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Rice starch vs. rice flour: Differences in their properties when modified by heat–moisture treatment

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ABSTRACT

Starch and flour from the same rice grain source (with 20, 25 and 30% moisture content) were exposed to heat–moisture treatment (HMT) at 100 °C for 16 h in order to investigate whether there were differences in their susceptibility to modification by HMT and, if any, to determine the main causes of the differences. HMT had a far greater effect on paste viscosity of flour than of starch. A significant increase in paste viscosity after removal of proteins from HMT flour – as well as images of fast green-stained HMT flour gels – indicated that an important role was played by proteins in affecting properties of the modified samples. Greater effects of HMT on thermal parameters of gelatinization and gel hardness values of flours were observed – more so than those for starches. Following this observation, it was ascertained that components in rice flour other than rice starch granules also underwent alterations during HMT.
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Heat–moisture treatment (HMT) is a physical modification technique applied to starches. It is considered to be natural and safe compared to chemical modification. Numerous studies have demonstrated the effects of such treatment on the structure and physicochemical properties of cereal, tuber and legume starches, including significant changes in X-ray diffraction pattern, crystallinity, starch chain interactions, granule swelling, amylose leaching, viscosity, gelatinization parameters, retrogradation, and acid and enzyme hydrolysis (Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994; Hormdok & Noomhorm, 2007; Jiranuntakul, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2011; Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012; Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009; Watcharatewinkul, Uttapap, Puttanlek, & Rungsardthong, 2010). Changes in these properties would affect the versatility of starch in food products such as fried batter food, noodles, and other healthy food products.

Flours are fine, powdery materials obtained by grinding and sifting the starch-containing plant organelles, such as those from grains, seeds, roots, tubers, and fruits. Usually, flours contain almost the same components as the raw materials, except for moisture content. Components often found in flours include starch, non-starch polysaccharide, sugar, protein, lipid, and inorganic materials. Commercial rice flour is produced either by dry or wet milling of broken rice, whereas rice starch is generally obtained by the alkaline steeping method with multi-stage purification. Such a treatment results in a significant reduction of protein content as well as other components in rice starch. As reported by Singh, Okadome, Toyoshima, Isobe, and Ohtsubo (2000), the protein content of rice starch (0.2–0.9%) was much lower than that of rice flour (5.2–6.87%). It has been claimed that protein components account for the differences in thermal and pasting properties of rice starch and rice flour (Hamaker & Griffin, 1993; Lim, Lee, Shin, & Lim, 1999; Zhu, Liu, Sang, Gu, & Shi, 2010).

The effects of HMT on various aspects of rice starch properties have been reported by several researchers (Hormdok & Noomhorm, 2007; Khunae, Tran, & Sirivongpaisal, 2007; Shih, King, Daigle, An, & Ali, 2007; Zavareze, Storck, Suita de Castro, Schirmer, & Dias, 2010), whereas relatively little work has been done on properties of rice flour (Cham & Suwannaporn, 2010; Lorlowhakarn & Naivikul, 2006). None of the reviewed works involved comparison of starch and flour from the same source of rice kernels (the same variety, batch, etc.) in terms of susceptibility to modification by HMT. Therefore, in order to obtain information on properties of HMT rice starch compared to HMT rice flour, as well as to obtain a better understanding of the role of the components in flour (other than starch) on properties of HMT products, rice starch and rice flour from the same source – with moisture contents of 20, 25 and 30% – were subjected to HMT at 100 °C for 16 h. The treated products were then analyzed for their paste and gel properties as well as thermal properties. The magnitude of change in these attributes of starch

Abbreviations: HMT, heat–moisture treatment/heat–moisture treated; PB, protein body; T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH, gelatinization enthalpy.

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and flour by HMT was compared and discussed in relation to the composition of rice kernels, especially the protein component.

1. Materials and methods

1.1. Materials

Rice grains (Prachinburi variety) were obtained from Prachinburi Rice Research Center, Prachinburi, Thailand. Porcine pancreatic α-amylase (EC 3.2.1.1, 28 U/mg solid) and amyloglucosidase (EC 3.2.1.3, 300 U/ml) were purchased from Sigma–Aldrich (St. Louis, MO, USA). A GLUCOSE liquicolor complete kit was purchased from Human Diagnostics (Wiesbaden, Germany). Protease (E-BSPRT) at a concentration of 50 mg/ml was purchased from Megazyme International Ireland (Bray, Ireland).

