Carbohydrate Polymers 110 (2014) 128–134

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of dry heat treatment on the physicochemical properties and structure of proso millet flour and starch

Qingjie Sun*, Min Gong, Ying Li, Liu Xiong

School of Food Science and Engineering, Qingdao Agricultural University, Qingdao, Shandong Province, 266109, China

ARTICLE INFO

Article history:
Received 2 December 2013
Received in revised form 1 March 2014
Accepted 30 March 2014
Available online 5 April 2014

Keywords:
Dry heat treatment
Millet flour
Millet starch
pasting
Morphological
Structural properties

ABSTRACT

Proso millet (*Panicum miliaceum* L.) flour and starch were heated in a dry state at 130 °C for 2 or 4 h. The effects of dry heat treatment (DHT) on the pasting, morphological and structural properties of the samples were evaluated. Dry heat treatment had a more significant effect on the pasting viscosity of flour than starch; it increased the pasting viscosity of the flour while it only increased the final viscosity of the starch. After dry heating, the onset of gelatinization and the peak temperatures of the samples increased significantly while the endothermic enthalpy decreased. Scanning electron microscopy showed that the gel structure of the samples became more compact and the particles were plumper when compared with the native ones. Crystallinity of the samples decreased while the X-ray diffraction patterns remained the same after DHT.

1. Introduction

Millets, such as proso millet (*Panicum miliaceum* L.), have excellent nutritional properties and can become a basic resource for crop breeding programs and food diversification (Young-Il et al., 2010). Proso millet, which is also called millet, hog millet, and yellow hog, can be used in many different fields. But now millet is desirable for human food because it is easily digestible and is gluten-free. It can be ground into flour and used to bake flatbreads, tabbouleh or to brew beer (Badau, NkaMa, & Jideani, 2005). The proso millet is rich in protein, mineral substances, and vitamins, and its nutritive parameters are comparable or better than common cereals. Moreover, the quantities of nutrients in the millet are very similar to the recommended ratio of protein, saccharide, and lipids (Kalinova & Moudry, 2006).

Starch, in its native form, has a relatively limited usage in many industries. Physical and chemical modifications are commonly used to produce modified starches with special properties. Although chemically modified starches are available for industrial purposes, most industries (especially the food and pharmaceutical industries) prefer starches without chemical modification. Therefore, physically modified starch, by use of moisture, heat, shearing, or radiation, has gained a wider acceptance for no chemical reagents using (Zavareze, Storck, de Castro, Schirmera, & Dias, 2010). Depending on the presence of moisture, heat treatment can change the granular and molecular structure of the starch (Chung, Min, Kim, & Lim, 2007). Heating starches under dry conditions is a method for producing modified starches. Dry heating treatment (DHT) is a physical modification that changes the physicochemical properties of starch, without destroying its granule structure. Compared with chemical methods, dry heat is a simple, safe, and healthy method. Chiu, Schiermeyer, Thomas, and Shah (1998) introduced a dry heating process for formulating physically modified starches. They reported that thermally treated starches yield a functionality equivalent to that obtained by chemical cross-linking (Chiu et al., 1999; Li et al., 2013). Besides, Sun, Si, Xiong, and Chu (2013) found that the gel structure of the potato starch got compacter after drying-heating with CMC (130 °C, 2 h or 4 h). Heat treatment obviously improved the functional properties of starches.

To sum up, the effect of dry heat treatment or dry heating with ionic gums (Li et al., 2013; Sun et al., 2013) on pasting and thermal properties of starch have been studied, but the changes in the structural and morphological properties of starch and the comparison between flours and starches before and after dry heating have received little attention. To clarify the effects of DHT on the millet flour or starch, and compare the difference between the flours and the starches containing other constituents through dry heating, more studies are needed.

* Corresponding author at: School of Food Science and Engineering, Qingdao Agricultural University, 700 Changcheng Road, Chengyang District, Qingdao, 266109, China. Tel.: +86 532 88030448; fax: +86 532 88030449.
E-mail address: phdsun@163.com (Q. Sun).

http://dx.doi.org/10.1016/j.carbpol.2014.03.090
0144-8617/

In this study, the proso millet flour and proso millet starch (8%, w/w, moisture content) were heated in a dry state at 130 °C for 2 h or 4 h. The effects of the DHT on pasting, morphological and structural properties of the proso millet flour and starch were examined.

2. Materials and methods

2.1. Materials

Proso millet grains (Millet Lu 1) were obtained from Qingdao Academy of Agricultural Sciences, Qingdao, China. All analytical grade chemicals were used as obtained without further purification.

