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Milling of rice grains: Effects of starch/flour structures on gelatinization and pasting properties

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ABSTRACT

Starch gelatinization and flour pasting properties were determined and correlated with four different levels of starch structures in rice flour, i.e. flour particle size, degree of damaged starch granules, whole molecular size, and molecular branching structure. Onset starch-gelatinization temperatures were not significantly different among all flour samples, but peak and conclusion starch-gelatinization temperatures were significantly different and were strongly correlated with the flour particle size, indicating that rice flour with larger particle size has a greater barrier for heat transfer. There were slight differences in the enthalpy of starch gelatinization, which are likely associated with the disruption of crystalline structure in starch granules by the milling processes. Flours with volume-median diameter ≥56 μm did not show a defined peak viscosity in the RVA viscogram, possibly due to the presence of native protein and/or cell-wall structure stabilizing the swollen starch granules against the rupture caused by shear during heating. Furthermore, RVA final viscosity of flour was strongly correlated with the degree of damage to starch granules, suggesting the contribution of granular structure, possibly in swollen form. The results from this study allow the improvement in the manufacture and the selection criteria of rice flour with desirable gelatinization and pasting properties.

1. Introduction

Rice (*Oryza sativa* L.) is one of the most widely grown cereal crops for food. Rice heads are mostly consumed as cooked polished grains for staple food in many countries, whereas broken rice grains are commonly milled or ground into flour and used as an ingredient in baby foods, noodles, puddings, and many Asian cuisines. The largest component in rice grains is starch (>80%, dry weight basis), which is an important factor determining the quality of rice products. The structures of starch in rice grains can be simplified into six hierarchical levels (Dona, Pages, Gilbert, & Kuchel, 2010; Tran et al., 2011): individual linear branches of starch molecules (Level 1), macromolecular branched structure (Level 2), alternating crystalline and amorphous lamellae (Level 3), growth rings (Level 4), individual starch granules (Level 5), and a whole grain (Level 6). Although a whole rice grain contains not only starch granules, but also non-starch components, including lipids, proteins, and non-starch polysaccharides, it is included as one of the starch structural levels in the present study due to the fact that the interactions between starch and non-starch components, such as entrapment by cell-wall or protein matrices and starch–lipid complex, can affect the structures and properties of starch. Levels 1 and 2 are the molecular structure and comprise mainly two types of glucose polymers, namely highly branched amylopectin with a larger number of short branches and smaller amylose with few long branches. Furthermore, these six levels are not the only levels of starch structures in the grains. There are other levels, including superhelical (Oostergetel & van Bruggen, 1993) and blocklet structures (Gallant, Bouchet, & Baldwin, 1997), which are excluded here as they are not commonly studied and might complicate the discussion of the results from the present study.

Abbreviations: ANOVA, Analysis of variance; AUC, Area under the curve; CM10C2, Rice flour produced by two cycles of 10-min cryogenic milling; CM10C3, Rice flour produced by three cycles of 10-min cryogenic milling; CM10C4, Rice flour produced by four cycles of 10-min cryogenic milling; CM5C1, Rice flour produced by one cycle of 5-min cryogenic milling; CM5C2, Rice flour produced by two cycles of 5-min cryogenic milling; DP, Degree of polymerization; DSC, Differential scanning calorimetry/calorimeter; ΔH, Enthalpy of starch gelatinization; HM1000P1, Rice flour produced by one pass through a hammer mill with 1000-μm screen; HM1500P1, Rice flour produced by one pass through a hammer mill with 1500-μm screen; HM500P1, Rice flour produced by one pass through a hammer mill with 500-μm screen; HM500P2, Rice flour produced by two passes through a hammer mill with 500-μm screen; HM500P3, Rice flour produced by three passes through a hammer mill with 500-μm screen; $N_{de}(\bar{X})$, SEC number molecular size distribution of debranched starch; R, Correlation coefficient; $\bar{R}_h$, Average hydrodynamic radius; RVA, Rapid visco analyser; SEC, Size exclusion chromatography; T_c, Conclusion starch-gelatinization temperature; T_o, Onset starch-gelatinization temperature; T_p, Peak starch-gelatinization temperature; $\bar{X}$, Average DP.

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Milling or grinding to break cereal grains (Level 6 starch structure) into flour can cause damage to starch granules (Level 5 structure) (Dhital, Shrestha, & Gidley, 2010a; Hasjim, Srichuwong, Scott, & Jane, 2009; Tran et al., 2011), disruption of starch crystalline lamellae (Level 3 structure) (Dhital, Shrestha, Flanagan, Hasjim, & Gidley, 2011; Morrison, Tester, & Gidley, 1994), and degradation of starch molecules (Levels 1 and 2 structures) (Dhital et al., 2011; Morrison & Tester, 1994; Tran et al., 2011; Yin & Stark, 1988). It is well documented that grinding of isolated starch granules alters starch gelatinization and pasting properties. Gelatinization temperature, enthalpy of gelatinization, and RVA pasting viscosity decrease with the increase of grinding time (Chen, Lii, & Lu, 2003; Dhital et al., 2010a, 2011; Han, Campanella, Mix, & Hamaker, 2002; Morrison et al., 1994), which is associated with the damage to starch granules (Level 5 structure) and/or the disruption of starch crystalline lamellae (Level 3 structure). Grinding of isolated starch granules, although it allows the study of grinding effects on starch structures and properties without the interference from the non-starch components in cereal grains, is not a common practice in food industry and does not replicate the grinding of cereal grains, where the protein and cell-wall matrices in the grains may provide protection to starch granules against structural degradation during grinding, and the size of grains (mm) is much larger than the size of isolated starch granules (μm). Furthermore, the use of ground isolated starch granules neglects the effects of flour particle size (Level 6 starch structure) on starch gelatinization and pasting properties, which is important in understanding the cooking quality of flour. Hence, it is crucial to study the effects of grinding on starch gelatinization and pasting properties using flour because of the complexity in the starch structures in grains and flour compared with those of isolated starch granules.

