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ORIGINAL ARTICLE

Physicochemical, thermal and structural properties of heat moisture treated common buckwheat starches

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Abstract Common buckwheat starch modified by heat moisture treatment at different temperatures was analysed for functional, pasting, structural, thermal, gel textural and morphological properties. Heat moisture treatment decreased swelling power, solubility and oil absorption capacity while amplified water absorption capacity of buckwheat starch. Lower whiteness index with higher a* and b* values were observed for treated starches. Modified starches showed increased paste clarity and reduced syneresis. A declining order of paste clarity and freeze-thaw stability of native and treated starches was noticed during storage period. RVA analysis showed reduced viscosities (peak, trough, breakdown, final and setback viscosity) for hydrothermally treated starches. Increased gel hardness was observed for modified starches and starch sample treated at 85 °C produced the hardest gel. FTIR spectrums of native and treated starch samples showed peaks at similar wavenumbers. Micrographs revealed the polygonal shape of native starch granules with flat areas on surface. Increased agglomeration in heat moisture treated starch samples was noticed in scanned images of starches. X-ray diffraction analysis showed 'A' type crystalline pattern in native starch of common buckwheat and no alteration in crystalline pattern due to hydrothermal treatment was observed. Relative crystallinity of native buckwheat starch decreased during heat moisture treatment and the minimum value was recorded for starches treated at 85 °C. Differential scanning calorimetry showed raised gelatinisation temperatures (T_O, T_P and T_C) and reduced ΔH values for hydrothermal treated starches.

Keywords Common buckwheat starch · Hydrothermal treatment · Pasting properties · X-ray diffractometry · Thermal properties

Introduction

Starch is the major food reserved polysaccharide in plants and is composed of glucose polymers—amylose and amylopectin, the ratio of which depends on origin of starch. Starch is widely used raw material in food industries and its applications are chiefly governed by its granular structure, pasting behaviour, gelatinization and some functional properties like solubility, swelling, water and fat absorption capacity. Starch from each source is unique in nature having different characteristics determining its suitability for particular application. Versatility of starch has made it a requisite tool in creating innovative foods for future. Irrespective of sources, native starches are undesirable for many applications due to their inability to withstand processing conditions. So as to meet the new technological requirements of modern industries, modification of starch by physical, chemical, enzymatic treatments or genetic transformation is in trend. Starch modification is done with a purpose of improving the functional characteristics of starches and tailoring them to specific applications. Heat moisture treatment of starch is a physical method of starch modification involving heat treatment (80–120 °C) at restricted moisture level (10–30%) for a time period ranging from 15 min to 16 h. During this treatment,

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physical damage of starch regarding size and shape of granules doesn't takes place due to controlled application of heat and moisture. Numerous studies have revealed the effects of physical and chemical modification treatments on the properties of cereal, tuber and legume starches, including noticeable alteration in morphology, X-ray diffraction pattern, relative crystallinity, amylose leaching, starch chain interaction and gelatinisation parameters (Jiranuntakul et al. 2011; Balasubramanian et al. 2014; Ali et al. 2016; Sarkar 2016). Alteration of starch properties by physical modification methods enhances the suitability of starch for innovative food and non-food applications. Increased water barrier properties and tensile strength of edible films prepared from hydrothermally modifies amaranth and buckwheat starches were observed in previous studies (Sindhu and Khatkar 2018a, b; Sindhu et al. 2018).

Common buckwheat (*Fagopyrum esculentum*) is a non-glutinous pseudocereal well known for its nutritional value and is one of the two varieties chiefly grown and consumed globally. Starch is the major component of buckwheat endosperm, which plays a significant role in appearance, structure and quality of food products prepared from buckwheat. Buckwheat seeds mainly contain starch varying from 59 to 69% that is 15–25% amylose; rest is amylopectin (Skrabanja et al. 2004). Buckwheat could be an emerging source of starch with different physico-chemical, textural, structural and gelatinisation characteristics. As literature on investigations of native and modified starches of different sources such as rice, barley, potato, beans, tubers etc. is present while scarce information is available on modification of buckwheat starch. Therefore, present investigation was aimed at isolation and modification of common buckwheat starch by heat moisture treatment at different temperatures as well as evaluation of effects of modification treatments on various properties of starch.

Materials and methods

Materials

The grains of common buckwheat (*Fagopyrum esculentum*) were purchased from National Bureau of Plant Genetic Resources Regional Station, Shimla, India. All chemicals used in this research work were of analytical reagent grade.

