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Morphology and physicochemical properties of mechanically activated rice starch

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ABSTRACT

The morphology and physicochemical properties of mechanically activated rice starch (MARS) isolated from three rice cultivars were investigated by scanning electron microscopy, X-ray diffractometry, gel permeation chromatography and Rapid Visco Analysis. The shape of rice starch granule changed from native polyhedron to anomalistic state during mechanical activation. It was suggested that the hydration of starch and moisture was an important factor for granules agglomeration which appeared more easily with higher moisture content. Mechanical force resulted in destroying of starch crystal structure which disappeared basically after activated for 10 h. As the mechanical activation time prolonged, the amylopectin and amylose of rice starch were both decomposed gradually, thus causing the increase of cold-water solubility and reducing power and the decrease of BV. Meanwhile, the pasting temperature and the viscosity of MARS decreased, including peak viscosity, final viscosity, breakdown viscosity and setback viscosity. The crystalline and molecular structure of rice starch with 6.02% moisture content were more easily destroyed by mechanical force than those with 1.05% and 11.05% moisture content, which resulted in higher cold-water solubility and reducing power, lower BV, pasting temperature, peak viscosity, final viscosity, breakdown viscosity and setback viscosity.

1. Introduction

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and annual renewal (Yu, Dean, & Li, 2006). Native starch has been used in food systems to a limited degree, and this restriction of use is imposed by its properties. Chemical or physical modification has been used to expand the usefulness of starches (Wurzburg & Szymanski, 1970). Since the regulation of chemically modified starch for food, especially baby food is quite strict and there are environmental concerns on wastewater (Devi, Fibrianto, Torley, & Bhandari, 2009), more and more physical modifications appear, such as ball milling, heat-moisture treatment, extrusion, pulsed electric fields treatment and sonication (Chung, Liu, & Hoover, 2009; Han, Zeng, Zhang, & Yu, 2009; Jackson, Gomez, Waniska, & Rooney, 1990; Morrison & Tester, 1994; Zuo, Knoerzer, Mawson, Kentish, & Ashokkumar, 2009).

Mechanical activation as a physical modification can be utilized to damage and micronize starch. Microgranular starches produced a creamy mouth feel, a desirable attribute in low-fat and fat-free food formulations (Malinski, Daniel, Zhang, & Whistler, 2003). They were also utilized as bonding agents (Zhao & Whistler, 1994), plastic sheets (Wilhelm, Themeier, & Lindhauer, 1998) and a carrier material in cosmetics (Whistler, 1995). In the previous studies, mechanical force of ball milling could gradually change the molecular structure, crystal structure, cold-water solubility, morphological and thermal characteristics of starches (Chen, Lii, & Lu, 2003; Devi et al., 2009; Huang, Lu, Li, & Tong, 2007; Jane, Shen, Wang, & Maningat, 1992; Morrison & Tester, 1994; Sanguanpong et al., 2003; Tamaki, Hisamatsu, Teranishi, Adachi, & Yamada, 1998). Morphological structure is one of the important properties of mechanically activated starch. Some investigators reported that the granules retained integrity or reduced slightly granule size when the starch was ball-milled (Jane et al., 1992; Sanguanpong et al., 2003). In contrast, Tamaki et al. (1998) suggested that the granules lost their original flatness and smoothness and became rough during ball milling. Moreover, Huang et al. (2007) found that the granules agglomerated with a definite shift to larger granule size. The differences were probably due to the different ball milling conditions, sources of starch and moistures of starch before ball milling treatment.

It has been reported that ball milling treatment could change some physicochemical properties of rice starch (Chen et al., 2003; Devi et al., 2009). However, there are few reports on the information which related to the changes of molecular weight, reducing power and blue value (BV) of rice starch during ball milling.

The objectives of this study were to discover the effects of starch moisture content before mechanical activation on the granules agglomeration and physicochemical properties of rice starch when the mechanical activation time prolonged.

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2. Materials and methods

2.1. Materials and reagents

Three rice cultivars were used (Indica rice from Changlong Cereals Industry Co., Ltd. Wuhan, China; Japonica rice from Hunan Jinjian Cereals Industry Co., Ltd. Changde, China; Glutinous rice from Hongan County, Hubei Province, China). All the reagents were of analytical grade.

2.2. Methods

2.2.1. Isolation and purification of rice starch

Isolation and purification of rice starch were performed according to the method of Yamamoto, Sawada, and Onogaki (1973) with some modifications. The main steps were as follows:

Ten kilograms of rice was soaked in 0.3% NaOH solution for 24 h (the weight ratio of 0.3% NaOH solution to rice was 3:1.). The mixture was wet-milled by a miller and filtered through a nylon mesh sieve (150 μm). Then the slurry stood at room temperature for 12 h. After the supernatant was discarded, the slurry was added 0.3% NaOH solution to maintain a constant total weight (40 kg), and the sequence was repeated four times. The slurry was then adjusted to pH 7.0 using 0.5 M HCl solution, and washed with water five times. After the supernatant was discarded, the slurry was centrifuged at 2000g for 10 min. The precipitation was collected and air-dried at 40 °C for 12 h as the native starch (0 h). The native starch was milled and passed through 150 μm screen. Chemical compositions of the isolated rice starches were determined according to American Association of Cereal Chemists standard methods (AACC International, 2003) and shown in Table 1.