Many studies have shown the effects of flour particle size (Level 6 starch structure) (Mahasukhonthachat, Sopade, & Gidley, 2010; Marshall, 1992), damaged starch granules (Level 5 structure) (Dhital et al., 2011, 2010a; Morrison et al., 1994), and molecular structure (Levels 1 and 2 structures) (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005a, 2005b; Vandeputte, Derycke, Geeroms, & Delcour, 2003) separately on starch gelatinization properties and starch or flour pasting properties. However, existing literatures to date have not addressed the starch structure – gelatinization/pasting property relationships at four different levels of starch structures in a single study. Furthermore, it is not well understood whether the effects of the flour particle size is (partially or completely) contributed by the damage to starch granules and/or the degradation of starch molecular structure. The objective of this study is to understand which level of starch structures is the dominant factor determining the starch gelatinization properties of rice flour and flour pasting properties. This will provide a better insight in the effects of flour particle size, damaged starch granules, and molecular degradation, as separate entities, on the properties of rice flour.

In a previous study (Tran et al., 2011), a series of rice flours were produced from rice grains using cryogenic milling and hammer milling. The resulting flours had different flour particle sizes, degrees of damaged starch granules, and degrees of molecular degradation as summarized in Table 1. The hammer-milling process resulted in a greater damage to starch granules (Level 5 structure) than the cryogenic-milling process when the grains were ground to a similar volume-median flour particle diameter (Level 6 structure). Starch molecular structure (Levels 1 and 2 structures) was little or not affected by the cryogenic-milling process, whereas the degradation of both amylopectin and amylose molecules was clearly observed in the hammer-milled flours as analyzed using size exclusion chromatography (SEC) (Supplementary Data Figure S1). The preferential cleavage of longer branch chains with degree of polymerization (DP) >10,000, such as those of amylose, during the grinding of rice grains, especially by the hammer-milling process, was shown using the method of Vilaplana and Gilbert (2010), which reduces the SEC number molecular size distribution of debranched starch (individual branches, Level 1 structure) to a single parameter. These rice flours were used in the present study to provide variations in starch structures at four different levels in order to achieve the aforementioned objective of the study.

2. Materials and methods

2.1. Materials

Polished long-grain rice grains were purchased from a local grocery store. The starch content of the rice grains was 83% (w/w, dry flour basis) as determined by Total Starch (AA/AMG) assay kit (Megazyme International Ltd., Co. Wicklow, Ireland). The amylose content was 15% (w/w, dry starch basis) as determined from the ratio of the area under the curve (AUC) of amylose branches to the total AUC of both amylose and amylopectin branches in the SEC weight molecular size distribution of enzymatically debranched starch (Supplementary Data Figure S1A). The grains were ground into flour using cryogenic or hammer milling as described by Tran et al. (2011). The cryogenic milling of rice grains was performed using a Freezer/Mill 6870 (SPEX CertiPrep, Metuchen, NJ, USA) at $10\,s^{-1}$ in liquid nitrogen bath in cycles of 5- and 10-min to total cryogenic milling times of 5, 10, 20, 30, and 40 min. The hammer milling of rice grains was performed by passing the rice grains through a hammer mill (Janke & Kunkel, IKA-Labortechnik, Staufen, Germany) with 500-, 1000-, or 1500-μm screen at ambient temperature. The temperature of the rice flour immediately after passing through the hammer mill with 500-μm screen was about 40–45 °C, which should minimize any heat damage by hammer milling on flour/starch structures. The cryogenic- and hammer-milling treatments are summarized in Table 1 along with the structural attributes of the resulting rice flours as determined in the previous study (Tran et al., 2011): volume-median diameter of flour particles (Level 6 starch structure) analyzed using a Mastersizer 2000 with Hydro MU (Malvern Instruments Ltd., Malvern, UK), damage to starch granules (Level 5 starch structure) analyzed using Starch Damage assay kit (Megazyme International Ltd.), average hydrodynamic radius ($\bar{R}_h$) of whole (fully branched) starch molecules (Level 2 starch structure) calculated from the SEC weight molecular size distribution, and slope of the SEC number molecular size distribution of longer (amylose) branches with DP between 5×10^3 and 20×10^3 determined by plotting the SEC number molecular size distribution of debranched starch (Level 1 starch structure) as ln ($Nde(X)/X$) against DP X. Higher slope represents fewer longer branches. The SEC weight molecular size distributions of whole (fully branched) starch and the SEC number molecular size distributions of debranched starch from all rice flour samples are shown in Supplementary Data figure S1B and C, respectively. The starch contents of all rice flour samples did not vary significantly (Tran et al., 2011), implying that the grain composition was not significantly affected by the cryogenic- and hammer-milling processes. Since commercial starch granules and laboratory-isolated starch granules inevitably contain some degree of damage (Dhital et al., 2010a; Hasjim et al., 2009), it is not possible to obtain undamaged starch control for comparison with the samples in the present study.

2.2. Isolation of starch granules from rice flour

Starch granules were isolated from rice flour by laboratory-scale wet milling following the method of Syahariza, Li, and Hasjim (2010). A screen with 53-μm openings was used to filter the flour

Table 1
Grinding treatments of rice grains and starch structures of the resulting rice flours.[a]

Flour sample	Treatment description	Starch structures			
		Level 6: volume-median particle diameter of flour (μm)[a]	Level 5: degree of damaged starch granules (%)[a]	Molecular structures	
				Level 2: average hydrodynamic radius ($\bar{R}_h$, nm)[a]	Level 1: slope of amylose branches ($5000 < DP < 20{,}000$)[a]
CM5C1	1 cycle of 5-min cryogenic milling	149	4.2	19.1	4.61×10^{-4}
CM5C2	2 cycles of 5-min cryogenic milling	115	5.4	21.8	4.66×10^{-4}
CM10C2	2 cycles of 10-min cryogenic milling	34	11.6	21.6	4.61×10^{-4}
CM10C3	3 cycles of 10-min cryogenic milling	32	12.0	19.8	4.44×10^{-4}
CM10C4	4 cycles of 10-min cryogenic milling	30	14.9	23.6	4.45×10^{-4}
HM1500P1	1 pass through hammer mill with 1500-μm screen	564	4.4	–[b]	4.88×10^{-4}
HM1000P1	1 pass through hammer mill with 1000-μm screen	478	5.6	20.9	5.02×10^{-4}
HM500P1	1 pass through hammer mill with 500-μm screen	158	17.0	16.6	5.57×10^{-4}
HM500P2	2 passes through hammer mill with 500-μm screen	56	25.2	15.6	5.42×10^{-4}
HM500P3	3 passes through hammer mill with 500-μm screen	42	26.1	17.4	5.54×10^{-4}