Isolation of starch

Cleaned grains of buckwheat were soaked in NaOH solution (0.25%) in ratio of 1:6 for a period of 18 h at room temperature. Steeped grains were cleaned using distilled water before grounding in kitchen blender. The slurry produced was filtered through 100 mesh and 270 mesh sieves. Filtrate was centrifuged at 8000 rpm for 20 min at 15 °C and supernatant was removed. From the pallet in centrifuge tube upper yellowish coloured layer was scrapped away and lower whitish layer of starch was remixed in distilled water for centrifugation. Later step was repeated 4–5 times to achieve pure white starch. Starch suspension was washed with ethanol once in repeated washing steps to remove lipids from starch. Starch was dried at below 40 °C for 10–12 h in hot air oven, conditioned at room temperature for 2 h in desiccator and packed in air tight container till further analysis.

Heat moisture treatment of starch

Starch was subjected to hydrothermal treatment according the method of Franco et al. (1995) with slight modifications. Starch was fixed to 30% moisture content by uniformly addition of calculated volume of distilled water. Starch was sealed in polyethylene pouches and kept undisturbed for 12 h at 10 °C. After the incubation, starch was filled in different air tight glass containers and heated for 6 h at 85 and 120 °C. Occasionally containers were shaken during heating for uniform heat distribution within starch. Treated starch samples were cooled in desiccator and dried at 40 °C for 6 to 8 h. Starches were again equilibrated at room temperature for 4 h, ground and sieved using 75 µm sieve. Heat moisture treated starch samples were stored in well labelled air tight containers at room temperature.

Swelling power and solubility

Starch sample (0.2 g) in 10 ml water was heated for 1 h at 90 °C with constant stirring followed by cooling to room temperature and centrifugation at 5000 rpm for 10 min. Sediment in paste form was weighed and supernatant transferred into pre-weighed petri dish. The residue obtained after drying of supernatant represented the amount of starch solubilised in water (Balasubramanian et al. 2014). Following formula was used for calculation of swelling power

$$\text{Swelling power} = \frac{\text{Wt. of sediment paste} \times 100}{\text{Wt. of sample on dry basis} \times (100 - \%\,\text{solubility})}$$

Water and oil absorption capacity

Water absorption capacity (WAC) and oil absorption capacity (OAC) of starch samples were determined by using the method of Ige et al. (1984). Starch suspension

(5%) was allowed to stand for 40 min with agitation after every 10 min and centrifuged for 25 min at 3250 rpm. The supernatant was discarded and weight of sediment in centrifuge tube was noted. For determination of oil absorption capacity (OAC), mixture of starch and oil was allowed to stand for a period of 30 min and centrifuged at 3200 rpm for 25 min. Volume of supernatant was measured indicating the unabsorbed oil.

Color parameters

Color characteristics of starch were determined using CR-300 Chroma meter (Minolta, Japan). White and black tiles given with the chroma meter were taken as standard. Whiteness index was calculated using the formula $WI = 100 - \left[(100 - L)^2 + a^2 + b^2\right]^{1/2}$.

Paste clarity

Method of Perera and Hoover (1999) was followed for determination of starch paste clarity. Starch (0.5 g) in 50 ml distilled was heated at 90 °C in water bath for a period of 1 h with continuous stirring. Suspensions were allowed to cool at room temperature and stored at refrigeration temperature for a period of 5 days. Light transmittance of starch suspensions was measured at 640 nm after every 24 h using UV–Vis Spectrophotometer. Distilled water was treated as blank for light transmittance measurement.

Freeze thaw stability

Freeze thaw stability of starch samples was measured by following the method of Balasubramanian et al. (2014). Aqueous suspension of starch (5%, w/w) was heated at 90 °C for 1 h with constant agitation. After cooling, the paste was weighed (20 g) into pre-weighed centrifuge tubes and centrifuged at 1000 rpm for a period of 10 min to take out free water. Starch paste in centrifuge tubes after removal of supernatant were subjected to four freeze- thaw cycles and subsequent to each cycle centrifugation was done at speed of 4000 rpm for 30 min. In each freeze thaw cycles, samples were kept for 20 h at − 18 °C in deep freezer followed by thawing for 4 h at 30 °C. Water released (%) subsequent to each freeze thaw cycles was calculated as syneresis.

$$\text{Syneresis } (\%) = \frac{\text{Wt. of water released} \times 100}{\text{Wt. of sample}}$$

Pasting properties

Rapid Visco Analyser (Perten Instruments, Australia) generated curves were used to determine the pasting properties of native and modified starch samples. Starch slurry prepared in aluminium canister by dispersing 3 g starch (14% moisture basis) in 25 gm double distilled water was homogenized manually to prevent lump formation before RVA run. The suspension was subjected to a programmed heating and cooling cycle.