The moisture contents (wet basis) of native starches were adjusted to 11%, 6% at 55 °C, and then adjusted to 1% at 105 °C. The exact moisture contents were measured at 135 °C for 2 h (AACC International, 2003). The native starches with various moisture contents were obtained as follows: Indica rice starch (IRS) 11.05%, IRS 6.02% and IRS 1.05%, Japonica rice starch (JRS) 6.16%, JRS 0.95%, Glutinous rice starch (GRS) 6.11% and GRS 1.20%.

2.2.2. Preparation of mechanically activated of rice starch (MARS)

Thirty grams starch was activated by ball-mill (Rolling-type, QM-1SP2, China Nanjing University Instrument Plant) with 4 jars (agate, $\Phi 10 \times 9$ cm) and balls (agate, $\Phi 10$ mm, 70 g, and $\Phi 6$ mm, 30 g for each of the 4 jars). Milling was performed at 450 r/min and room temperature. The samples were collected at 1, 5, 10, 25, 50 and 100 h. The temperatures of all MARS were tested below 35 °C after activation.

2.2.3. Scanning electron microscopy (SEM) and average granule size

The samples were fixed onto metallic sample holders using silver conductive adhesive, sputtered with a layer of platinum and observed by SEM (JSM-6390LV, NTC, Japan). The diameters of at least 200 granules were measured, whose average value was calculated as the average granule size.

Table 1
Chemical compositions of rice starch samples (dry basis, %).[a]

	Total starch	Moisture content	Crude protein	Crude fat	Ash
IRS[b]	86.35 ± 0.98	12.51 ± 0.06	0.56 ± 0.02	ND[c]	0.48 ± 0.04
JRS[d]	87.45 ± 0.44	11.84 ± 0.02	0.58 ± 0.03	ND	0.72 ± 0.08
GRS[e]	87.63 ± 0.89	11.26 ± 0.10	0.62 ± 0.02	ND	0.38 ± 0.04

[a] Each value is the mean ± SD over three measurements.
[b] IRS, Indica rice starch.
[c] ND, Not detected.
[d] JRS, Japonica rice starch.
[e] GRS, Glutinous rice starch.

2.2.4. X-ray diffraction

The X-ray diffraction patterns of MARS were measured using a JDX-10P3A diffractometer (Japan) under the following conditions: Cu Kα radiation, 30 kV, 20 mA and scanning regions of the diffraction angle 2θ 0–55°, scanning velocity 0.02°/s.

$$\text{Crystallinity } (\%) = \text{Ic}/(\text{Ia} + \text{Ic}) \times 100$$

where Ia = amorphous area on the X-ray diffractogram, Ic = crystallized area on the diffractogram (Cheetham & Tao, 1998; Fujita, Yamamoto, Sugimoto, Morita, & Yamamori, 1998).

2.2.5. Gel permeation chromatography (GPC) and visible absorption spectrum (VAS)

The molecular weight distributions of MARS were analysed according to Lu's (1996) method with some modifications. The main steps were as follows:

One hundred milligrams of MARS was dispersed in 5 mL of 0.25 M KOH in a boiling water bath for 10 min. After cooled to room temperature, the mixture was adjusted to pH 7.0 with 0.1 M HCl solution and made up to 50 mL with distilled water. The dispersion was filtered through a microfiltration membrane (0.25 μm pore size). An aliquot of the filtrate (4 mL) was fractionated by ascending chromatography on a Sepharose CL-2B 300 (Sigma, USA) column (1.7×75 cm) operating with a peristaltic pump (Shanghai Huxi Analysis Instrument Factory Co., Ltd., China) at a flow rate of 16 mL/h with 0.05 M NaCl solution containing 0.02% sodium azide as the eluent. Fractions of 4 mL each were collected. The aliquots (1 mL) of the fractions were used for determination of carbohydrate by using a phenol–sulfuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1951).

VAS was checked as follows: 2 mL aliquot of peak value fractions of amylopectin or amylose (2 mL distilled water as control) were added 0.2 mL 0.1 M HCl solution and 0.5 mL aqueous I_2–KI solution (1 mL iodine solution containing 2 mg I_2 and 20 mg KI). The solution was then made up to 10 mL with distilled water, vortexed for 10 s and stood at room temperature for 20 min to react. Finally, the reaction mixture was scanned from 480 to 680 nm using a UV–vis spectrophotometer (UV-1700 PharmaSpec, Shimadzu Corporation, Japan).