2.2. Proso millet flour and starch preparations

The grains were ground into flour using cryogenic milling as described by Hasjima, Li, and Dhitala (2013). The proso millets were steeped in two times distilled water at 4 °C for 2 h, then the water was drained off and the millets were ground with a blender. The milled millet flour was dried in an oven at 40 °C for 48 h, and then passed through a 100-mesh screen. The proso millet starch was prepared using the alkaline steeping method (Ju, Hettiarachchy, & Rath, 2001; Santhanee et al., 2013) with some modifications. Proso millet grains were steeped in 0.3% sodium hydroxide solution and kept at 4 °C for 24 h. The supernatant was discarded and the steeped millets were ground with a blender, then passed through a 100 mesh screen. The slurry was centrifuged at 3000 rpm for 15 min. Then, the supernatant was decanted and the precipitate was re-slurried with water and centrifuged. The step of washing with water was repeated three times. Next, the starch cake was re-suspended in water, neutralized with 1 N hydrochloric acid to pH 7. The supernatant was decanted and the neutralized starch was removed and dried in an oven at 40 °C for 48 h. Standard AOAC methods (1990) were used for the measurement of nitrogen, ash, and lipid. Protein was determined from estimation of total nitrogen using a conversion factor of 6.25. The measurement of the chemical composition (%, dry basis) of the flour and starch was determined according to the method of Puncha-arnon and Uttapap (2013). Protein, lipid, ash, carbohydrate and amylose content in millet flour were 11.43%, 0.91%, 1.3%, 84.82% and 1.5% (dwb, %), whereas those in starch were 0.48%, 0.01%, 0.20%, 97.69% and 1.61% (dwb, %), respectively.

2.3. Modifications using dry heat treatment

The flours and starches were modified by DHT according to Lim, BeMiller, and Lim (2003). The millet flour and starch samples were kept in Petri dish and dried at 40 °C in an air dry oven until the moisture content reached to 8%. Then, all the samples were heated in an electric oven at 130 °C for 2 h or 4 h, respectively. The oven used was 876A-2 digital vacuum oven, Shanghai, China. After DHT, the flours and starches were covered with plastic wraps to prevent them from being affected by damp conditions. Untreated millet starch and flour were used as controls. The measurement of the chemical composition of the DHT samples was according to the same method above. Protein, lipid, ash, carbohydrate and amylose content in DHT2F were 11.44%, 0.9%, 1.31%, 84.83% and 1.5% (dwb, %), in DHT4F were 11.43%, 0.89%, 1.32%, 84.82% and 1.51% (dwb, %), whereas those in DHT2S and DHT4S were the same at 0.48%, 0.01%, 0.20%, 97.7% and 1.61% (dwb, %), respectively. The moisture content of the DHT2 samples and DHT4 samples were 5% and 3%, respectively.

2.4. Paste viscosity

The flour and starch (3.0 g, 14 g/100 g moisture basis) were weighed directly in the RVA canister and distilled water was added to obtain a sample weight of 28.0 g. The slurry was then manually homogenized using the plastic paddle to avoid lump formation before the RVA run. The slurry was heated from 50 °C to 95 °C at a rate of 12 °C/min and maintained at 95 °C for 2.5 min. It was then cooled to 50 °C at the same rate, and held at 50 °C for 2 min. Parameters including peak viscosity (PV), viscosity at the end of 2.5 min at 95 °C or trough viscosity (TV), final viscosity (FV) at the end of cooling, breakdown (BD = PV – TV), setback (SB = FV – TV), and pasting temperature were recorded. All tests were replicated three times.

2.5. Differential scanning calorimeter (DSC)

The thermal properties of samples produced via the heat treatment described above were investigated using a differential scanning calorimeter (DSC 1, Mettler-Toledo, Schwerzenbach, Switzerland) as described by Chanvrier et al. (2007) with minor modifications. Indium was used as the calibration standard. Each product sample (4 mg) and distilled water (8 mg) were placed in a stainless-steel pan, then the container hermetically sealed and then kept at 4 °C for 24 h. Samples were heated at 10 °C/min from 25 °C to 115 °C to observe for the presence of any residual enthalpy gelatinization peak. The endothermic enthalpy (ΔH), onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) were determined.