Textural properties of starch gels

The gel formed in the canister subsequent to RVA analysis of starch was kept in the same canister, sealed with parafilm to avoid moisture loss and stored at refrigeration temperature for 24 h. The textural properties were analysed by texture profile analysis (TPA) programme using texture analyzer (TA-XT 2i Stable Micro Systems, UK) equipped with Texture Expert software. Gel in the canister was compressed at a speed of 0.5 mm/s to a distance of 10 mm with a cylindrical plunger (P/25) of 25 mm diameter. Force was applied twice to generate a force–time curve from which different parameters of gel texture were determined.

Morphological properties

Scanning electron microscope (JCM-6000PLUS, JEOL, USA,) was used to obtain the micrographs of starch samples. Before scanning starch granules were coated with gold under vacuum.

Thermal properties

Thermal characteristics of starch samples were analysed by Differential Scanning Calorimeter (DSC 25, TA Instruments) equipped with analysis software named Trios. In 40 µl capacity aluminium pan distilled water was added to the starch (3–4 mg) to attain starch suspension containing 70% water. Hermetically sealed pans were kept for 24 h at room temperature to ensure equilibration of the starch and water. DSC analyzer was calibrated using indium and an empty aluminium pan was used as reference. The samples were scanned from 30 to 130 °C at a rate of 10 °C/min.

X-ray diffractometry

The X-ray diffraction patterns of starch samples were observed using MiniFlexII X-ray diffractometer (Rigaku Denki Co., Tokyo, Japan). Starch samples were scanned at 5–50° (2θ) with a rate of 5°/min, at target voltage of 40 kV and a current of 30 mA.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the starch samples were recorded using FTIR spectrometer (Spectrum BX, Perkin Elmer, USA). The starch sample was mixed with KBr and pressed to form a pellet. FTIR spectra were collected in 400–4000 cm^{-1} region.

Statistical analysis

All experiments were done in triplicate and data obtained were analysed using Analysis of Variance. Duncan test was conducted to analyse the significant difference ($p < 0.05$) among experimental mean values. Principal component analysis (PCA) was conducted to reduce the complexity of data sets to a small number of independent principal components. All statistical analysis of data were done using SPSS software version 16.0 (SPSS Inc).

Results and discussion

Functional properties

The impact of modification treatments on functional properties of common buckwheat starch is represented in Table 1. Values of swelling power and solubility of buckwheat starches ranged from 10.73 to 18.77 g/g and 12.64–31.32% respectively. Swelling power and solubility of buckwheat starch showed significantly lower values for heat moisture treated starch samples and progressive decrement was observed with increase in severity of temperature in hydrothermal treatment. Sarkar (2016) reported decrement in swelling power and solubility of hydrothermally modified starches of common buckwheat. Li et al. (2011) suggested that formation of stiff clusters of more arranged amylopectin side chain due to interactions between functional groups of starch leads to lower swelling power. Reduced solubility of starch might be due to the additional interactions among amylose–amylose and amylose-amylopectin chains of starch during hydrothermal treatment.

In hydrothermally treated starch samples, water absorption capacity ranged from 144.54 to 376.41% and oil absorption capacity varied from 71.57–166.98%. Water absorption capacity showed significantly increased values while oil absorption capacity showed significantly decreased values for treated starch samples relative to native starch and intensity of change was increased with increasing temperature of heat moisture treatment. Similar results were reported in previous studies by Malik and Saxena (2016) for common buckwheat starch. Increased hydrophilic tendency of starch molecules might be due to little extension of amorphous regions resulted from hydrogen bond disruption between crystalline and amorphous areas at the time of heat-moisture treatment.