1.2. Starch and flour preparations

Rice starch was prepared by the alkaline steeping method (Ju, Hettiarachchy, & Rath, 2001), with some modifications. Dehulled rice grains were steeped in distilled water at 4 °C for 24 h. The supernatant was discarded and the steeped rice grains were ground with a blender, then passed through a 63 μm screen. The slurry was allowed to stand at 4 °C for 48 h. The supernatant was removed and the starch cake was re-suspended in 0.35% sodium hydroxide solution and kept at 4 °C for 48 h. The supernatant was decanted and the starch layer was re-slurried with water. The starch slurry was passed through a 63 μm sieve and allowed to stand at 4 °C for 24 h. The steps of washing with water were repeated three times. The starch cake was re-suspended in water, neutralized with 1 M hydrochloric acid to pH 7, and stored at 4 °C for 24 h. The supernatant was decanted, and the neutralized starch was re-suspended in water and placed at 4 °C for 24 h. Finally, the supernatant was removed and the starch cake was dried in an oven at 40 °C for 24 h. For rice flour, rice grains were ground with a blender, then passed through a 106 μm screen.

1.3. Chemical composition of starch and flour

Standard AOAC methods (1990) were used for the measurement of moisture, nitrogen, ash, and lipid. Protein was determined from estimation of total nitrogen using a conversion factor of 6.25. Phosphorus content was determined by a colorimetric chemical method (Smith & Caruso, 1964). Apparent amylose content was determined by a procedure described by Hoover and Ratnayake (2001). The amylose content was calculated from a standard curve prepared by using mixtures of pure amylose and amylopectin fractionated from rice starch (over a range of 0–100% amylose). Total starch was determined according to the method of McCleary, Gibson, and Mugford (1997).

1.4. Heat–moisture treatment

Rice starch and flour samples were adjusted to the desired moisture content (20, 25 or 30%) by soaking 200 g of starch in 600 ml of water overnight at 4 °C. The excess water in equilibrated slurry was then drawn out by vacuum suction to obtain a cake with moisture content around 40%. The cake was then air-dried to allow the moisture content to drop to the desired level. Moist samples (native and moistened rice starches and flours) in 250 ml screw-capped bottles were heated at 100 °C for 16 h. After HMT, the starches were dried at 40 °C overnight. Untreated rice starch and flour were used as controls.

1.5. Pasting properties

Pasting properties of starch slurry at a concentration of 8% (w/w) were determined by a Rapid Visco Analyzer (RVA-3D; Newport Scientific, Narrabeen, Australia) with a paddle rotated at a fixed speed of 160 rpm. The starch slurry was heated from 40 to 92.5 °C at a rate of 3 °C/min, maintained at 92.5 °C for 15 min, and then cooled to 40 °C at the same rate.

1.6. Light microscope

Samples were stained with fast green (0.1% for 20 min) and then rinsed with water, followed by iodine (0.2% iodine for 10 s), to observe the protein and starch in samples. The stained samples were examined under a light microscope at 200×.

1.7. Preparation of deproteinized rice flour

HMT rice flours were deproteinized by two methods: alkaline steeping and enzyme hydrolysis. Removal of protein by alkaline steeping was carried out according to the procedure described in Section 1.2. For enzyme hydrolysis, proteins in flour were hydrolyzed with protease as follows: a slurry of 2.24 g of HMT rice flour in 14.0 g of water was prepared in a Rapid Visco Analyzer (RVA) canister and its pH was adjusted to pH 7.8 with 0.1 N NaOH. Protease solution (0.1 ml) was then added, and the concentration of slurry was brought up to 8% before incubating at 37 °C for 30 min. Pasting properties of the deproteinized samples were then determined with an RVA. The control samples were done in parallel by using an equivalent amount of bovine serum albumin (BSA) instead of protease.

1.8. Texture analysis

After RVA testing, the canister containing starch/flour paste was covered with paraffin film and kept at 4 °C for 24 h. Texture of the gel was then determined using a Shimadzu EZ-S 50N Texture Analyzer (Shimadzu, Kyoto, Japan). Gel in the canister (with a dimension of 20 mm in height and 38 mm in diameter) was compressed at a speed of 2.0 mm/s to a distance of 15 mm with a cylindrical probe 20 mm in diameter. The obtained textural parameters were means of at least three measurements.

1.9. Differential scanning calorimetry

The thermal properties of starch/flour were determined by a differential scanning calorimeter (DSC 1; Mettler-Toledo, Schwerzenbach, Switzerland). The starch/flour (3 mg) was weighed in an aluminum pan (ME-00026763; Mettler-Toledo) and water (6 mg) was added. The pan was sealed and allowed to stand for 24 h at 4 °C. The scanning temperature range and heating rate were 25–100 °C and 5 °C/min, respectively. An empty pan was used as a reference. The transition temperatures reported were the onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c). The enthalpy change on gelatinization (ΔH) was estimated by integrating the area between the thermograms and a baseline under the peak, and was expressed in terms of J/g of dry starch.