[a] The volume-median particle diameter of flour was analyzed using a Mastersizer 2000 with Hydro MU (Malvern Instruments Ltd., Malvern, UK), the degree of damaged starch granules was analyzed using Starch Damage assay kit (Megazyme International Ltd., Co. Wicklow, Ireland), the $\bar{R}_h$ of whole (fully branched) starch molecules was obtained from SEC weight molecular size distribution, and the slope of amylose branches (DP of between $5000 < \bar{X} < 20,000$) was determined by plotting SEC number molecular size distribution as $\ln(N\mathrm{d}(\bar{X})/\bar{X})$ against DP $\bar{X}$. Adapted from Hasjim et al. (2012) and Tran et al. (2011).
[b] Not included because of incomplete starch extraction/dissolution, underestimating the actual the $\bar{R}_h$ of whole (fully branched) starch molecules.

particles after being milled in sodium bisulfite solution using a domestic blender for 5 min. The flour particles that remained on the screen were returned into the blender for a second milling and filtered through the 53-μm screen. The two fractions of filtrate were combined and the proteins and lipids in the filtrate were removed using 0.1 M NaCl solution (90%) and toluene (10%) until the toluene layer was clear of protein residues, followed by several washings with water and ethanol.

2.3. Gelatinization properties of starch

Starch gelatinization properties were analyzed in triplicate using a differential scanning calorimeter (DSC, DSC 1, Mettler Toledo, Schwerzenbach, Switzerland) following the method of Li, Hasjim, Dhital, Godwin, and Gilbert (2011) with modification as follows. Rice flour or isolated rice starch granules (~3 mg, dry weight basis) was placed in a 40-μL aluminum pan, and water was added to give a sample-to-water weight ratio of 1 to 3. The pan was sealed, and the sample was allowed to equilibrate overnight in a refrigerator at 4 °C. In the DSC, the sample was held at 10 °C for 1 min followed by heating from 10 to 95 °C at a rate of 5 °C/min. Indium was used for calibration, and an empty aluminum pan was used as reference. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy of gelatinization (ΔH) were determined from the endotherm of starch gelatinization using the built-in software (STARe system, Mettler Toledo).

2.4. Pasting properties of flour

Flour pasting properties were analyzed in triplicate using a Rapid Visco Analyser (RVA, RVA model 4, Newport Scientific Pty. Ltd., Warriewood, NSW, Australia) following the method of Li et al. (2011) with modification as follows. Rice flour (2.0 g, dry weight basis) was mixed with distilled water (a total weight of 25 g) in an RVA canister. Two heating profiles were used, which had total heating times of 23 and 30 min. For the 23-min heating profile, the flour suspension was held in the RVA at 50 °C for 1 min, heated from 50 to 95 °C at a rate of 6 °C/min, held at 95 °C for 5 min, cooled from 95 to 50 °C at a rate of 6 °C/min, and held at 50 °C for 2 min. For the 30-min heating profile, the flour suspension was treated the same way as in the 23-min heating profile, except the flour suspension was held at 95 °C for 10 min instead of 5 min and held at 50 °C for 4 min after cooling instead of 2 min. The heating process was accompanied by a constant shear at 960 rpm for the first 10 s followed by a constant shear at 160 rpm until the end of the analysis. Pasting temperature (temperature at where viscosity starts to develop), peak viscosity (maximum viscosity during heating and holding at 95 °C), trough (the minimum viscosity between peak viscosity and final viscosity), breakdown (difference between peak viscosity and trough), final viscosity (maximum viscosity during holding at 50 °C after cooling), and setback (difference between final viscosity and trough) were identified from the RVA viscogram using the Thermocline Version 2.2 software (Newport Scientific).

2.5. Statistical analysis

The mean values of the gelatinization and pasting properties were analyzed by Minitab 16 (Minitab Inc., State College, PA, USA) using analysis of variance (ANOVA). The General Linear Model and Tukey's Pairwise Comparisons with confidence level at 95.0% were used in performing the ANOVA. The correlation coefficients (R) between the (gelatinization and pasting) properties and four different levels of starch structures (Levels 1, 2, 5, and 6 structures) were also analyzed using Minitab 16. The $\bar{R}_h$ of whole (fully branched) starch molecules from the rice flour produced by hammer milling with 1500-μm screen (HM1500P1) was excluded from the correlation test because of its large flour particle size (volume-median particle diameter of 149 μm, Table 1), inhibiting the complete

starch extraction/dissolution for an accurate molecular structure characterization and underestimating the actual $\bar{R}_h$ (Tran et al., 2011).

3. Results and discussion

In a previous study, the same rice flour samples were successfully used to understand the roles of starch structures in the solubility and swelling properties of rice flours (Hasjim, Li, & Dhital, 2012). The results showed that the molecular degradation caused by grinding techniques was not the precondition for increased starch solubility in cold and hot water (at 30 and 90 °C, respectively) with increasing damage to starch granules, as previously suggested (Morrison & Tester, 1994; Stark & Yin, 1986; Yin & Stark, 1988). In the present study, the gelatinization and pasting properties were correlated separately for the first time with four different levels of starch structures in rice flour: volume-median particle diameter of flour, degree of damaged starch granules, $\bar{R}_h$ of whole starch molecules, and slope of amylose branches (Levels 6, 5, 2, and 1 structures, respectively). This was not attainable in the past, but recent developments, including the technique to extract starch from flour without introducing artifacts to the starch structures (Syahariza et al., 2010) and the method to reduce molecular size distributions of starch to single parameters (Vilaplana & Gilbert, 2010), have made this possible.