Color parameters

Color is an important quality characteristic of any ingredient used in food products that determines its end use. Color values recorded for native and treated starches are presented in Table 1. All color parameters were found to be considerably influenced by modification treatments indicated by variations in L*, a* and b* values of treated and untreated starch samples. L* value indicating the brightness ranged from 92.48 to 99.70 in starch samples. Native starch had shown slight greenish tint and yellowness in color which were observed to be decreased by heat moisture treatment at lower temperature (85 °C) while increased in starches treated at higher temperature (120 °C). Heat moisture treated starches showed lower L* resulted in significantly decreased whiteness index than native starch. Similar results of color values were reported by Sarkar (2016) and Balasubramanian et al. (2014) for hydrothermally modified starches extracted from common buckwheat and pearl millet, respectively. Change in color values might be attributed to the occurrence of Millard reaction during hydrothermal process between reducing sugars from heated starch and amino groups in the protein. Pigments present in starch if passed to the final product could reduce its appearance quality and thus acceptability of that product. More whiteness is the desired feature in case of starch as an ingredient in food products like pie filling, edible films and puddings to meet the consumer preference.

Paste clarity

Light transmittance of starch pastes is an essential quality aspect that differs noticeably with botanical source of starch. Heat moisture treatment showed increased transparency of starch pastes as compared to native starch and progressive increment in paste clarity was noticed with raise in temperature of treatment. Results are in conformity with the findings of study conducted on buckwheat starch by Sarkar (2016) observed improved paste clarity following heat moisture treatment. Balasubramanian et al. (2014) reported increased paste clarity of heat moisture treated starch of pearl millet. Data revealed a significantly decreasing trend of paste clarity of native as well as modified starch samples during storage which was in consistence with the reports of earlier studies by Sarkar (2016) on heat moisture treated buckwheat starch. Jacobson et al. (1997) suggested that factors like leaching of amylose and amylopectin chains, swelling of granules,

Table 1 Functional and color properties of native and modified starches of common buckwheat

Treatments	SP (g/g)	S (%)	OAC (%)	WAC (%)	L*	A*	b*	WI
NS	18.77 ± 0.4[a]	31.32 ± 0.81[a]	166.98 ± 6.39[a]	144.54 ± 7.1[a]	99.70 ± 0.00[a]	0.39 ± 0.01[a]	3.82 ± 0.00[a]	97.66 ± 0.06[a]
HMTS (at 85 °C)	12.55 ± 0.24[d]	16.21 ± 1.02[b]	99.74 ± 0.54[b]	240.89 ± 3.22[b]	98.14 ± 0.17[b]	0.21 ± 0.0[b]	3.45 ± 0.05[b]	96.07 ± 0.12[b]
HMTS (at 120 °C)	10.73 ± 0.09[e]	12.64 ± 0.28[c]	71.57 ± 1.09[c]	376.41 ± 7.63[c]	92.48 ± 0.00[c]	1.25 ± 0.01[c]	9.30 ± 0.15[c]	87.97 ± 0.11[c]

NS native starch, *HMTS* heat moisture treated starch, *SP* swelling power, *S* solubility, *WAC* water absorption capacity, *OAC* oil absorption capacity: *L** black to white, *a** green to red, *b** blue to yellow, *WI* whiteness index

All values are mean of triplicate determinations ± standard deviation mean. Values within same column with different letters are significantly different ($p \leq 0.05$)

chain length of amylose and amylopectin could be responsible for reduced starch paste transmittance during storage (Supplementary Figure 1).

Freeze-thaw stability

Release of water due to rearrangement of starch molecules during cooling and storage of starch pastes is known as syneresis. The syneresis measured as percentage of water released by centrifugation of starch paste on same day of paste preparation was reduced in modified starches. Decreasing trend of syneresis was observed with increasing severity of heat moisture treatment. However, Balasubramanian et al. (2014) reported increase in syneresis in hydrothermally treated pearl millet starch. Increased capacity for water retention could be the reason for reduction in syneresis of heat moisture treated starch samples.

Intensity of syneresis depends on various factors such arrangement of amylose fraction, chain length of amylopectin and degree of polymerization of the amylose and amylopectin. As expected, percentage of liberated water increased significantly in native and modified starches with the progressive sequence of freeze-thaw cycles. Ali et al. (2016) observed the rising trend of syneresis in rice and corn starches during sequential freeze-thaw cycles. During freeze-thawing, a phenomenon of phase separation and formation of ice crystals takes place. As the size of ice crystals increases the rate of syneresis rises more rapidly. The phenomenon of syneresis primarily associated with aggregation of amylose molecules by inter- and intra-molecular hydrogen bonding. The objective of study of freeze-thawing was to simulate the conditions that could happen during the processing and storage of food products (Supplementary Figure 2).