1.10. Statistical analysis

All analyses of starch and flour characteristics and properties were carried out with three replications. Experimental data were analyzed using one-way analysis of variance (ANOVA) and expressed as mean values ± standard deviations. A Duncan's test was conducted to examine significant differences among

Table 1
Chemical compositions (dwb) of rice starch and flour.

Characteristics	Composition (%, dry basis)	
	Rice starch	Rice flour
Protein (%)	0.38 ± 0.01	6.22 ± 0.12
Lipid (%)	0.01 ± 0.01	0.24 ± 0.01
Ash (%)	0.19 ± 0.01	0.18 ± 0.01
Phosphorus (ppm)	12.85 ± 0.82	102.60 ± 2.95
Amylose (%)	25.01 ± 0.79	nd
Total starch (%)	95.24 ± 0.52	84.66 ± 0.39

nd: not determined.

experimental mean values ($P \leq 0.05$). The software used for all analyses was SPSS version 16.0.

2. Results and discussion

2.1. Chemical composition

The chemical compositions of the starch and flour samples are presented in Table 1. Rice flour contained noticeably higher amounts of protein, lipid and phosphorus compared to rice starch. Protein, lipid, ash and phosphorus in rice flour were 6.22%, 0.24%, 0.18% and 102.6 ppm, whereas those in rice starch were 0.38%, 0.01%, 0.19% and 12.8 ppm, respectively. Purified rice starch had much higher contents of total starch (95.24%) compared to rice flour (85.66%). Previous studies have shown that rice starch contained 98% starch, 0.07–0.68% protein, 0.01–0.35% ash and 13–47 ppm phosphorus (Zhu et al., 2010), whereas rice flour contained 71–91% starch, 7–11% protein, 0.87–8.1% lipid and 0.46–1.1% ash (Dias, Zavareze, Spier, Suita de Castro, & Gutkoski, 2010; Gunaratne & Hoover, 2002; Zhu et al., 2010). Differences in the chemical compositions of flour and starch would influence their paste and gel properties, as well as the susceptibility of flour and starch to HMT.

2.2. Pasting properties of HMT rice starch and rice flour

RVA viscographs of native and HMT rice starches are shown in Fig. 1A and the corresponding pasting parameters are summarized in Table 2. Pasting temperature, peak viscosity, breakdown and setback of native rice starch were 76.8 °C, 103.7 RVU, 25.8 RVU and 151.5 RVU, respectively. After HMT, pasting temperature of treated starch with a moisture content of 20% increased slightly, while significant increases were observed for treated starches with moisture contents of 25% and 30%. On the other hand, increases in levels of moisture treatment caused a progressive decrease in the peak viscosity of HMT starches. Reduced viscosity and increased pasting temperature after HMT were consistent with previous reports on other starches: rice and corn (Jiranuntakul et al., 2011), canna (Watcharatewinkul et al., 2009), and lentil, potato and yam (Hoover & Vasanthan, 1994). These studies indicated that structural rearrangement and starch-chain associations contributed to these changes. In addition, phase separation between amylose and amylopectin, compaction of granular matter by vapor pressure force, and chemical bonding/interactions that occur during HMT might be other factors influencing the strength of HMT starch (Watcharatewinkul et al., 2009).

The pasting profile of untreated rice flour was similar to that of untreated rice starch, except that the flour sample had a higher pasting temperature and a slightly lower breakdown, could develop viscosity faster when cooled down, and had much lower setback than the starch sample (Fig. 1B). Pasting temperature, peak viscosity, breakdown and setback of untreated rice flour were 81.9 °C, 100.4 RVU, 11.3 RVU and 80.7 RVU, respectively (Table 2). Lim