3.1. Gelatinization properties of starch

Starch gelatinization is the transition of the semi-crystalline structure (Level 3 starch structure) in native starch granules to an amorphous structure (Cooke & Gidley, 1992). Starch gelatinization properties were analyzed both from the rice flour samples and from the starch granules isolated from selected rice flour samples using laboratory-scale wet milling. The comparison between the starch gelatinization properties of the flour samples and those of the isolated starch granule samples shows whether flour particle size (Level 6 starch structure) or starch granular/molecular structures (Levels 1, 2, and 5 structures) are the dominant factor(s) determining starch gelatinization properties.

The T_o of all rice four samples were about 63 °C (Table 2), which were not significantly different despite the various grinding treatments (Table 1). Except for the $\bar{R}_h$ of whole starch molecules in the cryogenically milled rice flours, no significant correlations were observed between the T_o with the volume-median particle diameter of flour, the degree of damaged starch granules, the $\bar{R}_h$ of whole starch molecules, and the slope of amylose branches (Levels 6, 5, 2, and 1 structures, respectively) among all rice flour samples as a whole and among the cryogenically milled or the hammer-milled rice flours separately (Table 3 and Supplementary Data Figure S2). It was reported that T_o was slightly or not significantly affected by the particle sizes of rice flours (Marshall, 1992) and those of the cryogenically milled and hammer-milled sorghum flours (Mahasukhonthachat et al., 2010). Significantly lower T_o, however, were observed among some of the starch granule samples isolated from the rice flours by laboratory-scale wet milling (Table 4 and Fig. 1). Furthermore, the T_o of the rice flour samples were 4–15 °C higher than those of their respective isolated starch granule samples (Tables 2 and 4, respectively), which is likely attributed to the presence of non-starch components in the rice flours, such as protein and cell-wall materials (Ghiasi, Hoseney, & Varriano-Marston, 1983; Marshall, 1992), affecting the heat transfer for starch gelatinization.

The T_o of the isolated starch granule samples from the hammer-milled rice flours were, in general, lower than those of the isolated starch granule samples from the cryogenically milled rice flours, because the starch granules (Level 5 structure) in the

Table 2
Starch gelatinization and flour pasting properties of cryogenically milled rice flours and hammer-milled rice flours.[a]

Flour sample	Starch gelatinization properties				Flour pasting properties					
	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g dry starch)	Pasting temperature (°C)	Peak viscosity (cP)	Trough (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)
CM5C1	63.6 ± 0.3 a	68.9 ± 0.5 b–d	73.9 ± 0.2 de	11.35 ± 0.67 ab	91.6 ± 0.5 b	ND[b]	ND	ND	2333 ± 45 b	ND
CM5C2	63.2 ± 0.1 a	68.4 ± 0.2 c–e	74.2 ± 0.3 d	14.40 ± 0.26 a	90.6 ± 0.1 b	ND	ND	ND	2236 ± 15 b	ND
CM10C2	63.2 ± 0.3 a	67.6 ± 0.5 e	72.3 ± 0.5 ef	7.36 ± 3.54 b	89.9 ± 0.3 b	1182 ± 13 a	997 ± 3 a	184 ± 14 a	1960 ± 5 c	962 ± 7 a
CM10C3	63.4 ± 0.2 a	68.0 ± 0.1 de	72.2 ± 0.2 f	8.07 ± 0.92 b	90.1 ± 0.1 b	1139 ± 31 a	939 ± 22 b	200 ± 15 a	1891 ± 39 cd	952 ± 25 a
CM10C4	62.8 ± 0.1 a	67.9 ± 0.1 de	72.5 ± 0.1 ef	9.60 ± 1.01 ab	90.7 ± 0.8 b	1050 ± 35 b	849 ± 2 c	201 ± 34 a	1810 ± 21 d	961 ± 19 a
HM1500P1	62.7 ± 0.7 a	69.9 ± 0.3 a	82.8 ± 0.1 a	10.79 ± 3.40 ab	94.5 ± 0.6 a	ND	ND	ND	2448 ± 17 a	ND
HM1000P1	63.0 ± 0.4 a	69.7 ± 0.4 ab	80.8 ± 1.4 b	10.67 ± 0.53 ab	91.5 ± 0.3 b	ND	ND	ND	2332 ± 58 b	ND
HM500P1	63.0 ± 0.0 a	68.4 ± 0.3 c–e	74.9 ± 0.8 cd	7.37 ± 1.79 b	90.8 ± 1.0 b	ND	ND	ND	1701 ± 30 e	ND
HM500P2	63.3 ± 0.4 a	69.1 ± 0.4 a–c	76.0 ± 0.2 c	7.42 ± 0.84 b	91.5 ± 1.4 b	ND	ND	ND	1293 ± 57 f	ND
HM500P3	63.1 ± 0.2 a	68.9 ± 0.1 b–d	75.0 ± 0.7 cd	7.07 ± 0.64 b	90.3 ± 0.3 b	921 ± 19 c	822 ± 9 c	99 ± 10 b	1637 ± 24 e	815 ± 15 b

[a] Mean ± standard deviation from triplicate. Values in the same column with different letters are significantly different at $p < 0.05$.
[b] Not detected as there is no defined peak viscosity during heating and holding at 95 °C.

Table 3
Correlation coefficients between (gelatinization and pasting) properties and starch structures in rice flours.[a]

Property	Volume-median particle diameter (Level 6)			Degree of damaged starch granules (Level 5)			Average hydrodynamic radius (Level 2)			Slope of amylose branches (Level 1)		
	All	CM only	HM only	All	CM only	HM only	All	CM only	HM only	All	CM only	HM only
Starch gelatinization												
T_o	−0.483	0.549	−0.795	−0.018	−0.649	0.783	−0.286	−0.992**	−0.577	−0.193	0.288	0.661
T_p	0.832**	0.941*	0.840	−0.204	−0.855	−0.739	−0.409	−0.544	0.742	0.394	0.393	−0.964**
T_c	0.943**	0.934*	0.965**	−0.298	−0.908*	−0.903*	−0.236	−0.226	0.885	0.323	0.721	−0.997**
ΔH	0.382	0.769	0.982**	−0.760*	−0.727	−0.948*	0.515	0.032	0.915	−0.458	0.559	−0.978**
Flour pasting												
Pasting temperature	0.823**	0.812	0.778	−0.382	−0.624	−0.698	−0.316	−0.335	0.230	0.091	0.233	−0.837
Final viscosity	0.671*	0.976**	0.963**	−0.948**	−0.993**	−0.950*	0.597	−0.543	0.971*	−0.516	0.792	−0.875

All, cryogenically milled and hammer-milled flour samples as a whole; CM, cryogenically milled flour samples; HM, hammer-milled flour samples.
[a] Correlation values with * and ** are significant at $p < 0.05$ and 0.01, respectively.

