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Characterization of hydrothermal and acid modified proso millet starch

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ABSTRACT

The aim of this study was to characterize modified proso millet (*Panicum miliaceum*) starch in order to explore its prospect as an ingredient for food applications. The current study determined the effect of hydrothermal modification (HTM) at 30 g/100 g moisture level and acid modification (AM) with HCl on extracted proso millet starch physicochemical and functional properties. Amylose content reduces with AM while HTM showed negligible effect. HTM starch had higher water binding capacity (WBC) whereas AM starch showed reduction in WBC. Additionally, the solubility and swelling power of HTM starch decreased with increase in temperature, and in AM starch solubility increased sharply but swelling power increases at 80 °C but significantly ($P < 0.05$) reduces at 90 °C. HTM caused increase in gelatinization temperature with a mean value of 87.17 °C compared to 78.61 °C in native starch. AM reduced onset (69.71 °C) and gelatinization temperature (77.26 °C), and it increased the range (26.56 °C) significantly ($P < 0.05$) with no effect on ΔH_G. Pasting profiles of native proso millet starch changed significantly ($P < 0.05$) upon modifications and reduction in peak viscosity was observed in both modifications. AM reduced the holding strength, final viscosity, setback and breakdown whereas HTM reduced only breakdown and no change was observed in other parameters.

1. Introduction

Interest in millet utilization has increased due to the various rediscovered health benefits and also due to its increasing use as non-gluten ingredient in food applications (Zhu, 2014). Millet has many advantages over other cereals such as higher resistance to pest and diseases, adaptability to a wide range of climatic conditions and grows well in high temperatures and dry conditions (Saleh, Zhang, Chen, & Shen, 2013). Besides having agronomic advantages, millets have better amino acid composition and high nutritive value which is comparable to that of major cereals such as wheat, corn and rice (Klopfenstein & Hoseney, 1995, pp. 125–168; Parameswaran & Sadasivam, 1994). Millet is widely consumed as food in African countries, China and Indian subcontinent, however it is not part of human diet in USA and mainly used for animal and bird feed (Lyon, 2008). Proso millet is the major variety of millet grown in the US with a total production of 418,145 tons in 2013 (FAO, 2013). Proso millet, considered an underutilized grain in USA, can serve as source of starch as it is reported to contain 60–67% starch (Santra, 2013). Due to the vast application of starches in food systems, different sources with good functional properties are being explored.

Starch is a naturally renewable, inexpensive and biodegradable material which is used to alter the textural properties of several foods (Radley, 1976, pp. 51–115). It has various industrial applications such as thickener, binder, encapsulating agent, stabilizer and gelling agent (Radley, 1976, pp. 51–115). However, it is the modified starch that is used mostly in industrial applications due to undesirable characteristics of native starch upon cooking whereas modification improves gelling tendency, clarity and texture (Bemiller, 1997). Starch modification alters physical and chemical properties to improve functionality of native starch (Hermansson & Svegmark, 1996). Hydrothermal modification (HTM) involves controlled application of heat and moisture, which causes physical modification of starches without gelatinization and damage to the starch granules with respect to size, shape or birefringence (Stute, 1992). Acid modification (AM) of starch is a chemical modification process involving hydrolysis of starch using hydrochloric acid, which breaks the glycosidic linkages of α-glucan chains, changing the structure and characteristics of native starch (Hoover, 2000). AM is used to modify physicochemical properties of native starch

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for applications in various industries such as food and textile (Radley, 1976, pp. 51–115). Acid hydrolysis is widely used for production of starch gum candies, paper, cationic and amphoteric starches (Wurzburg, 1986). Understanding the properties, and potential uses of proso millet starch significantly contributes to the further expansion of millets as alternative functional crop (Zhu, 2014). The present study was undertaken to explore the behavior of native and modified starches as affected by different modifications methods. Most studies on millet starch have focused on pearl millet and other major millet varieties but no work has been done to investigate the effect of hydrothermal and acid modification on proso millet starch.

2. Materials and methods

2.1. Raw materials

Proso millet flour was purchased from Bob's Red mill (Milwaukie, OR, USA) and stored at ambient temperature (24–28 °C). All chemicals used for the analyses were of analytical grade (Sigma Aldrich, St. Louis, MO, USA).

2.2. Starch isolation

Starch was isolated using alkaline steeping method (Sira & Amaiz, 2004; Wang & Wang, 2001a, b). Proso flour (100 g) was steeped in 200 ml of 0.1 g/100 g NaOH for 18 h. Mixture was blended for 2 min using waring blender and passed through a sieve (U.S. 100 sieve size) and centrifuged at 2000 rpm for 15 min. The top layer was carefully decanted and the bottom layer was re-slurried and washed thrice with 0.1 g/100 g NaOH, while removing the upper layer carefully every time. The starch was washed with deionized water, then treated with 0.1 mol/L HCl to pH 6.5, and washed with deionized water four times, centrifuged, dried in an oven at 45 °C for 48 h.