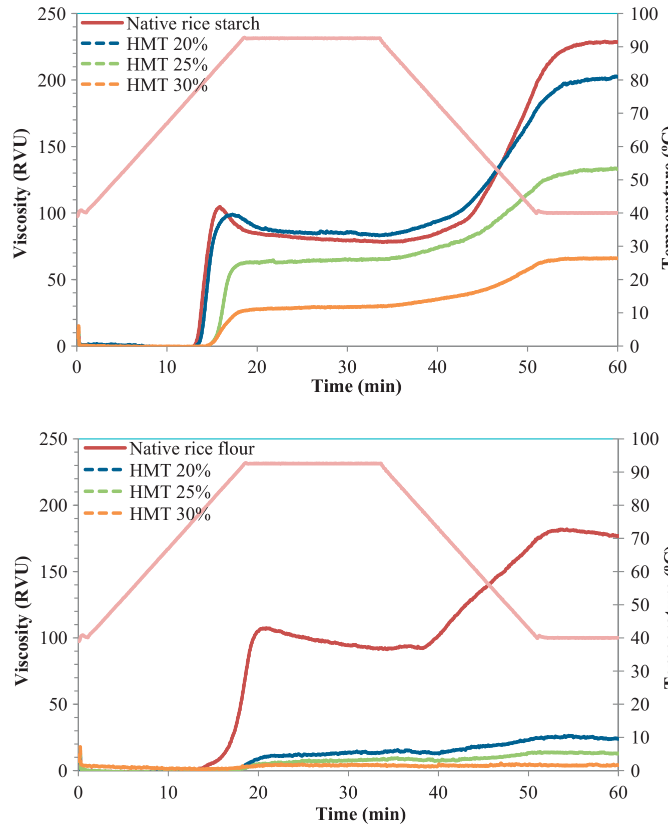

Fig. 1. RVA pasting profiles of native and HMT rice starches and flours.

et al. (1999), Xie, Chen, Duan, Zhu, and Liao (2008), and Zhu et al. (2010) have demonstrated that rice protein is primarily responsible for the differences in pasting properties between rice flour and rice starch. As shown in Fig. 1B, the effect of HMT on paste viscosity was much more pronounced in rice flour than in rice starch. Significant changes in pasting profile of HMT rice flour were found; viscosities of all treated flour were very low, and almost approached zero in the case of flour having 30% moisture content during treatment. All viscograms showed no clearly defined peak/trough; therefore, pasting parameters – such as peak viscosity, breakdown and setback – could not be determined. Since protein is the second major component in flour (after starch), and can be denatured by heat treatment, it was postulated in this study that protein in rice flour would also undergo alteration by HMT along with the starch granules, and that some interactions might occur between them during heat treatment. Accordingly, these changes would account for the differences in paste and gel properties of HMT rice starch and rice flour. In view of this, the untreated and HMT rice flours were stained with fast green, followed by iodine, to observe the changes in protein and starch granules by HMT.

2.3. Light microscopy of stained samples

Images of untreated and HMT rice flours stained with fast green and iodine and examined by light microscope (200×) are shown in Fig. 2. Green and blue colors appearing on stained samples represent the existing protein and starch, respectively. Most of the stored protein in rice endosperm is glutelin, with the remainder consisting of prolamin, albumin and globulin. Glutelin and prolamin accumulate in the 2–3 μm semi-ellipsoidal and 1–2 μm spherical bodies, called protein body II (PB-II) and protein body I (PB-I), respectively (Tanaka, Sugimoto, Ogawa, & Kasai, 1980). It is well known that

Table 2
RVA pasting parameters of native and HMT rice starches and flours.

Characteristics	Pasting temperature (°C)	Peak viscosity (RVU)	Breakdown (RVU)	Setback (RVU)	Final viscosity (RVU)
Native rice starch	76.8 ± 0.2	103.7 ± 1.4	25.8 ± 1.3	151.4 ± 1.1	229.4 ± 1.0
HMT20%	77.1 ± 0.2	99.4 ± 0.7	15.8 ± 0.1	119.5 ± 0.3	203.0 ± 1.0
HMT25%	81.8 ± 0.4	64.8 ± 0.4	0.6 ± 0.2	70.4 ± 1.7	134.5 ± 2.3
HMT30%	81.5 ± 0.1	30.3 ± 1.9	0.3 ± 0.1	37.7 ± 0.6	67.6 ± 2.4
Native rice flour	81.9 ± 4.0	100.4 ± 9.9	11.3 ± 6.7	80.7 ± 0.3	169.8 ± 10.2
HMT20%	86.8 ± 4.4	13.5 ± 1.6	0.6 ± 0.5	12.5 ± 0.3	25.5 ± 2.3
HMT25%	92.0 ± 0.1	6.9 ± 0.9	0.4 ± 0.3	6.5 ± 0.4	13.0 ± 0.4
HMT30%	0.0	0.0	0.0	0.0	0.0
Deproteinized by alkaline dissolution					
Native rice flour	76.8 ± 0.2	103.7 ± 1.4	25.8 ± 1.3	151.4 ± 1.1	229.4 ± 1.0
HMT20%	78.8 ± 0.1	39.7 ± 1.6	36.2 ± 0.5	17.1 ± 0.8	58.8 ± 1.4
HMT25%	80.0 ± 0.1	20.0 ± 0.1	24.1 ± 0.9	4.3 ± 0.3	39.9 ± 1.1
HMT30%	82.0 ± 0.4	9.9 ± 0.2	10.2 ± 1.2	0.8 ± 0.4	19.3 ± 0.6
Deproteinized by protease hydrolysis					
Native rice flour	77.4 ± 0.1	91.9 ± 0.8	79.1 ± 0.1	32.2 ± 1.1	138.8 ± 1.9
HMT20%	82.2 ± 0.1	49.4 ± 3.9	32.0 ± 1.3	4.9 ± 0.2	76.5 ± 2.8
HMT25%	83.1 ± 0.1	23.8 ± 0.9	17.9 ± 0.5	2.6 ± 0.1	39.2 ± 0.4
HMT30%	85.8 ± 0.4	6.7 ± 1.2	4.6 ± 0.8	0.5 ± 0.1	10.8 ± 0.4