Table 4
Gelatinization properties of starch granules isolated from selected cryogenically milled rice flours and hammer-milled rice flours.[a]

Starch sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g dry starch)
CM5C1 starch	58.5 ± 0.6 ab	63.9 ± 0.3 a	70.2 ± 0.6 a	11.07 ± 2.31 a
CM10C2 starch	58.9 ± 0.3 a	64.4 ± 0.4 a	70.3 ± 0.6 a	12.54 ± 0.88 a
CM10C4 starch	59.1 ± 0.3 a	64.6 ± 0.4 a	70.5 ± 0.7 a	12.54 ± 0.99 a
HM1500P1 starch	57.8 ± 0.8 b	64.2 ± 0.2 a	70.7 ± 0.5 a	13.24 ± 1.06 a
HM500P1 starch	47.8 ± 0.5 c	64.2 ± 0.5 a	69.7 ± 0.4 a	6.36 ± 1.32 b
HM500P3 starch	57.7 ± 0.5 b	64.0 ± 0.3 a	69.8 ± 0.3 a	10.12 ± 1.25 a

[a] Mean ± standard deviation from triplicate. Values in the same column with different letters are significantly different at $p < 0.05$.

hammer-milled rice flours were more severely damaged (Chen et al., 2003; Morrison et al., 1994). The T_o of isolated starch granules reflects the heat stability of starch crystalline structure (Level 3 structure), i.e. length of double helices of amylopectin branches that form the crystalline lamellae (Srichuwong et al., 2010, 2005a), and the damage to starch granules (Level 5 structure) has been reported to be accompanied by the disruption of starch crystalline structure (Level 3 structure) (Chen et al., 2003; Dhital et al., 2011; Morrison et al., 1994).

An additional smaller starch-gelatinization endotherm at lower temperature was observed from the starch granules isolated from the rice flour produced by one pass through the hammer mill with 500-μm screen (HM500P1) overlapping with the main gelatinization endotherm (Table 4 and Fig. 1), which was reproducible in three measurements and was not observed in other isolated starch granule samples, implying that there might be two populations of starch granules in the HM500P1 flour. The damage to starch granules (Level 5 structure) in rice flour is not uniform within a single flour particle (Level 6 structure) as damaged starch granules are mostly, if not all, located at the surface of the flour particle which comes in contact with the grinding force, and the starch granules in the inner part of the flour particle are relatively intact. Damaged starch granules, containing (partially) disrupted crystalline structure, have a lower gelatinization temperature than intact starch granules (Chen et al., 2003; Dhital et al., 2011; Morrison et al., 1994). The additional endotherm was not observed in the starch granules isolated from the rice flour produced by three passes through the hammer mill with the same 500-μm screen (HM500P3) although the starch granules of the HM500P3 flour were more severely damaged than those of the HM500P1 flour (Table 1), suggesting an artifact caused by the laboratory-scale wet-milling process in isolating the starch granules from the rice flour. Damaged starch granules have smaller size than intact starch granules (Dhital et al., 2010a; Hasjim et al., 2009), hence they have slower sedimentation rate (Dhital, Shrestha, & Gidley, 2010b) and are likely removed with the non-starch components during wet-milling process. The results suggest that wet milling might not be an appropriate method to isolate starch granules from milled flour for accurate structure and property characterization.

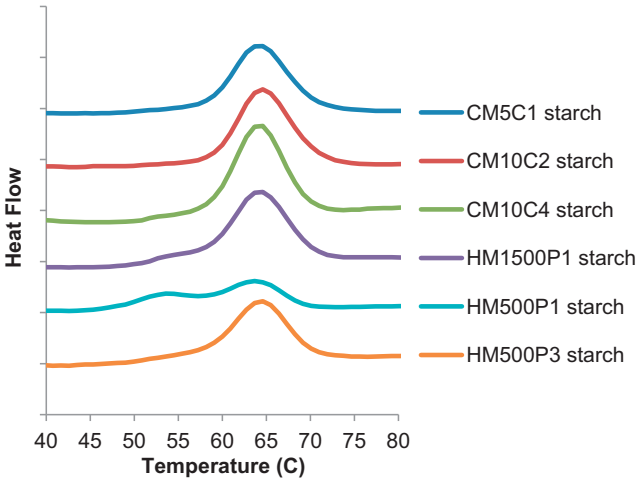

Fig. 1. DSC thermograms of starch granules isolated from selected cryogenically milled rice flours and hammer-milled rice flours.

