch samples were fixed on SEM stub with double-sided adhesive tape and then coated in a vacuum with thin gold layer before investigation. The PXRD diffractograms of native and modified tapioca starches were obtained using a powder x-ray diffractometer (model Miniflex II, Rigaku Co., Japan) at 30 kV, 40 mA over the range of 5-45° 2θ by the scanning speed of 2 degrees/min using Cu Kα radiation wavelength of 1.5406 Å.

The solubility and swelling power of the starches were assessed using established methods (7). Starch was weighed (W_0) into a centrifuge tube with coated screw cap to which 10 mL of distilled water were added. The tube was heated at 80°C in an oil bath for 30 min. The tube was cooled to room temperature and centrifuged for 15 min at 2,200 rpm. The supernatant was decanted and dried to constant weight (W_1) in a hot-air oven at 100°C. The wet starch sediment was weighed (W_2) to obtain the swelling of the starch. The solubility and swelling power were calculated as follows:

$$\text{Solubility (\%)} = \frac{W_1}{W_0} \times 100 \quad \text{Swelling power (g/g)} = \frac{W_2}{W_0 (100 - \text{solubility})} \times 100$$

Results and Discussion

Scanning electron microscopy. The granule appearance of the native and modified tapioca starches after freeze drying was investigated using SEM, as shown in Fig. 1. The SEM micrograph of native tapioca starch (Fig. 1A) showed typical granules of spheroid forms, 10-20 μm in size, while the modified starches showed deformation of granular structure as aggregates of broken granules and the formation of a film-like structure (Fig. 1B-1H). The dry sample obtained from ultrasonically treatment showed more disrupted granules when compared with heat-treated starch. In addition, the increase of ultrasound amplitude and sonication time tended to more destroy the granules which showed a smoother surface. These results suggested that the high power ultrasonic treatment caused substantial changes in the physical nature such as deformation and loss of granule structure.

PXRD diffratograms of modified starches. The crystallinity of starch granule was assessed by powder x-ray diffractometry. The PXRD diffractograms of native and treated tapioca starches are presented in Fig. 2. The diffractogram of native tapioca starch showed typical feature characteristics of A-type crystallinity starch with strong peaks 2θ at about 15°, 17°, 18°, and 23° (8), which indicated that tapioca starch is a typical semi-crystalline material. The diffractograms of treated tapioca starches showed a decreased intensity of crystallization peak, i.e., ultrasonically treated tapioca starches a more decrease than heat-treated tapioca starches. This result indicates that the crystalline structure of tapioca starch was destructed after ultrasonic treatment. The crystalline structure was then transformed into amorphous structure in which the ultrasonically treated tapioca starches showed more amorphous structure than heat-treated tapioca starches. However, PXRD diffractograms of tapioca starches treated ultrasonically with different ultrasound amplitudes (50 and 100%) and sonication times (10, 20 and 30 minutes) were not significantly different.

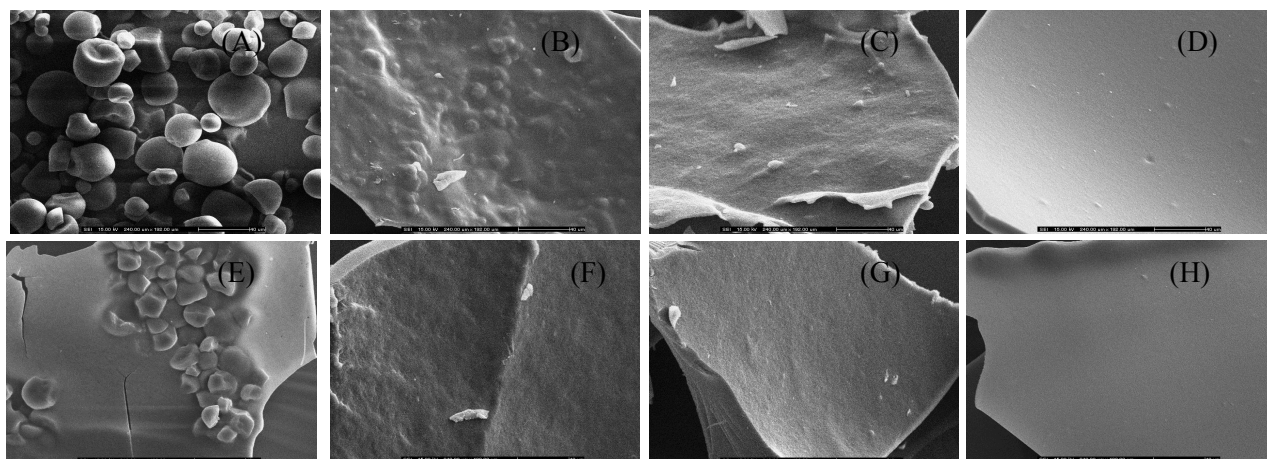


Figure 1. SEM images of the native and modified tapioca starches; (A) native, (B) heat-treated, ultrasonically treated with amplitude of 50% for (C) 10, (D) 20, (E) 30 min and ultrasonically treated with amplitude of 100% for (F) 10, (G) 20, (H) 30 min.