the starch in plants is stored in the form of granules with varying size and shape depending on the botanical source. Rice starch granules have a polyhedral shape with a diameter range of 1–7 μm. As shown in Fig. 2, the image of untreated rice flour is entirely different from those of HMT flours. The compound starch granules in untreated flour were mostly uniformly dispersed, with the protein bodies distributed among them. However, most of the protein bodies were observed as agglomerations rather than as singular bodies. These agglomerations might occur during the dry-milling of the rice kernel. As a result of HMT, the starch granules clumped together, forming small lumps. The degree of clumping was greater with an increase in the moisture content in flour samples during heat treatment. Similar results were found for the protein bodies. It was observed that the protein bodies were deformed and spread over the lumps of starch granules. Due to their fragile nature (Varatharajan, Hoover, Liu, & Seetharaman, 2010), protein bodies can easily be denatured by heating at 100 °C. The enlarged photo (1000×, Fig. 2 inset) of HMT rice flour with 30% moisture content reveals that the denatured protein bodies spread over, and adhered to, the surfaces of the starch granule clumps. These protein layers were presumably the main cause of the differences in pasting properties between HMT rice starch and rice flour. To verify this supposition, the proteins in HMT rice flour were removed by dissolution in alkaline solution and by enzyme hydrolysis. The pasting profiles of deproteinized HMT flours were then compared with those of HMT starches.

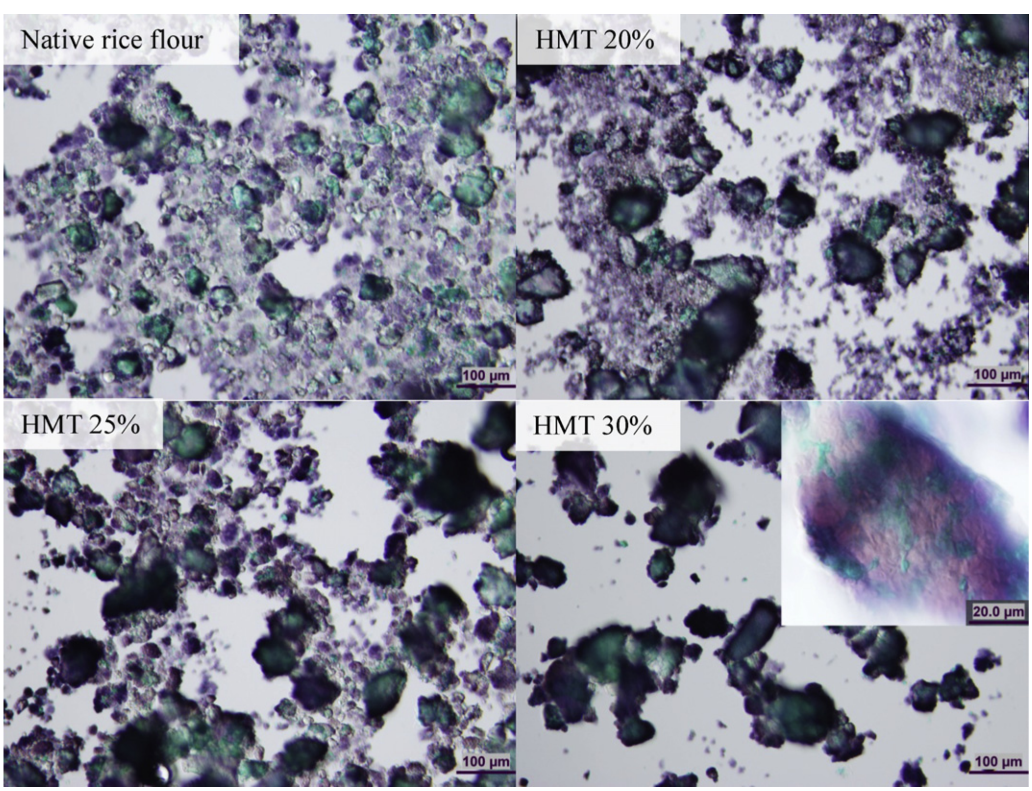

Fig. 2. Light microscopy of native and HMT rice flours stained with fast green and iodine (200×).