2.6. Scanning Electron Microscopy (SEM)

The pastes of the millet flours and starches before and after DHT after gelatinization with RVA should be quickly freeze dried. The microstructure of samples after freeze drying for 48 h was observed by scanning electron microscopy (SEM). In addition, the morphology of the flour and starch samples before and after DHT was observed by SEM using the method described by Kim et al. (2008). A dry flour sample was placed on a double-sided Scotch tape, mounted on an aluminum specimen holder, and coated with a thin film of gola under vacuum. Samples were observed under a Jeol scanning electron microscope (JSM 840, Jeol, Japan), and the accelerating voltage was 2 kV.

2.7. X-ray diffraction pattern

The crystal structure of the flour and starch samples was studied with an X-ray diffractometer (Bruker AXS Model D8 Discover) using the conditions described by Watcharatewinkula, Puttanlekb, Rungsardthongc, and Uttapap (2009). Both native and DHT samples were equilibrated in a saturated relative humidity chamber for 24 h at room temperature. The X-ray diffraction was performed on an X-ray diffractometer with copper Ka radiation. Signals of the reflection angle of 2θ, from 4 °C to 45 °C, were recorded. The overall degree of crystallinity was quantified as the ratio of the area of crystalline reflection to the overall diffraction area (Yu, Ma, Menager, & Sun, 2012).

2.8. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of native and DHT samples were recorded on a FTIR spectrophotometer (NEXUS-870, Thermo Nicolet Corporation) as described by Kunal et al. (2008). All the samples (8%, w/w, moisture content) were mixed with KBr and pressed into pellets. The pellets were then subjected to Attenuated Total Reflectance (ATR) spectroscopy in the range of 4000–400 cm^{-1}. Intensity

measurements were performed on the spectra by recording the height of the absorbance bands from the baseline.

2.9. Statistical analysis

All experiments were conducted at least in triplicate, with mean values and standard errors determined for these experiments. All the test data were analyzed using the Analysis of Variance (ANOVA) and Origin Pro 7.5 statistics program, then expressed as mean values ± standard deviations. Differences were considered at a significant level of 95% ($p < 0.05$).

3. Results and discussion

3.1. Pasting properties of native and DHT millet flour and starch

The pasting properties and viscogram data of the flours and starches with and without DHT are shown in Fig. 1 and Table 1. Dry heat treatment increased the PV of the flours greatly while slightly decreased the PV of the starches when compared with the native samples (Table 1). After DHT, the PV increased from 652 cP (NF) to 2155 cP (DHT2F) and 2685 cP (DHT4F), increasing about two to three folds compared with the native flour. The same tendency was also observed in the TV, BD, FV, and SB of all the heat treated flours. The pasting temperature of the native starch was 76 °C, which was close to the proso millet named "Andong 48ho" (amylose content was 1.2%) reported by Kim, Choi, Kang, and Kim (2012). Compared with the native starch, dry heat treatment had slightly decreased the PV but increased the TV and FV obviously. The BD of the DHT starches decreased from 1854 cP (NS) to 1188 cP (DHT2S) and 1062 cP (DHT4S). The reduction of BD indicated that the DHT starches had more resistance to high temperatures and shearing and that it had higher pasting stability. Gunaratne and Corke (2007) proposed that when gelatinized starch paste was subjected to cooling, the extent of the viscosity increase was mainly governed by the rapid re-association of linear amylose chains via formation of a gel matrix. The FV of the starch increased by about 50% after DHT compared to the native starch. Iromidayo, Olu-Owolabi, Adeniyi Afolabi, and Adebowale Kayode (2011) reported that the increment in the final viscosity was due to the aggregation of the amylose molecules, since the setback value was the recovery of the viscosity during cooling.

Pasting properties were significantly different among the flour and starch samples (Fig. 1). The pasting curves of the DHT flours were obviously higher than that of the native flour. The pasting curve of the starch did not show a significant change after DHT; however, the viscosity curve of the DHT flours were close to those of the native starch and DHT starches. This result suggests that dry heating flour could be used instead of starch in higher viscosity products in practical applications, as it contains rich nutrients such as protein and vitamins, but avoids the inconvenience of starch extraction. These changes in the pasting characteristics indicated that starch molecules had some degree of re-association and interaction with non-starch ingredients during thermal treatments. It also suggested that the shear-stabilization of the starch granule was provided by the DHT, which was similar to the modified starches obtained by chemical cross-linking. Almost no change was observed in the chemical composition analysis, and the differences of pasting characteristics may be attributed to the changes in the structure (Li, Shoemaker, Ma, & Shen Zhong, 2008; Lim et al., 2003), which need further investigations in the future. Previous reports suggested that an ester bond could be formed when the starch and non-starch components were dry heated, similar to the interaction of starch and gum cross-linking during dry heating treatments (Li et al., 2008; Lim et al., 2003). The effect of DHT on flours and starches can be applied to products that require a higher final viscosity or better viscosity stability.