Pasting properties

Pasting parameters of hydrothermally modified and native starch samples are depicted in Table 2. Viscosity of starch is an important property and is a fundamental aspect for applicability of starch to food processing. Results revealed that modification treatments notably reduced viscosities of starch as compared to native one. Increasing temperature of treatment progressively decreased the peak, breakdown, and final and setback viscosity of hydrothermally modified starch samples. Swelling of starch granules and leached amylose content are key factors determining the viscosity development throughout the pasting process. Peak viscosity of starch decreased from 4237 to 1919 cP during hydrothermal treatments. As decreased swelling power and solubility was observed in heat moisture treated starch

samples, consequently, reduction in peak viscosity was expected.

Breakdown viscosity of native starch was 1971 cP which decreased to 6.3cP in heat moisture treated starch samples. Lower breakdown viscosity of heat moisture treated starches showed the higher stability of starches for heating and shearing action. Noticeable least value of breakdown viscosity (6.3 cP) exhibited by heat-moisture treated (at 120 °C) starch sample represented it as the most stable starch during heating and shearing action among tested samples. Similar results of peak and breakdown viscosity were reported by Liu et al. (2015) and Zavareze et al. (2012) for heat moisture treated starches of tartary buckwheat and potato, respectively. Setback viscosity is the measure of recrystallization/retrogradation of gelatinized starch during cooling. Significantly reduced values of setback viscosity were observed for heat moisture treated starches of common buckwheat. Setback viscosity is influenced by leached amylose content, size of granules and existence of stiff, undamaged swollen granules. Zavareze et al. (2010) confirmed that heat moisture treated starches exhibited intensifying reduction in setback viscosity with increasing amylose content in starches because hydrothermal treatment supported additional interactions between starch molecules which lessen amount of leached amylose and decreased the setback viscosity value.

Capacity of starch to form thick paste on cooling after cooking the starch paste is represented by final viscosity. Hydrothermal treatment significantly decreased final viscosity from 4021 to 2759 cP and a trend of progressive decrement was noticed with rise in temperature of treatment. RVA analysis of heat moisture treated starches showed significant raise in pasting temperature and peak time which were consistent with findings of Zavareze et al. (2010) for hydrothermally modified rice starches of different cultivars. Increase in pasting temperature supported by hydrothermal treatment specified the strengthening of bonds and interactions between nearby chains of amylopectin increasing the crystallinity of starch granules. Altered crystallinity and association of starch molecules in amorphous regions during heat moisture treatment could also be the reasons for changes in pasting behaviour of starches.

Gel textural properties

Results of texture profile analysis of gels of native and heat moisture treated starches are presented in Table 3. Hardness of gels measured as force applied to cause deformation was found to be 9.65 g for native starch of buckwheat. Hydrothermally modified starches showed significantly increased gel hardness and starches treated at 85 °C exhibited the highest value. Values of adhesiveness increased due to heat moisture treatment at 85 °C while decreased on further raising the treatment temperature up to 120 °C. Heat moisture treated starch samples exhibited reduced values of springiness and cohesiveness while increased values of gumminess and chewiness. Gel formation mainly depends on swelling factor of starch granules and increased gel hardness in hydrothermally starch samples could be attributed to the decreased swelling power relative to native starch. Results of gel hardness of hydrothermally modified starch samples were in conformity with the findings of Malik and Saxena (2016) for buckwheat starch following heat moisture treatment. It was suggested that increased interactions between starch chains in amylose portion during hydrothermal modification supported the development of more junction zones in the continuous phase of gels resulted in higher gel hardness (Hormdok and Noomhorm 2007). In previous studies decreased gel hardness, adhesives, cohesiveness, gumminess and chewiness were reported in heat moisture treated starches extracted from buckwheat (Liu et al. 2014). Heat moisture treatment at different temperature might have influenced these factors differently that could be the reason for variation in gel textural characteristics of treated buckwheat starches.