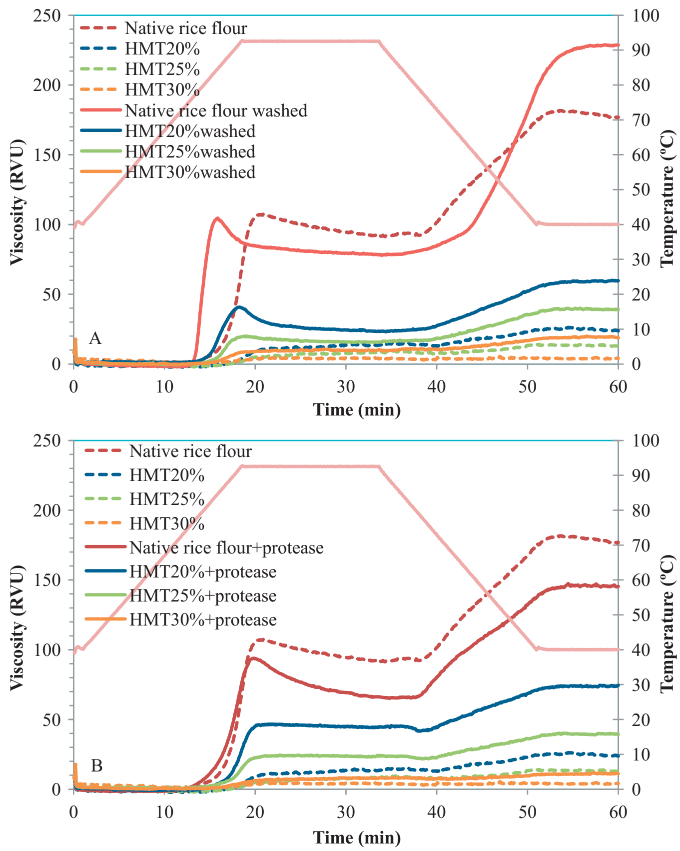

Fig. 3. RVA pasting profiles of HMT rice flours deproteinized by alkaline dissolution (A) and enzyme hydrolysis (B).

2.4. Pasting properties of deproteinized HMT rice flour

Pasting profiles of deproteinized HMT flours are shown in Fig. 3 and the corresponding pasting parameters are given in Table 2. Removal of proteins from HMT flours by dissolving in alkaline solution resulted in an increase of viscosity of all HMT flour samples. However, their viscosities remained lower than those of HMT starches, due to incomplete removal of the salt- and/or alcohol-soluble proteins, and even alkali-soluble proteins. As shown in Table 3, most of the proteins (5.5–5.8% dwb) still remained in HMT rice flours after alkaline dissolution. Integration of proteins with other components in flour during HMT might impede protein dissolution. Similar results were found for HMT flours treated with protease, but with slightly greater efficiency of protein removal, i.e. the protein content remaining in HMT flour was in a range of 4.64–4.82% dwb. Viscosities of the hydrolyzed flour samples, especially HMT flour with 20% moisture content, increased significantly, but could not attain the viscosity values of HMT starches. (The presence of BSA with equal amounts of enzyme had no/little effect on the viscosity of HMT flour [data not shown].) HMT proteins very likely could not be readily hydrolyzed by protease as a result of their structural deformation. Rice albumin, globulin and glutelin have been reported to be denatured at 73.3, 78.9 and 82.2 °C, respectively (Ju et al., 2001). Denaturation of rice proteins results in an increase of their surface hydrophobicities, due to exposure of hydrophobic groups folded inside the intact native protein molecule (Mine, 1997).

In relation to the results obtained from these experiments, together with information from previous studies as mentioned above, it can be concluded that rice proteins played an important role in the different characteristics of HMT rice flour and rice starch. During HMT at 100 °C, protein bodies were deformed and denatured. Interactions that occurred between denatured proteins, and between proteins and starch granules, consequently caused the association of the protein networks with the surfaces of starch granules (Fig. 2). These protein layers, in cooperation with the increased hydrophobicity, retarded the swelling of HMT starch granules in flour. Therefore, paste viscosities of HMT flours were much lower than those of HMT starches treated under the same conditions. The role of proteins in pasting characteristics was consistent with previous reports. Lim et al. (1999), for example, reported that reducing the protein content in rice flour increased its peak viscosity. Tan and Corke (2002) proposed that protein content was negatively correlated with peak viscosity and hot paste viscosity. Chrastil (1990) reported that disulfide bonding increased during storage of rice at high temperatures.