2.2.6. Determination of cold-water solubility (25°C)

The cold-water solubility of sample was performed at 25 °C for 20 min according to Huang et al. (2007).

2.2.7. Determination of reducing power

Twenty-five milliliter distilled water was added to 0.50 g starch (dry basis). The starch dispersion was stirred in boiling water bath for 20 min, and then centrifuged at 2000g for 10 min. The supernatant was used to analyze reducing sugar of MARS by 3,5-dinitrosalicylic acid (DNS) colorimetry (Miller, 1959) with glucose as a standard.

$$\text{Reducing power } (\%) = \text{reducing sugar/starch} \times 100$$

2.2.8. Determination of BV

BV of MARS was measured according to the method of Zhao, Xiong, Qiu, and Xu (2007).

2.2.9. Pasting properties from Rapid Visco Analysis (RVA)

Paste viscosity of the MARS was determined using Rapid Visco Analyzer (Model 3D, Newport Scientific, Warriewood, Australia) with the method of Song, He, Ruan, and Chen (2006). The viscosity parameters were calculated according to the methods of the literatures (Lai, 2001; Limpisut & Jindal, 2002).

Pasting temperature (PT): temperature indicating an initial increase in viscosity.
Peak viscosity (PV): maximum viscosity during the heating cycle.
Final viscosity (FV): final viscosity at 50 °C.
Breakdown viscosity (BD): PV minus final viscosity at 95 °C.
Setback viscosity (SB): FV minus final viscosity at 95 °C.

2.3. Statistical analysis

The experiment data were analysed with Microsoft Excel 2003 (Microsoft Corporation, USA), Microcal Origin 6.0 (Microca Corporation, USA) and Statistical Analysis Syastem Software 8.1 (SAS Institute, Inc., USA).

3. Results and discussion

3.1. Morphology of MARS

SEM photographs of MARS samples treated by ball milling for different times are shown in Fig. 1, and their average granule sizes in Table 2.

Table 2
Average granules size of MARS[a] (μm).

Mechanical activation time (h)	IRS[b] 1.05%	JRS[c] 0.95%	GRS[d] 1.20%	IRS 6.02%	IRS 11.05%
0	4.44	4.16	5.00	4.48	4.48
5	3.06	2.58	2.71	4.48	4.49
10	2.90	2.19	2.16	3.32	5.11
50	2.14	1.73	1.81	3.94	7.08
100	2.46	1.92	2.18	6.39	11.84

[a] MARS, mechanically activated rice starch.
[b] IRS, Indica rice starch.
[c] JRS, Japonica rice starch.
[d] GRS, Glutinous rice starch.

According to the SEM photographs, the structure of a native rice starch granule was a polyhedron with pronounced edges (Fig. 1a0, b0, c0, d0 and e0). The surface was smooth and had no cracks. When subjected to mechanical activation, the starch granules appeared to be damaged (Fig. 1a1–a4, b1–b4 and c1–c4) because of the pressure and friction action of the balls which rolled and fractured the surface of the starch granules.

With low moisture contents (IRS 1.05%, JRS 0.95% and GRS 1.20%), the starch granule sizes became small (IRS from 4.44 to 2.14 μm; JRS from 4.16 to 1.73 μm; GRS from 5.00 to 1.81 μm) when the mechanical activation time prolonged from 0 to 50 h. However, the starch granule sizes became a little larger when