In contrast to T_o, the T_p and T_c among the rice flour samples (Table 2) were significantly affected by the grinding treatments (Table 1) with greater differences among the hammer-milled rice flours than among the cryogenically milled flours. The ranges of T_p and T_c for the flour samples were 67.6–69.9 °C and 72.2–82.8 °C, respectively. Significant positive correlations were observed between the T_p and the volume-median particle diameter of flour (Level 6 structure) of all rice flour samples as a whole and of only the cryogenically milled rice flour samples and significant negative correlation was observed between the T_p and the slope of amylose branches (Level 1 structure) of only the hammer-milled rice flour samples (Table 3 and Supplementary Data Figure S3). The T_c and the volume-median diameter of flour particles (Level 6 structure) were significantly and positively correlated for all rice flour samples as a whole and for the cryogenically milled and the hammer-milled rice flour samples separately (Table 3 and Supplementary Data Figure S4). Significant negative correlations between the T_c and the degree of damaged starch granules (Level

5 structure) were only observed among the cryogenically milled or the hammer-milled rice flour samples separately, but not among all rice flour samples as a whole. Furthermore, significant negative correlation was observed between the T_c and the slope of amylose branches (Level 1 structure) of only the hammer-milled rice flour samples. There were, however, no significant differences in the T_p and T_c among the isolated starch granule samples (Table 4 and Fig. 1). This indicates that the differences in the T_p and T_c among the rice flour samples (Table 2) were associated with the particle size of the flours (volume-median particle diameter, Level 6 structure), which showed the strongest correlations with the T_p or T_c (Table 3 and Supplementary Data Figures S3 and S4), similar to the observations reported by Marshall (1992). The apparent significant correlations observed at starch branching and granular structures (Levels 1 and 5 structures, respectively) were likely due to the changes at these levels of starch structures occurring with the particle size reduction of rice grains (Level 6 structure), especially by the hammer-milling process (Tran et al., 2011). Similar to T_o, the T_p and T_c of the rice flour samples were 3–6 °C and 2–12 °C, respectively, higher than those of their respective isolated starch granule samples (Tables 2 and 4), which were attributed to the effects of non-starch components in the rice flour on starch gelatinization properties (Ghiasi et al., 1983; Marshall, 1992).

The higher T_p and T_c of the rice flour samples (Table 2), especially those with larger volume-median particle diameter (Level 6 structure) (Table 1), can be attributed to the greater physical barrier for heat transfer to gelatinize the starch granules in the inner part of the flour particles (Karlsson & Eliasson, 2003), resulting in an apparent greater heat stability. Whereas, the similar T_o among all rice flour samples (Table 2) reflect the heat stability of the starch granules near the surface of flour particles that are more accessible to heat. Water diffusion or penetration has also been postulated to alter the starch gelatinization temperature of grains and flour (Marshall, 1992). This was not the case in the present study as the flour particles were equilibrated with excess water overnight before the thermal analysis using DSC, allowing enough time for water diffusion and penetration into the flour particles. The results show that, although gelatinization properties are associated with the crystalline structure of starch granules, the presence of non-starch components in grains or flour can evidently affect starch gelatinization temperature.

Enthalpy change (ΔH) during starch gelatinization is the amount of energy needed to convert the crystalline structure (Level 3 structure) in native starch granules to an amorphous structure, thus it reflects the degree of crystallinity of the starch granules (Cooke & Gidley, 1992; Dhital et al., 2011; Morrison et al., 1994). The ΔH of the rice flour samples ranged from 7.4 to 14.4 and from 7.1 to 10.8 J/g dry starch for the cryogenically milled and the hammer-milled rice flours, respectively (Table 2). There were no significant differences in the ΔH among all rice flour samples, except the ΔH of the rice flour produced by two cycles of 5-min cryogenic milling (CM5C2). Similarly, there were no significant correlations observed between the ΔH and the four different levels of starch structures in the cryogenically milled rice flours (Table 3 and Supplementary Data Figure S5), and there were no significant differences in the ΔH of the isolated starch granule samples from the cryogenically milled rice flours (Table 4 and Fig. 1). Significant correlations, however, were observed between the ΔH and three different levels of starch structures in the hammer-milled rice flours: positively with the volume-median particle diameter of flour, negatively with the degree of damaged starch granules, and negatively with the slope of amylose branches (Levels 6, 5, and 1, respectively) (Table 3 and Supplementary Data Figure S5). The apparent correlations were likely due to the disruption to starch crystalline structure (Level 3 structure), which occurred with the damage to starch granules during hammer milling (Chen et al., 2003; Dhital et al., 2011; Morrison et al., 1994). Furthermore, the starch granules isolated from the HM500P1 flour had significantly lower ΔH than other isolated starch granule samples and showed an additional smaller gelatinization endotherm at lower temperature (Table 4 and Fig. 1), indicating that the hammer-milling process caused a greater disruption to starch crystalline structure (Level 3 structure) than the cryogenic-milling process. Similar to the T_o, the ΔH of the isolated starch granules from the HM500P3 flour was not significantly different from those of the isolated starch granules from the HM1500P1 flour and from the cryogenically milled rice flours, which again implies that the laboratory-scale wet milling used to isolate starch granules from the HM500P3 flour might have removed the severely damaged starch granules along with the non-starch components.

3.2. Pasting properties of flour

RVA measures the changes in the apparent viscosity of a sample during heating and cooling in sufficient water, which are then interpreted as pasting properties. The increase in the apparent viscosity is due to the ability of flour particles to absorb water and to swell, filling up the space in the RVA canister. Although starch gelatinization might be the major factor contributing to the swelling of rice flour particles as amorphous starch can absorb more water than semi-crystalline starch, and the rice flours used in the present study contain 83% starch, DSC and RVA in practice measure completely different quantities, that are thermal transition and apparent viscosity, respectively. Furthermore, on the contrary to starch gelatinization, which is only associated with starch crystalline structure (Level 3 structure), the swelling of flour particles is contributed not only by starch but also by other components in the flour, such as proteins and non-starch polysaccharides, which structures might be altered by the grinding processes. Hence, there is no unique relationship between pasting and starch gelatinization properties of a flour sample and they should be treated as independent groups of properties.

Two RVA heating profiles with total heating times of 23 and 30 min were tested with the HM1500P1 flour and the rice flour produced by hammer milling with 1000-μm screen (HM1000P1), which had the largest particle sizes among all rice flour samples (Table 1). The differences between the two heating profiles are longer holding time at 95 °C (10 vs. 5 min) and longer holding time at 50 °C after cooling (4 vs. 2 min) in the 30-min heating profile compared with the 23-min heating profile. The viscograms from the two heating profiles were similar for the HM1500P1and HM1000P1 flours, except the longer holding time at 95 °C allowed the viscogram to reach a plateau before the viscosity increased during cooling, and the longer holding time at 50 °C after cooling showed a more defined peak of final viscosity (Fig. 2A). Batey and Curtin (2000) also reported that increasing the holding time at 95 °C longer than 4 min caused only small changes in the trough and the final viscosity of wheat-flour viscogram. Therefore, the 30-min heating profile was used to compare the pasting properties of rice flours in the present study.