FTIR (Fourier-transformed infrared) spectroscopy

The spectral peak characteristics due to different types of bond stretches on spectrums of buckwheat starches were

Table 2 Pasting properties of native and modified starches of common buckwheat

	PV (cP)	TV (cP)	BV (cP)	FV (cP)	SV (cP)	PT (°C)	Pt (min)
NS	4237 ± 22^{a}	2265 ± 201^{a}	1971 ± 24^{a}	4021 ± 75^{a}	1756 ± 12^{a}	73.2 ± 0.4^{a}	4.1 ± 0.0^{a}
HMTS (at 85 °C)	2251 ± 8^{b}	1888 ± 2^{b}	362 ± 24^{b}	3383 ± 12^{b}	1495 ± 114^{b}	80.7 ± 0.0^{b}	5.0 ± 0.3^{b}
HMTS (at 120 °C)	1919 ± 2^{c}	1913 ± 2^{b}	6.3 ± 0.5^{c}	2759 ± 1^{c}	846 ± 9.2^{c}	81.2 ± 0.4^{c}	6.3 ± 0.2^{c}

NS native starch, *HMTS* heat moisture treated starch, *PV* peak viscosity, *TV* trough viscosity, *BV* breakdown viscosity, *FV* final viscosity, *SV* setback viscosity, *PT* pasting temperature, *Pt* pasting time, *cP* centipoise

All values are mean of triplicate determinations ± standard deviation mean. Values within same column with different letters are significantly different ($p \leq 0.05$)

Table 3 Gel textural properties of native and modified starches of common buckwheat

Treatments	HRD (g)	ADH (g/s)	SPG	GMM (g)	CHW (g)	COH
NS	9.63 ± 1.03[a]	− 2.01 ± 0.5[a]	1.59 ± 0.01[a]	4.76 ± 0.69[a]	7.62 ± 1.18[a]	0.49 ± 0.01[a]
HMTS (at 85 °C)	16.71 ± 0.34[b]	− 6.94 ± 0.88[b]	1.32 ± 0.02[b]	6.78 ± 0.23[b]	8.99 ± 0.51[b]	0.40 ± 0.00[b]
HMTS (at 120 °C)	12.25 ± 0.76[c]	− 1.24 ± 0.28[a]	1.24 ± 0.06[b,c]	4.29 ± 0.58[a]	5.36 ± 1.02[c]	0.34 ± 0.02[c]

NS native starch, *HMTS* heat moisture treated starch, *HRD* hardness, *ADH* adhesiveness, *SPG* springiness, *GMM* gumminess, *CHW* chewiness, *COH* cohesiveness

All values are mean of triplicate determinations ± standard deviation mean. Values within same column with different letters are significantly different ($p \leq 0.05$)

interpreted in the light of available literature (Chi et al. 2008; Ali et al. 2016; Kumar and Khatkar 2017). The spectrums of heat moisture treated starches were similar to native starch spectrum with no noticeable change in peaks. A discernible wide band around 3250–3500 cm^{-1} appeared on all spectrums which might be attributed to the O–H stretching of alcohols and phenols in free form. The peak found on the spectra of all starch samples around 2931–2932 cm^{-1} were assigned to asymmetric stretching of C-H bonds. Spectral peak noticed around 1241–1244 cm^{-1} for native and modified starch samples could be attributed to vibration modes offered by amylose and amylopectin. These bands were chiefly attributed to C–O stretch of C–O–H in starch. Band at 1242 cm^{-1} on the diffractogram of starch was assigned to the CH_2OH (side chain) related mode as well as the C–O–H deformation mode (Cael et al. 1975) (Supplementary Figure 3).

Thermal properties

Results of differential scanning calorimetry of native and modified starches of buckwheat are represented in Table 4. Hydrothermally modified starches exhibited significantly increased gelatinisation temperatures relative to native starch of buckwheat. Increasing trend of gelatinisation temperatures was observed with raising temperature of heat moisture treatment. The highest values of peak (79.42 °C) and end (92.02 °C) gelatinisation temperature among native and hydrothermally modified starches were recorded for samples treated at 120 °C. Shift of gelatinisation temperatures towards elevated range could be attributed to the alterations in starch granules at structural level including destabilisation of crystalline lamella, leaching of amylose and lessening of amorphous zones during hydrothermal treatment leading to increased ratio of crystalline regions (Khunae et al. 2007). Moreover, the reduced mobility of the amorphous zones due to amylose–amylose and amylose-fat interaction following heat moisture treatment supported requirement of higher temperature for gelatinisation. Heat moisture treatments decreased swelling power and thus destabilising effect of amorphous region on crystalline melting decreased, subsequently, higher temperature required for melting of hydrothermally modified starch.

The values of ΔH, indicating the energy required for dissociation of double helices, decreased in starch samples modified by heat moisture treatments as compared to native starch. Liu et al. (2014) reported increased gelatinisation temperatures and decreased ΔH of buckwheat starches modified by hydrothermal treatment at varying moisture level. The disruption of double helices present in amorphous and crystalline regions and partial depolymerisation of amylose molecules in starch granules during heat moisture treatment could be the reasons for reduced ΔH values in treated starches (Gunaratne and Hoover 2002).