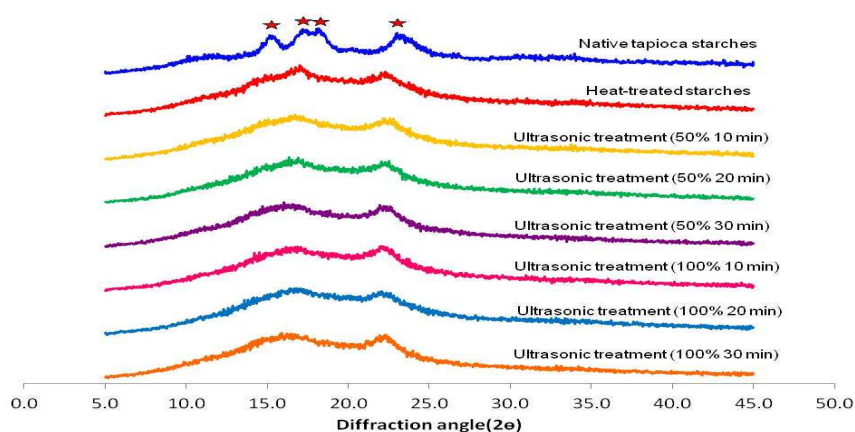


Figure 2. Powder x-ray diffractograms of native and modified tapioca starches.

Swelling power and solubility. The swelling power and solubility of native, heat-treated and ultrasonically treated tapioca starches are shown in Fig. 3. Ultrasonically treated starch has higher swelling power and solubility values, compared to native and heat-treated starches. The results demonstrated the higher water absorption capacity which is resulted from ultrasound disruption of the granule associated with higher facility for water entrance in starch granule leading to a higher water uptake. The major impact on starch granule disintegration is caused by the cavitation forces which can break the crystalline molecular structure and chains of tapioca starch by disrupting covalent bonds. Therefore, the water molecules could bind more to free hydroxyl groups of amylose and amylopectin by hydrogen bonds, which cause an increase in swelling power and solubility (9). Also, the increased solubility was observed when sonication time was increased but swelling power was not significantly different. The swelling power and solubility of ultrasonically treated starches were not significantly changed when the ultrasound amplitude was increased from 50 to 100 %.

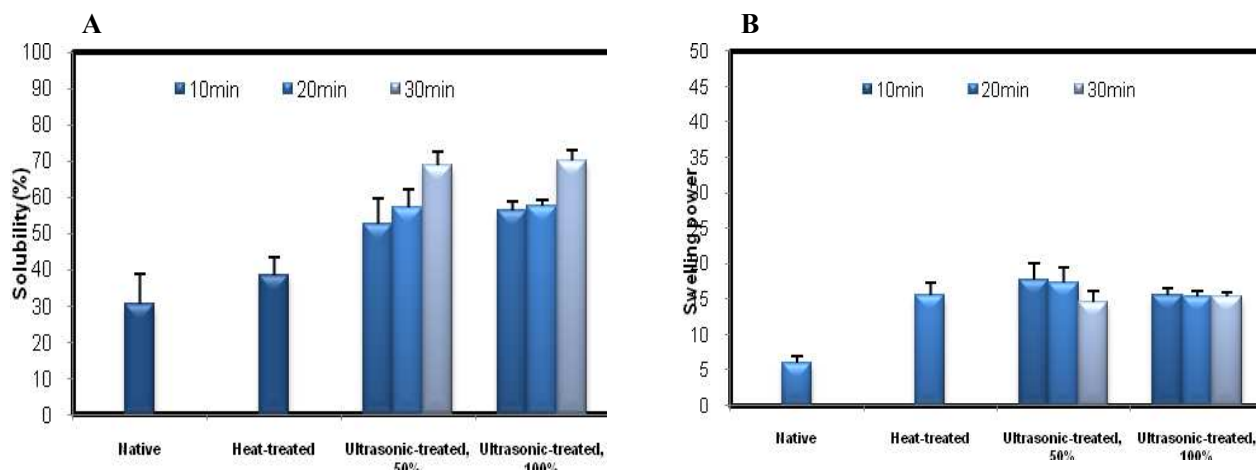


Figure 3. (A) Solubility and (B) swelling power of native and modified tapioca starches.

Conclusions

Compared to native tapioca starch, the modified starch with ultrasonic treatment has resulted in changes in the starch molecular structure followed by significant variations in physical properties. PXRD results showed a decrease in intensity of crystallization peak. SEM micrographs showed obvious impact of ultrasound on the structure of starch granules. The increase in solubility and swelling power of ultrasonically treated starch is associated with the water absorption capacity. The higher ability of water reach into starch granule due to it was disrupted by mechanically damages of ultrasound treatment which leads to a higher water uptake and retention.

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