The viscograms of the cryogenically milled and the hammer-milled rice flours are shown in Fig. 2B and C, respectively. Rice flour samples with volume-median particle diameters ≥56 μm (CM5C1, CM5C2, HM1500P1, HM1000P1, HM500P1, and HM500P2) (Table 1) did not show defined peak viscosity during heating and holding at 95 °C, hence the trough, breakdown, and setback were not able to be determined from these flours. Furthermore, except for the rice flour produced by hammer milling with 500-μm screen for two passes (HM500P2), rice flour sample with larger volume-median particle diameter, in general, had higher viscosity during cooling from 95 to 50 °C and higher final viscosity during holding at 50 °C after cooling. Cellulase treatment on the

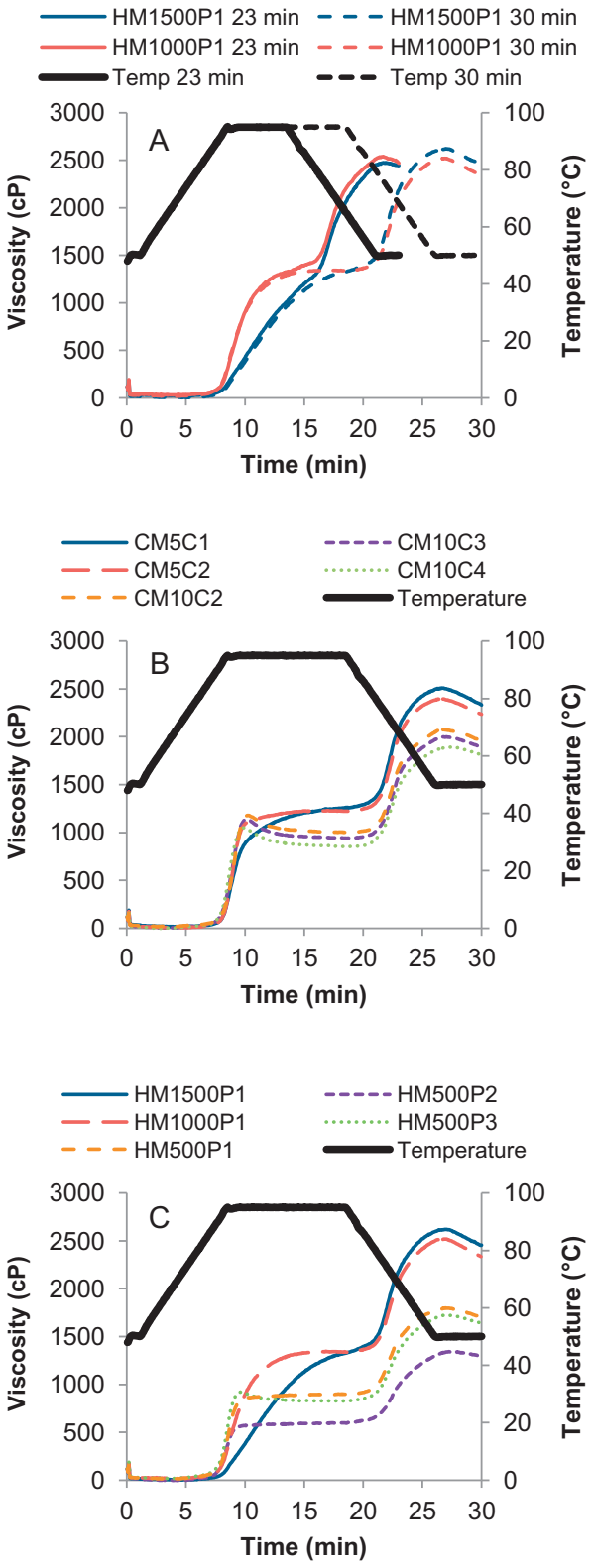

Fig. 2. (A) RVA viscograms of shorter (23 min, solid line) and longer (30 min, dashed line) pasting profiles. RVA viscograms of (B) cryogenically milled rice flours and (C) hammer-milled rice flours.

flour from aged rice grains was reported to produce a more defined peak viscosity during holding at 95 °C than the flour without cellulase treatment (Zhou, Robards, Helliwell, & Blanchard, 2003). Furthermore, chemical and enzymatic degradations of protein in rice flour were reported to lower overall pasting viscosity (peak viscosity, trough, and final viscosity), whereas the same treatments did not show any effects on the pasting properties of isolated starch (Fitzgerald, Martin, Ward, Park, & Shead, 2003; Hamaker & Griffin, 1990). Hence, the lack of defined peak viscosity during heating and holding at 95 °C and the higher viscosity during cooling and holding at 50 °C after cooling of rice flour with larger particle size could be attributed to the greater amount of native protein and/or cell-wall structure, stabilizing the starch paste and preventing the rupture of swollen starch granules by shear during heating in the RVA. The native protein and cell-wall structures might be disrupted when the grains were subjected to greater grinding force or longer grinding time to produce flour with smaller particle size, weakening the effects of protein and cell-wall structures on flour pasting properties. The HM500P3 flour, however, had an RVA viscogram similar to that of the HM500P1 flour, which overall pasting viscosity was higher than that of the HM500P2 flour (Fig. 2C). Although protein can stabilize starch paste and increase the overall pasting viscosity, protein matrix can restrict the swelling of starch granules during heating (Zhou et al., 2003). Passing the rice flour through the hammer mill with 500-μm screen for the third time might have caused a greater disruption of protein structure, allowing the starch granules to swell to a greater extent during heating. Further study is needed to obtain a better understanding in the changes of the protein and cell-wall structures of rice grains caused by grinding.