3.2. Thermal properties

The gelatinization parameters of native and DHT millet flour and starch are given in Table 2. The gelatinization onset (T_o) and peak temperature (T_p) of DHT samples were higher than those of the native samples, while the conclusion temperatures (T_c) were lower than those of the native ones. The T_o of the native starch was 68.65 °C, this was in accordance with Annor, Marcone, Bertoit, and Seetharaman (2014) who reported the T_o of the proso millet starches ranged from 62.8 to 70.6 °C. The T_p of the flour had the highest increase of about 4 °C after DHT, which was from 70.15 °C (NF) to 73.86 °C (DHT2F) and 74.69 °C (DHT4F). The gelatinization temperature range ($T_c - T_o$) of native flour (15.94 °C) was larger than that of native starch (11.76 °C), indicating that other components in the flour could also affect the gelatinization of the crystalline region. The $T_c - T_o$ of the flour decreased obviously after DHT and the smaller gelatinization temperature range was close to that of the native starch, while that of the DHT starch just had a slight change compared with the native one. These changes indicated that DHT had a more significant influence on the thermal properties of flour than of starch, and the difference may be attributed to the existence of the non-starch components such as protein in the flour. The protein in the native flour may have had some restrictions during starch gelatinization and it may have made the gelatinization temperature range wider as described by Puncha-arnon and Uttapap (2013), while the protein in the DHT flour may have been denatured and had no significant influence on the starch gelatinization, making the gelatinization similar to that of the starch samples. Great reductions were also observed in the endothermic enthalpy (ΔH) of both the flour and starch after DHT. The flour showed a higher decrease in ΔH from 15.03 J/g (NF) to 9.08 J/g (DHT2F) and 7.97 J/g (DHT4F), reflecting the reduction of crystallinity. The ΔH of starch likewise decreased from 16.10 J/g (NS) to 13.79 J/g (DHT2S) and 13.24 J/g (DHT4S). A similar result was reported by Chung et al. (2007) who found that adding xanthan to a starch–phosphate mixture prior to dry heat treatment resulted to reductions in the melting enthalpy. They suggested that this was related to the interactions between starch molecules and xanthan. This further confirmed the influence of the non-starch components on the millet properties during dry heat treatment. Annor et al. (2014) have reported the ΔH of millet starch granules ranged from 11.2 to 13.2 J/g, while Kim et al. (2012) reported the ΔH was 0.81–4.48 J/g. These differences of thermal properties may be attributed to the different varieties of the proso millet.

3.3. Morphological analysis

The scanning electron micrographs (SEM) of the millet flour and starch granules before and after DHT are presented in Fig. 2. The diameter of the starch particles was about 5–12 μm, which was in accordance with Yanez and Walker (1986) who reported the particle size of the proso millet varied from 6 to 11 μm. Scanning electron micrographs revealed that both the surfaces of the flour and starch granules after DHT (A2 and B2) were smooth and looked plumper compared with the native ones (A1 and B1). It might be that non-starch compositions interacted with the starch granules and attached to the surface of the starch granules during the dry heating process. After DHT, flour granules formed into big lumps under SEM observation (A2). The DHT starch granules, on the other hand, did not show the same trend compared with the native sample. This suggested that starch reacted with other components in the flours during the DHT process, which is consistent with previous reports (Chiu et al., 1998, 1999). Chiu et al. reported that

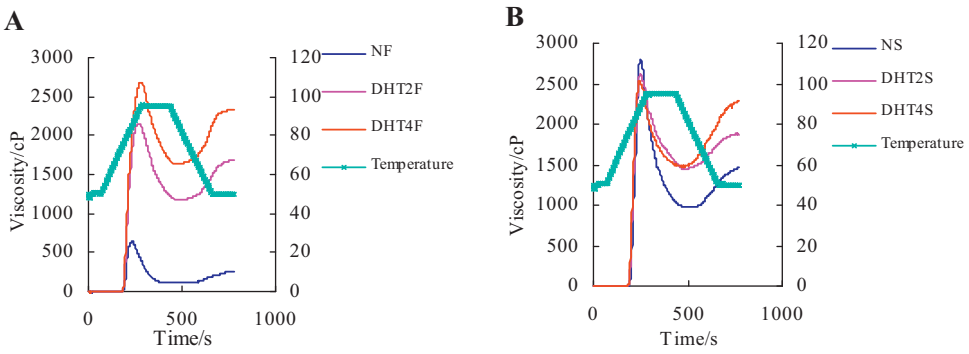

Fig. 1. Paste viscograms of proso millet flour samples (A) and starch samples (B): native flour (NF), flour treated at 130 °C for 2 h (DHT2F), flour treated at 130 °C for 4 h (DHT4F); native starch (NS), starch treated at 130 °C for 2 h (DHT2S), starch treated at 130 °C for 4 h (DHT4S).