Table 3
Protein content of HMT rice flours deproteinizedby alkaline dissolution and protease hydrolysis.

Starch sample	Protein content (%, dwb)	
	Alkaline dissolution	Protease hydrolysis
Native rice flour	0.39 ± 0.01	2.98 ± 0.24
HMT20%	5.80 ± 0.24	4.82 ± 0.06
HMT25%	5.71 ± 0.24	4.69 ± 0.01
HMT30%	5.50 ± 0.30	4.64 ± 0.18

2.5. Gel texture

Hardness values (as analyzed by a texture analyzer) of rice starch and flour gels after being kept at 4 °C for 24 h are summarized in Table 4. Native rice starch (1098 g) had much higher gel hardness than rice flour (439 g). Gel formation of starch paste mainly depends on swollen starch granules that hold water in the network within the granule. Amylose leaked from swollen granules plays a minor role, but it becomes more significant when the swollen granules disrupt. Other components in flour and starch samples – such as protein, lipid, and non-starch polysaccharides – would also take part in the network formation, either facilitating or impeding the process. In this study, the higher hardness of starch gel compared to flour gel was presumably due to its higher starch content, as well as a greater extent of granule swelling due to lower protein and lipid content.

Modification by HMT resulted in a reduction of gel hardness of both starch and flour samples. Under the same HMT conditions, starch samples exhibited much higher gel hardness than flour samples. An increase in the moisture content of samples during treatment tended to decrease the hardness of gels. It was speculated that starch granules of the HMT starch and flour samples with higher moisture content swelled less, and thus formed weaker gel. In the case of HMT flours, a sharp decrease in gel hardness was also affected by components other than starch. Protein layers that formed on the starch surface, as well as lipid complexes formed during HMT, could inhibit the swelling of starch granules. Biliaderis and Tonogai (1991) found that lipids formed complexes with amylose on the granular surface and thereby restricted granular swelling. Low gelatinization in fried batter was reportedly

Table 4
Hardness values of native and HMT rice starches and flours.

Starch sample	Hardness (gf)	Flour sample	Hardness (gf)
Native rice starch	1098 ± 148^{a}	Native rice flour	439 ± 20^{c}
HMT20%	1062 ± 33^{a}	HMT20%	259 ± 4de
HMT25%	901 ± 122^{b}	HMT25%	192 ± 5^{ef}
HMT30%	395 ± 12^{cd}	HMT30%	78 ± 3^{f}

Means with different letters (a–f) are significantly different ($P \leq 0.05$).

Table 5
DSC characteristics of native and HMT rice starches and flours.

Characteristics	Gelatinization (°C)					
	T_o	T_{p1}	T_{p2}	T_c	$T_c - T_o$	ΔH (J/g)
Native rice starch	69.2 ± 0.1	73.1 ± 0.1	–	77.9 ± 0.2	8.7 ± 0.1	14.9 ± 0.3
HMT20%	72.2 ± 0.4	75.9 ± 0.6	–	82.7 ± 0.9	10.5 ± 0.5	16.1 ± 0.2
HMT25%	76.2 ± 0.1	80.0 ± 0.1	86.3 ± 0.1	91.2 ± 0.2	15.1 ± 0.2	15.4 ± 0.4
HMT30%	77.9 ± 0.1	82.4 ± 0.1	89.8 ± 0.4	94.1 ± 0.2	16.2 ± 0.2	11.5 ± 0.5
Native rice flour	69.4 ± 0.4	73.2 ± 0.1	–	77.7 ± 0.2	8.4 ± 0.2	11.4 ± 0.6
HMT20%	74.4 ± 0.1	78.1 ± 0.1	83.1 ± 0.1	86.8 ± 0.7	12.4 ± 0.7	14.8 ± 0.1
HMT25%	77.0 ± 0.2	79.3 ± 0.1	85.2 ± 0.1	88.7 ± 0.9	11.7 ± 0.7	13.1 ± 0.2
HMT30%	79.8 ± 0.2	83.2 ± 0.1	88.5 ± 0.2	96.2 ± 0.3	16.4 ± 0.2	14.7 ± 0.1

due to amylose–lipid complex formation (Matsunaga, Kawasaki, & Takeda, 2003). Hamaker and Griffin (1993) explained that proteins with intact disulfide bonds made the swollen granules less susceptible to breakdown, either by imparting strength to the swollen granules or by reducing the degree of swelling.