Morphological properties

Micrographs of granules of native and modified starches of buckwheat obtained by scanning electron microscopy

Table 4 Thermal properties of native and modified starches of common buckwheat

	T_O (°C)	T_P (°C)	T_C (°C)	ΔH (J/g)
NS	64.92 ± 0.03[a]	69.65 ± 0.04[a]	77.90 ± 1.70[a]	2.97 ± 0.02[a]
HMTS (at 85 °C)	73.74 ± 0.06[b]	78.15 ± 0.13[b]	83.55 ± 0.08[b]	2.80 ± 0.10[b]
HMTS (at 120 °C)	73.04 ± 0.04[c]	79.42 ± 0.36[c]	92.02 ± 0.00[c]	2.35 ± 0.05[c]

NS native starch, *HMTS* heat moisture treated starch, T_O onset temperature, T_P peak temperature, T_C conclusion temperature, *ΔH* gelatinisation enthalpy

All values are mean of triplicate determinations ± standard deviation mean. Values within same column with different letters are significantly different ($p \leq 0.05$)

revealed that granules of native starch of buckwheat were polygonal in shape with diameter varying from 5.6 to 7.3 µm. Surface of native buckwheat starch granules was smooth with no any cavity or fissure. The size and shape of granules were consistent the finding of Sarkar (2016). Heat moisture treated samples showed some hollow space on the surface of starch granules which were in agreement with earlier studies (Liu et al. 2014, 2015) reported fissures on the starch granule surface of common and tartary buckwheat modified by hydrothermal treatment at different conditions of temperature and moisture. The micrographs exposed that hydrothermal treatments caused more aggregation of starch granules due to increased close packing than native starch granules resulted in cluster formation. Watcharatewinkul et al. (2009) observed that hydrothermal treatment changed loosely packed granules into close packing. The holes and cracks formation on the surface of granules could be due to strong interaction between amylose and amylopectin (Supplementary Figure 4).

X-ray diffractometery

X-ray diffractograms of treated and native starches of common buckwheat are given in Fig. 1. Measured up to the standard pattern of diffraction observed by Zobel (1964), buckwheat starches showed typical 'A' type crystallinity pattern with strong reflections at 2θ about 15°, 17°, 17.90° and 23° and small peak at about 20°. The strong peaks at around 15°, 17°, 18° and 23° on diffractograms are characteristics of cereals starches representing 'A' type crystalline pattern which were reported for starches of buckwheat, amaranth, maize and rice in previous studies (Singh et al. 2006, 2007, 2014; Li et al. 2014). It can be concluded from the figure that modification did not change the crystallinity pattern of buckwheat starch as the peaks on diffractograms of native and modified starches were observed at similar degree. However, the intensity of peaks was different in modified starches from native starch that was an indication of changed relative crystallinity of hydrothermally modified buckwheat starches.

Heat moisture treated starch samples showed decreased relative crystallinity and the lowest relative crystallinity value (9.65%) was exhibited by samples treated at 85 °C. Chen et al. (2017) reported that heat moisture treatment reduced the extent of branching in starch granules of maize and also found that parts of crystalline phases were changed into amorphous regions. Jiranuntakul et al. (2011) observed decreased relative crystallinity in heat moisture treated starches of corn, rice and maize and noticed more pronounced changes in waxy type starches. Therefore, reduction in relative crystallinity of buckwheat starch following heat moisture treatment might be attributed to the destruction of crystalline phase (amylopectin) and transformation of semi-crystalline parts into amorphous phase during treatment. Gelatinisation of starch during hydrothermal treatment could also be the reason for decreased crystallinity of starches. Contrary to present results, Liu et al. (2015) reported increased relative crystallinity in buckwheat starches following heat moisture treatment. Results of hydrothermally treated samples revealed that different conditions of treatment produced unique effects on crystallinity of starch. Therefore, it is important to select an appropriate condition of temperature and moisture to control relative crystallinity and disruption of granular structure.