Table 1
RVA pasting parameters of proso millet flours and starches before and after dry-heating treatment.[a]

Sample	Pasting temperature (°C)	Peak viscosity (cP)	Trough viscosity (cP)	Final viscosity (cP)	Breakdown (cP)	Setback (cP)
NF	75.2 ± 0^{a}	652 ± 4^{e}	108 ± 1^{e}	261 ± 2^{e}	543 ± 3^{e}	153 ± 1^{e}
DHT2F	74.7 ± 0.5^{b}	2155 ± 13^{d}	1173 ± 54^{c}	1689 ± 33^{c}	982 ± 33^{d}	516 ± 22^{d}
DHT4F	74.4 ± 0^{b}	2685 ± 52^{b}	1632 ± 6^{a}	2328 ± 20^{a}	1053 ± 11^{c}	696 ± 29^{b}
NS	76 ± 0.5^{a}	2822 ± 41^{a}	967 ± 0^{d}	1470 ± 6^{d}	1854 ± 41^{a}	501 ± 8^{c}
DHT2S	75 ± 0.3^{a}	2621 ± 24^{b}	1432 ± 6^{b}	1829 ± 2^{b}	1188 ± 18^{b}	597 ± 6^{c}
DHT4S	74.6 ± 0.4^{b}	2536 ± 58^{c}	1474 ± 48^{b}	2266 ± 7^{a}	1062 ± 10^{c}	742 ± 11^{a}

[a] NF: native flour; DHT2F: flour treated at 130 °C for 2 h; DHT4F: flour treated at 130 °C for 4 h; NS: native starch; DHT2S: starch treated at 130 °C for 2 h; DHT4S: starch treated at 130 °C for 4 h. All data represent the mean of three determinations. Mean ± standard deviation. Means with the same letter in each column are not significantly different ($p < 0.05$).

Table 2
Thermal characteristics of native and dry heat treated millet flours and starches.

Sample	T_o (°C)	T_p (°C)	T_c (°C)	$T_c - T_o$ (°C)	ΔH (J/g)
NF	67.62 ± 0.25^{f}	70.15 ± 0.09^{f}	83.56 ± 0.70^{a}	15.94 ± 0.96^{a}	15.03 ± 0.62^{b}
DHT2F	68.98 ± 0.12^{d}	73.86 ± 0.10^{b}	80.63 ± 0.20^{b}	11.65 ± 0.23^{b}	9.08 ± 0.26^{d}
DHT4F	69.23 ± 0.47^{b}	74.69 ± 0.21^{a}	80.27 ± 0.28^{b}	11.04 ± 0.76^{c}	7.97 ± 0.86^{e}
NS	68.65 ± 0.40^{e}	71.37 ± 0.83^{e}	80.4 ± 0.11^{b}	11.76 ± 0.53^{b}	16.10 ± 0.37^{a}
DHT2S	69.12 ± 0.20^{c}	72.85 ± 0.02^{d}	79.67 ± 0.40^{c}	10.55 ± 0.11^{d}	13.79 ± 0.13^{c}
DHT4S	69.45 ± 0.38^{a}	73.07 ± 0.07^{c}	79.65 ± 0.79^{c}	10.21 ± 0.40^{e}	13.24 ± 0.12^{c}

All data represent the mean of three determinations. Mean ± standard deviation. Means with the same letter in each column are not significantly different ($p < 0.05$).