2.6. Thermal properties

Thermal transition behaviors of native and HMT rice starch and flour are presented in Fig. 4 and the corresponding gelatinization parameters are given in Table 5. The gelatinization temperature range of native rice starch (69.2–77.9 °C) was very close to that of native rice flour (69.4–77.3 °C). However, enthalpy change of gelatinization of starch samples was higher than that of flour samples, due to the higher starch content. After HMT, the endotherms of both starch and flour samples were shifted to a higher temperature with a broader shape and gelatinization temperature (T_p) of HMT starch and flour increased with an increase of moisture content. These results were consistent with other studies (Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994; Watcharatewinkul et al., 2009). However, the thermograms of HMT rice flours were significantly different from those of HMT rice starches treated under the same conditions. The most obvious case was the sample with 20% moisture content during treatment. Under this condition, starch displayed one peak endotherm, whereas flour displayed a biphasic endotherm. Both starch and flour exhibited biphasic endotherms at higher moisture contents (25 and 30%). The biphasic endotherms of starches and flours indicated a greater inhomogeneity in structural organization caused by HMT. However, distinctive features of biphasic endotherms were observed in HMT starch and flour samples: the second peak was dominant in flour samples, while the opposite was found for starch samples. This indicated that HMT had a greater influence on the structure of flour than of starch. This finding again confirmed the role of non-starch components on properties of HMT flours. In addition to rearrangement of amylose and amylopectin inside starch granules, as suggested by many researchers (Hoover & Vasanthan, 1994; Khunae et al., 2007; Zavareze et al., 2010), interactions of starch granules and other components in flours during HMT would also strengthen the structure of HMT flours, as denoted by greater differences in enthalpy change before and after heat–moisture treatment of flour samples (1.7–3.4 J/g), as compared to the starch samples (0.5–1.2 J/g). An exceptional case was the HMT30% rice starch (starch sample containing 30% moisture content during treatment), where the enthalpy change was reduced after HMT. This might be due to partial gelatinization, which could occur in samples having high moisture content. The partial gelatinization of starch could also be a reason for the markedly reduced viscosity of HMT30% rice starch (Fig. 1).

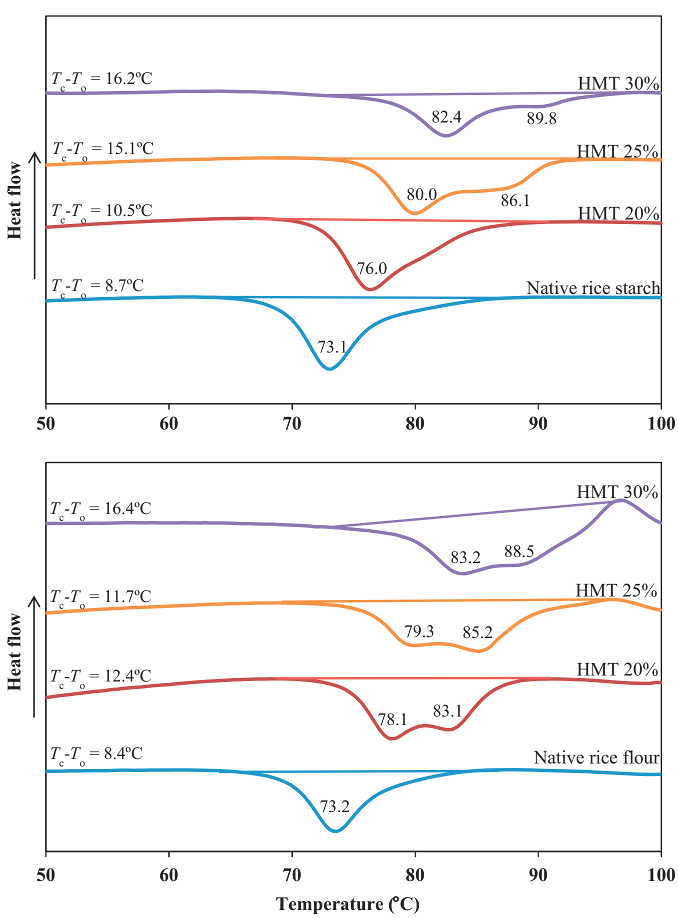

Fig. 4. Gelatinization thermograms of native and HMT rice starches and flours.

3. Conclusions

HMT had greater effects on paste and gel properties of rice flour, as well as on thermal properties, than on those of the corresponding starch. Removal of protein from HMT flours, resulting in higher paste viscosity, indicated the important role of protein in affecting the properties of HMT products. Other components in flours, such as lipids and non-starch polysaccharides, might also have an effect on the properties of HMT rice flours, and should be investigated in future studies.

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