The pasting properties of all rice flour samples are summarized in Table 2. There are significant differences in the peak viscosity, trough, breakdown, final viscosity, and setback among some rice flour samples, indicating that the flour pasting properties were affected by the milling treatments (Table 1). On the other hand, only the HM1500P1 flour showed a significantly higher pasting temperature than other rice flour samples, which were not significantly different among themselves. Although the pasting temperature of the rice flour samples might seem to follow the same trend as their T_o (Table 2), which is little or no effect with the milling treatments, the two properties measure completely different quantities. The pasting temperature is the temperature at where viscosity starts to develop during heating in the RVA, whereas the T_o is the onset temperature of the conversion of starch semi-crystalline structure to amorphous structure. Furthermore, there were substantial temperature differences between the two properties, ranging from 27 to 31 °C. Since peak viscosity was not detected in six out of ten rice flour samples, only pasting temperature and final viscosity were used for correlation analyses with the starch structures.

There were no significant correlations observed between the pasting temperature and the four different levels of starch structures in rice flour, except for a significant positive correlation between the pasting temperature and the volume-median particle diameter of rice flour when all flour samples were analyzed as a whole (Table 3 and Supplementary Data Figure S6). Furthermore, for the rice flour samples that did not show defined peak viscosity during heating and holding at 95 °C, the holding time required to reach plateau at 95 °C is in the following order: HM1500P1 > HM1000P1 > CM5C1 > CM5C2 > HM500P1 ≈ HM500P2 (Fig. 2B and C), which seems to be related to the flour particle size (Table 1). Rice flour samples with larger particle sizes have greater physical barrier to heat transfer as indicated by the higher T_c of these flour samples (Table 2) and, similarly, greater barrier to water diffusion or penetration than those with smaller particle size (Marshall, 1992). Hence, the rice flour sample with larger particle size has slower hydration rate and requires a longer time

to develop viscosity during heating, resulting in higher pasting temperature, and to reach a plateau viscosity at 95 °C.

Significant positive correlations were observed between the final viscosity and the volume-median particle diameter of rice flour (Level 6 structure), which were stronger when the cryogenically milled and the hammer-milled rice flours were analyzed separately than as a whole (R = 0.98, 0.96, and 0.67, respectively) (Table 3 and Supplementary Data Figure S7), suggesting that different structures of non-starch components contributing to the final viscosity of the cryogenically milled and hammer-milled rice flours, possibly due to different degradation mechanisms on the protein and/or cell-wall structure by the two grinding processes. Significant negative correlations were also observed between the final viscosity and the degree of damaged starch granules (Level 5 structure), which were similar whether the cryogenically milled and the hammer-milled rice flours were analyzed separately or as a whole (all R values were between −0.95 and −1.00) (Table 3 and Supplementary Data Figure S7), indicating that damage to starch granules is the most dominant factor influencing the final viscosity of rice flour. Isolated starch granules with higher degree of damage were reported to have lower peak viscosity, trough, and final viscosity (Chen et al., 2003; Dhital et al., 2010a), and the authors related this with the increase in the molecular degradation of starch (Levels 1 and 2 structures), occurring with the damage to starch granules. Larger starch molecules have shown to produce paste with greater viscosity (Shibanuma, Takeda, & Hizukuri, 1996). Although the results from the present study agree with this argument as a significant positive correlation was observed between the final viscosity and the $\bar{R}_h$ of whole starch molecules (Level 2 structure) in the hammer-milled rice flours, it was not observed when all rice flour samples were analyzed as a whole or when the cryogenically milled rice flours were analyzed separately (Table 3 and Supplementary Data Figure S7). Hence, the inability of damaged starch granules to retain water, possibly due to their smaller granule size (or volume) compared with intact starch granules, when they are heated at 95 °C (Tester, 1997) is a more plausible explanation for the relationship between final viscosity and damaged starch granules in the present study than the molecular degradation of starch caused by the grinding processes. The results also imply that starch granules (Level 5 structure) might still exist after heating, most likely in the swollen form, and contribute to the final viscosity of rice flour.

4. Conclusions

The present work is the first study to relate gelatinization and pasting properties with four different levels of starch structures in rice flour: volume-median particle diameter of flour, degree of damaged starch granules, $\bar{R}_h$ of whole starch molecules, and slope of amylose branches (Levels 6, 5, 2, and 1 structures, respectively). The particle size of flour (Level 6 structure) is the dominant factor determining the gelatinization temperature of rice flour, where it may act as a physical barrier for heat transfer. This is confirmed by the different trends observed for the gelatinization temperature of isolated starch granules, in which the factor of flour particle size is nonexistent. The significant correlations between ΔH and starch structures might be related to the degradation of starch crystalline structure (Level 3 structure) caused by the milling processes. Rice flour (Level 6 structure) with volume-median particle diameter ≥56 μm did not show a defined peak viscosity in the RVA viscogram during heating and holding at 95 °C, possibly due to the presence of native protein and/or cell-wall structure stabilizing the swollen starch granules against the rupture caused by shear during heating. In addition, rice flour with larger particle size also had higher pasting temperature and required a longer holding time at 95 °C to reach a plateau viscosity, implying that large flour particle has a greater physical barrier for both heat transfer and water diffusion. The final viscosity, however, is strongly affected by the damage to starch granules (Level 5 structure) and to lesser extents by flour particle size (Level 6 structure) and molecular size of whole starch (Level 2 structure), confirming that the differences in the final viscosity are not due to molecular degradation as previously suggested (Chen et al., 2003; Dhital et al., 2010a), but might be contributed by granular structure, most likely in swollen form.

The results from the present study suggest that comparison of grain flours from different botanical sources should take into account not only molecular structure of the components in the grains but also the structural changes caused by grinding process, such as flour particle size and damage to starch granules. The mechanistic understanding in the relationships between starch structures and starch properties during heating or cooking concluded from the present study can be used to improve the manufacture and the selection criteria of rice flour with desirable starch gelatinization and pasting properties.

Supplementary data

The SEC weight molecular size distributions of whole (fully branched) starch (Level 2 structure) and debranched starch (Level 1 structure) as well as the SEC number molecular size distributions of debranched starch (Level 1 structure) are shown in Supplementary Data Figure S1. The plots for the correlations listed in Table 3 are shown in the Supplementary Data Figures S2–S7.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.09.023.

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