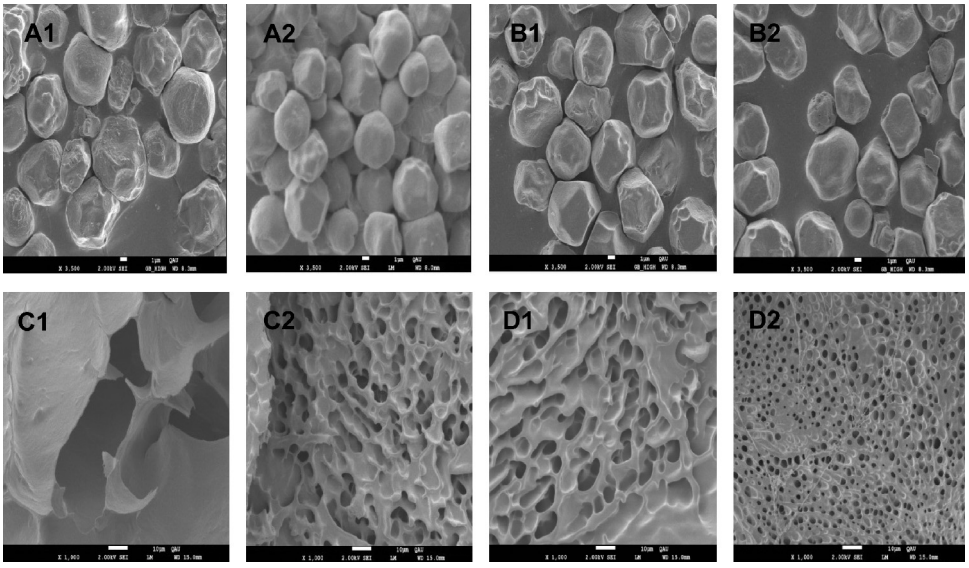

Fig. 2. SEM images of proso millet flour and starch particles and gels prepared before and after DHT (130 °C,4 h): (A1) flour particles; (A2) flour particles after dry heat treatments; (B1) starch particles; (B2) starch particles after dry heat treatments; (C1) gelatinized flour gel; (C2) gelatinized flour gel after dry heat treatments; (D1) gelatinized starch gel; (D2) gelatinized starch gel after dry heat treatments.

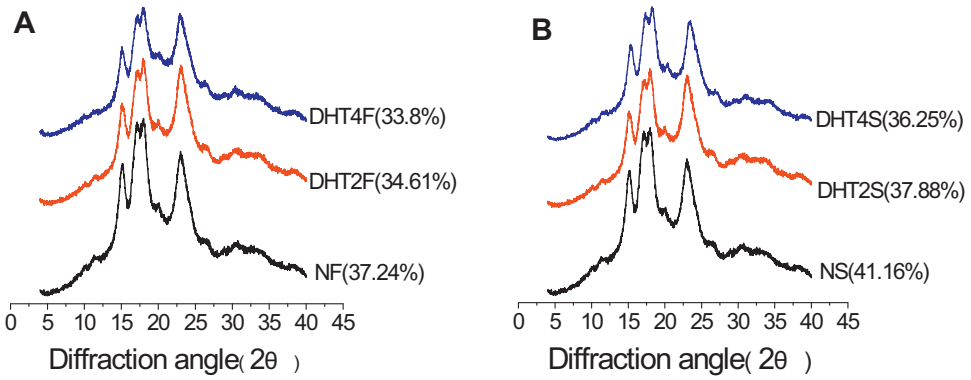

Fig. 3. X-ray patterns of proso millet flour samples (A) and starch samples (B): native flour (NF), flour treated at 130 °C for 2 h (DHT2F), flour treated at 130 °C for 4 h (DHT4F), native starch (NS), starch treated at 130 °C for 2 h (DHT2S), starch treated at 130 °C for 4 h (DHT4S).

heating dry starch or flour at >100 °C, preferably for several hours, provided functionality that is equivalent to chemical cross-linking (Chiu et al., 1998, 1999; Sun et al., 2013).

The lyophilized pastes of the flour and starch before and after drying heating as well as immediately after gelatinization were also observed by SEM. It was found that all the starch granules in the paste had been broken (C1, C2, D1 and D2) under SEM observation and that the starches and flours were entirely gelatinized. After dry heat treatment, the gel structure of the flour had more compact holes and it had formed into a stronger and closer structure (C2). The wall in the paste holes of untreated flour (C1) was thin, fragile, and could be easily destroyed. There were more small holes in the starch paste after 4 h of dry heating treatment (D2) compared with the native starch (D1). The denser structure of the DHT sample gels illustrated that the dry heating process made the interactions stronger in the flour/starch compositions. The SEM structure of the DHT flour gel was very different to the native gel but similar to that of the gelatinization native starch. These changes may provide further evidence that the non-starch components interacted with the starch during the dry heating process.