Principal component analysis (PCA)

Principal component analysis was done to extract the largest contributor to the variation in the original data. From

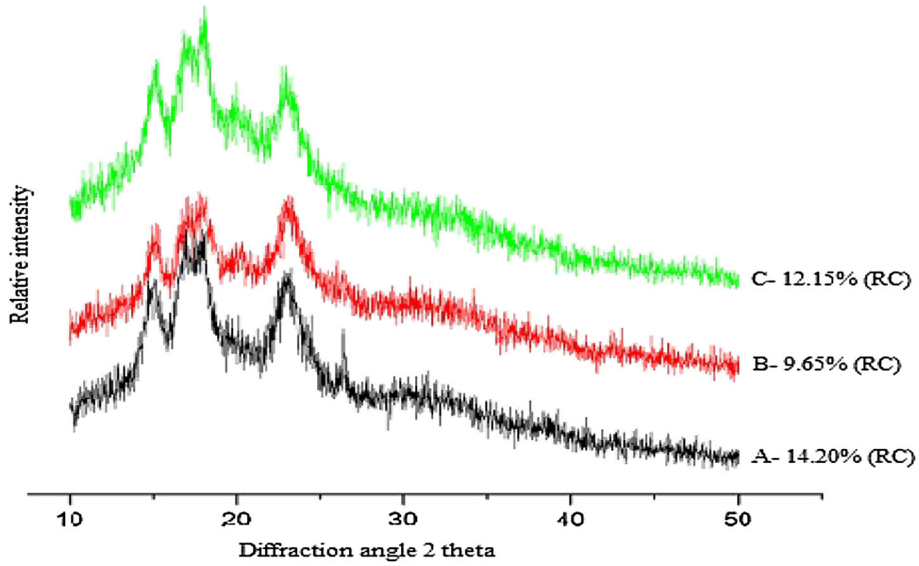

Fig. 1 X-ray diffractograms of native and modified starches of common buckwheat. **a** native starch; **b** heat moisture treated starch at 85 °C; **c** heat moisture treated starch at 120 °C

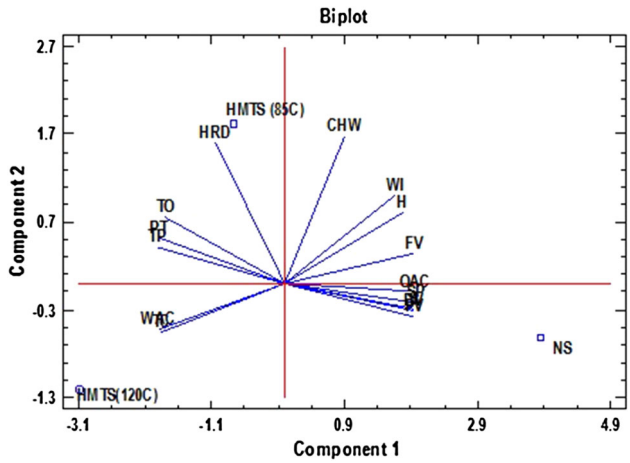

Fig. 2 Principal component analysis biplot for properties of native and modified starches of common buckwheat. *NS* native starch; HMTS 85: heat moisture treated starch at 85 °C; HMTS120: heat moisture treated starch at 120 °C

PCA two components were found to be responsible for total variations in present data. Results revealed that 82.9% of the variations can be explained by first principle component while 17% can be explained by second principle component. Native and modified starches located at different places in PCA biplot given in Fig. 2 indicated that treated starches were different from native starch of buckwheat in terms of measured parameters. Biplot showed high score of oil absorption capacity, solubility, swelling power, peak viscosity and whiteness index for native starch while high score of water absorption capacity and temperature of conclusion for starch treated at 120 °C. It was noticed that, the first principle component had high positive component loading from oil absorption capacity, solubility, swelling power, peak viscosity, breakdown viscosity and final viscosity. Hardness, chewiness, whiteness index, enthalpy change and onset temperature contributed to high positive component loading to the second principal component.

Conclusion

It could be concluded from the present study that heat moisture treatment significantly influence the functional, pasting, thermal and gel textural characteristics of common buckwheat starch. Heat moisture treatments by increasing paste clarity and reducing syneresis enhanced suitability of starch for cooked food products usually subjected to storage. Retrogradation, generally not required in starch based products, was reduced during heat moisture treatments indicated by decreased setback viscosity of hydrothermally modified starches. Reduced breakdown viscosity and increased pasting time and temperature represented improved thermal stability of modified starch samples. Crystallinity pattern and size and shape of starch granules were found to be unaffected by hydrothermal treatment of starch. Variations in functional, thermal and textural properties by hydrothermal treatment at different temperatures enhanced the applicability of common buckwheat starch for production of a wide variety of starch based food products.

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