2.3. Acid modification

Millet starch was modified according to the method described by Wang and Wang (2001a, b). HCl (0.14 mol/L) was added to 40 g starch and kept in water bath for 8 h at 50 °C and thereafter, 1 mol/L NaOH was used to adjust the pH to 6.5. Starch slurry was washed thrice with deionized water and then dried in an oven at 45 °C for 24 h.

2.4. Hydrothermal modification

Millet starch, conditioned to 30 g/100 g moisture content (dry basis) was added in glass bottle and kept at 4 °C for 12 h to equilibrate the moisture. Starch sample in sealed glass bottle was then heated for 3 h at 110 °C. The bottle was occasionally shaken to distribute the heat evenly and then cooled and dried for 4 h at 45 °C (Collado, Mabesa, Oates, & Corke, 2001).

2.5. Physico-chemical analysis

Moisture, protein, fat, ash were determined using AOAC standard methods (AOAC, 2005). Amylose content were determined using AACCI method 61–03.01 (AACC, 1997). Starch sample (100 mg) was mixed with 1 ml of 95 g/100 g ethanol and 9 ml of 1 mol/L NaOH and then transferred to 100 ml volumetric flask. Flasks were kept at room temperature for 10 min then heated in boiling water bath for 10 min and cooled for 2 h at room temperature. The resulting mixture was diluted to 100 ml using distilled water and mixed vigorously. An aliquot of starch solution (5 ml) was pipetted into 100 ml volumetric flask containing 50 ml distilled water. 1.0 mL of acetic acid (1 mol/L) and 2 mL iodine solution were added and diluted to 100 ml. After 20 min, absorbance was measured at 620 nm using blank to zero the spectrometer (EVO 60 ThermoFisher scientific, Waltham, MA USA). Standard curve was developed using standard amylose and amylopectin blends and used to measure amylose content.

2.6. Thermal properties

Degree of gelatinization was determined using differential scanning calorimetry (DSC – Q20, TA instruments, New Castle, Delaware, USA). Starch sample (10 mg, dry basis) was weighed into high volume stainless steel pans, followed by addition of 20 μl of distilled water. The pan was hermetically sealed and equilibrated at 4 °C for 24 h. Samples were kept at room temperature for one hour prior to scanning from 10 to 150 °C at 10 K/min (Krueger, Knutson, Inglett, & Walker, 1987).

After gelatinization, the samples were kept at 4 °C for 10 d and then reheated at the rate of 10 K/min from 10 °C to 150 °C to determine retrogradation properties.

2.7. Pasting properties

Pasting characteristics were determined using Discovery Hybrid Rheometer (DHR) with starch pasting cell (DHR-2, TA instruments, New Castle, Delaware, USA). A mixture of 3.5 g starch (14 g/100 g moisture) in 25 ml of distilled water was stirred at 160 rpm. Samples were held at 50 °C for 1 min and then heated to 95 °C at 4 K/min and held at 95 °C for 5min. Subsequently, samples were cooled to 50 °C at 4 K/min and held at 50 °C for 5 min. A plot of viscosity (Pa.s) vs. time (s) was used to determine pasting temperature, peak and final viscosity, holding strength, setback and breakdown.

2.8. Solubility and swelling power

Solubility and swelling power was determined using leach method (Leach, McCowen, & Schoch, 1959) modified by Balasubramanian, Sharma, Kaur, and Bhardwaj (2014); Kusumayanti, Handayani, and Santosa (2015) and Subramanian, Hoseney, and Bramel-Cox (1994). Starch (0.1 g) was heated in 10 ml of water at 70, 80, and 90 °C for 30 min. Samples were stirred occasionally to avoid lump formation and then centrifuged at 3000 rpm for 15 min. Supernatant was removed and starch sediment was weighed. Supernatant was dried for 2 h at 130 °C and then weighed.

$$Solubility(\%) = (W_{ss}*100)/W_s \quad (1)$$

Where, W_{ss} is the weight of soluble starch (g) and W_s is the weight of the sample (g).

$$Swelling\ power(\%) = (W_{sp}*100)/(W_s*(100 - \%solubility)) \quad (2)$$

where, W_{sp} is the weight of sediment paste (g) and W_s is the weight of sample (g).

2.9. Water binding capacity

Water binding capacity (WBC) was determined using the method described by Yamazaki (1953). A mixture of 2.5 g (dry basis) starch in 25 mL distilled water was stirred for 30 min and centrifuged at 3000 rpm for 10 min. Excess water was removed and then residue is weighed.