3.4. X-ray diffraction patterns

The X-ray diffraction patterns of all the samples were of the classic 'A' type, which was representative of grain starches with main reflections at 2θ of 15°, 17°, 18° and 23.5°, respectively (Fig. 3). Kim et al. (2012) also found that the proso millet starch showed a typical A-type crystallinity. The X-ray diffraction patterns of the flours (Fig. 3A) were similar to the starch samples (Fig. 3B) and the crystallinity of the heated flour samples decreased from 37.24% (NF) to 34.61% (DHT2F) and 33.8% (DHT4F), respectively, while the crystallinity of the heated starches separately decreased from 41.16% (NS) to 37.88% (DHT2S) and 36.25% (DHT4S), respectively. Among the flour samples treated with the same conditions, flours subjected to longer treatment time showed greater reductions in relative crystallinity, but the crystal type did not change after dry heat treatment (Fig. 3A). The relative crystallinity decreased with longer heating time, and these changes may suggest a decrease in the crystalline areas due to DHT and explain the greater thermal susceptibility evidenced by flours treated with dry heating. Similarly, the crystallinity of the starches also decreased greatly after dry heating, no other changes were apparent from the X-ray diffraction patterns (Fig. 3B). The decrease of crystallinity might have been due to the degradation of crystalline region or the increase of the amorphous region. Here, the crystallinity of the starch granules decreased after dry heat treatment, suggesting a partial reorganization of the amorphous region during dry heating. In addition, the imperfect crystallization and partially melting in the crystalline region and might have caused the decrease in crystallinity. The decrease of crystallinity in the starch granule may also account for the decrease in ΔH. Li et al. (2013) reported that the crystallinity of the waxy rice starch increased after dry heat treatment, but that with the addition of xanthan the amorphous region of the granule became more resistant to dry heating and the crystallinity did not change significantly. These differences in the results may be attributed to the differences in the structure of different starches. The decrease of the crystallinity might have also been due to the double helical movement during treatment, which might have disrupted starch crystallites and/or change crystallite orientation (Singh, Chang, Lin, Singh, & Singh, 2011). Apart from this, the influence of non-starch constituents and the thermal changes of the amorphous region during dry heating may also contribute to the lower crystallinity after DHT.

3.5. FTIR spectroscopy

The FTIR spectra of native and dry heating samples are presented in Fig. 4. The FTIR spectrum of flours and starches can show the level of sensitivity to DHT and the changes in structure on a molecular level. The strong absorption band in the range of 3500–3400 cm^{-1} was attributed to the O–H stretching of the starch and the peak width indicated the extent of formation of inter- and intra-molecular hydrogen bonds. The absorption peak of flours after DHT changed obviously from 3486 cm^{-1} (NF) to 3459 cm^{-1} (DHT2F) and 3423 cm^{-1} (DHT4F). The position of the peaks moved to a lower band in the flours after DHT, indicating that the interactions among the starches, and starches with other molecules, strengthened. The absorption peak of starches after DHT changed slightly from 3465 cm^{-1} (NS) to 3453 cm^{-1} (DHT2S) and 3447 cm^{-1} (DHT4S), but the width increased after the dry heating process. The wider peak of the DHT starch illustrated the increase in interactions among the starch molecules, and more hydrogen bonds were formed, leading to the strengthened gel network in the starch after the dry heating process (Fig. 2). The asymmetric stretching of C-H was observed at 2971 cm^{-1} and the absorption band at 1637 cm^{-1} was attributed to tightly bound water present in the starch (Shi, Wang, Li, & Adhikari, 2012). The FTIR spectrum of DHT4F (Fig. 4A) showed a more obvious peak at 2930 cm^{-1}(C–H stretching), and the peak moved to the left indicating the presence of hydrocarbon chromophores (Kunal et al., 2008). These changes were probably attributed to the –OH connected on the C interacting with other molecules, and the formation of the hydrogen bonds made –OH less attractive to the C–H bond. In addition, the intensity of the flours' absorption peak at 1267 cm^{-1} strengthened after DHT, while the DHT starches showed only a slight change at the same peak when compared with the native one. From the chemical

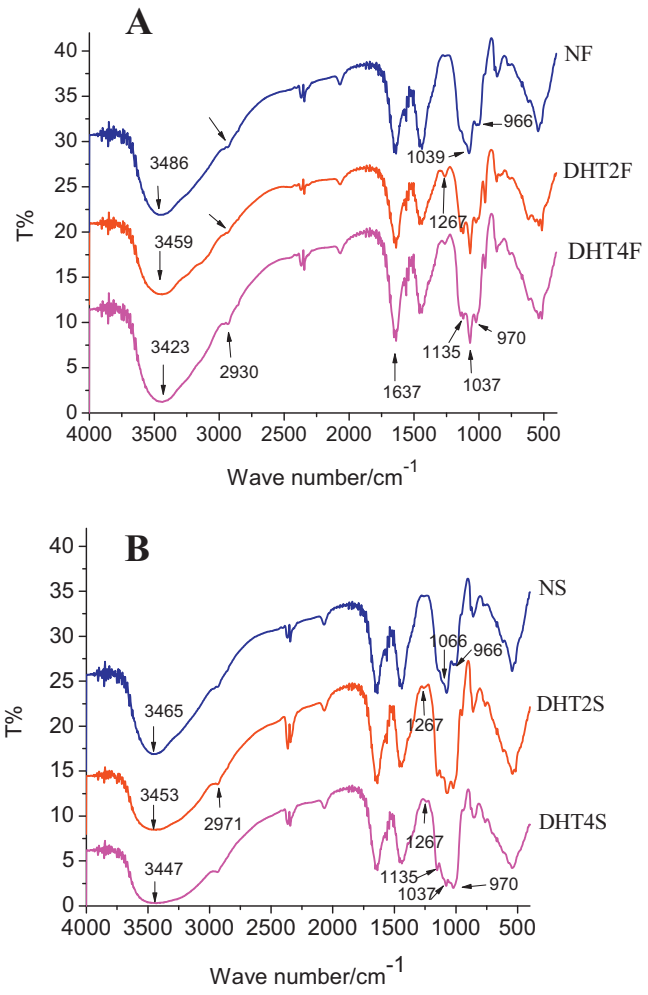

Fig. 4. FTIR spectra of proso millet flour samples (A) and starch samples (B): native flour (NF), flour treated at 130 °C for 2 h (DHT2F), flour treated at 130 °C for 4 h (DHT4F), native starch (NS), starch treated at 130 °C for 2 h (DHT2S), starch treated at 130 °C for 4 h (DHT4S).

composition analysis, almost no change has been observed in the component content. The greater change in the DHT flour may suggest the formation of hydrogen bonds or other bonds between the starch and non-starch compositions, which need to be investigated in the further study. The significant enhancement of the absorption peak in the DHT flours may be attributed to the strengthened of the stretching vibration of the C=O bond, C–O–C bond or C–C bond. The slight change in the starch samples indicated the presence of the functional group of non-starch constituents (such as proteins and lipids) in flours, which had a polymeric association with the polysaccharide functional groups in the starch during the dry heating process. In all the native samples, there were two peaks at about 966 cm^{-1} and 1039 cm^{-1}, but three peaks were observed in the DHT samples at about 970 cm^{-1}, 1037 cm^{-1}, and 1135 cm^{-1}, respectively. Other peaks, at 966 cm^{-1} in the native flour and 1066 cm^{-1} in the starch resulted from the angular deformation of C–H and C–C bond in the DHT flours and starches. Similarly, the peak at 1132 cm^{-1} resulted from the skeletal vibration of α-1-4 glycosidic linkage (C–O–C). The DHT flours and starches had three obvious peaks in the same range, indicating that new groups rose during the heating progress. The strengthening of the absorption peaks in the DHT flours may be attributed to the stretching vibration of the C=O bond in the esters generated between the –COOH in the protein and hydroxyl groups in the starches under DHT that was similar to a cross-linking reaction during the dry heating process. This was in accordance with previous reports, which studied the viscosity change and suggested that the ester bond might be formed when the starch and non-starch components had undergone heat treatment (Li et al., 2008; Lim et al., 2003). The peaks in the range of 950–1150 cm^{-1} can be considered as evidence of the cross-linking between the starch molecules and other non-starch constituents, especially for the protein in the flours.

4. Conclusions

Dry heat treatment to flour or starch can be useful for modifying their pasting and structural properties. As a physical modification method, the process is relatively safe and without the formation of any toxic by-products. Dry heat treatment had greater effects on the paste, thermal, morphological, and structural properties of proso millet flour than those of the corresponding starch. The DHT greatly increased the pasting viscosity of the flour, indicating that the non-starch ingredients played an important role. These results also suggested that dry heat treatment of starches and flours could be applied to products that require a higher final viscosity. Other than starch, other components in flours, such as protein, lipids, and non-starch polysaccharides, may also have effects on the properties of the proso millet flours during the dry heating process, and more studies should be conducted on this in the future.

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