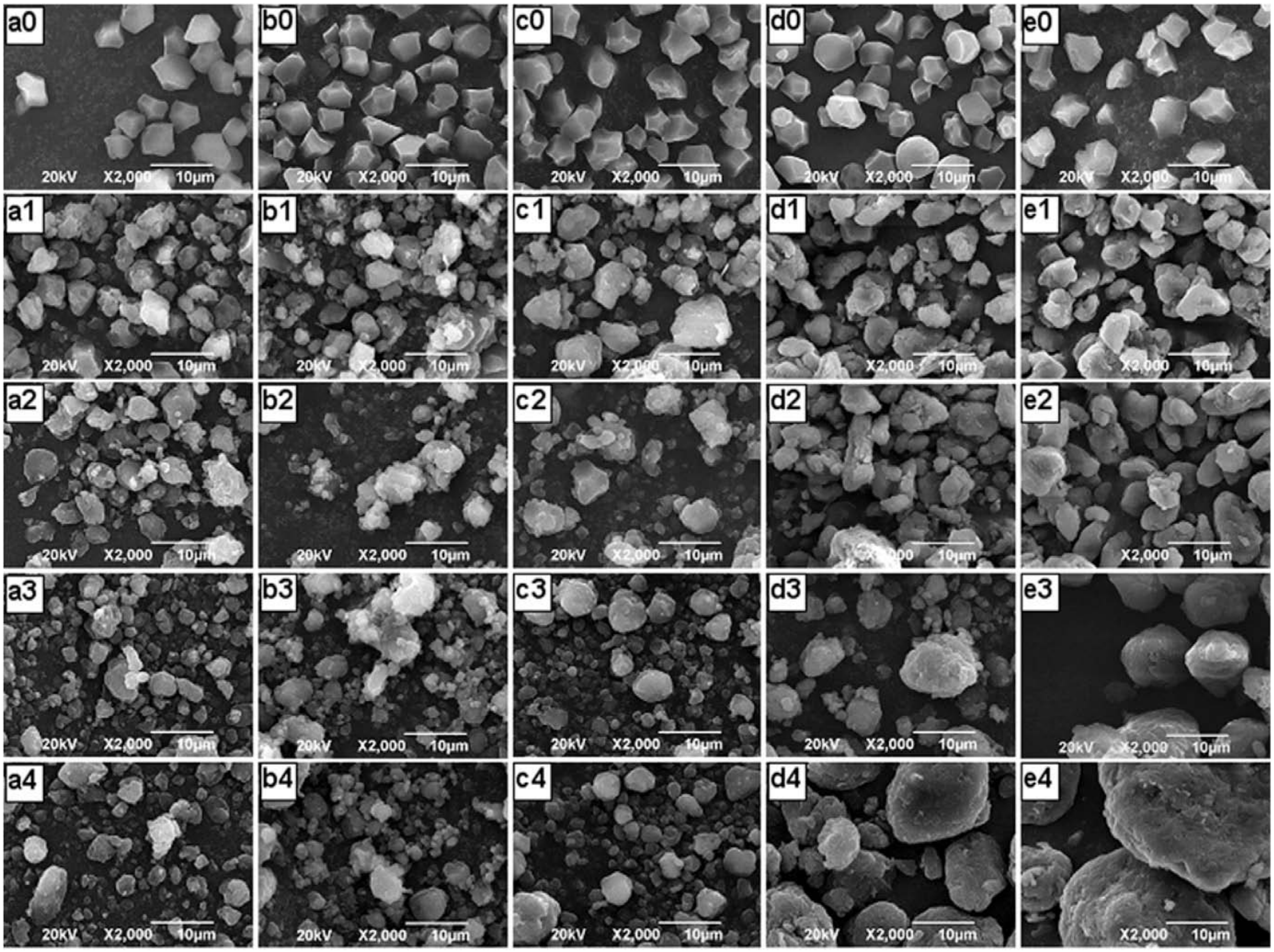

Fig. 1. Scanning electron microscopy (SEM) photographs of mechanically activated rice starch (MARS): (a) Indica rice starch (IRS) 1.05%; (b) Japonica rice starch (JRS) 0.95%; (c) Glutinous rice starch (GRS) 1.20%; (d) IRS 6.02%; (e) IRS 11.05%; 0–4 mechanical activation time 0, 5, 10, 50 and 100 h.

increasing mechanical activation time from 50 to 100 h. When treated by mechanical force with high moisture content (IRS 11.05%), the starch granules appeared to be swollen and agglomerated to be a larger granule sizes gradually from 5 to 100 h (from 4.49 to 11.84 μm) (Table 2). This was similar to the results of Tamaki et al. (1998) and Huang et al. (2007). Tamaki et al. (1998) found that the surface of maize starch granules lost its flatness and smoothness, and became rough as the ball milling time prolonged. Almost all of the granules retained their initial sizes and whole figures up to milling time of 80 h. Huang et al. (2007) discovered that when subjected to mechanical activation, the cassava starch granules appeared to be fractured and agglomerated into larger more amorphous granules. However, both the investigators did not consider the effect of moisture content on the granules agglomeration.

According to the average granule sizes of IRS 1.05%, IRS 6.02% and IRS 11.05%, the starch granule sizes became larger when the moisture content of starch increased at a same mechanical activation time (Table 2). The hydration of water and starch could be an important factor for granules agglomeration besides van der Waal's force and electrostatic force.

3.2. Crystalline structure of MARS

The native starch (MARS 0 h) showed a typical A-type pattern, which supported the crystalline property of native rice starch, with strong reflection peaks at 2θ about 15° and 23° and an unresolved doublet at 17°, 18° 2θ (Cheetham & Tao, 1998; Fiedorowicz & Para, 2006).

The crystalline structure of starch mainly consists of amylopectin side chain clusters that are formed by hydrogen bonds and arranged parallel with the structure of the double helixes (Fiedorowicz & Para, 2006; Gallant, Bouchet, & Baldwin, 1997; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). It is possible that some amylose also form a crystalline structure because of its double helixes structure (Vandeputte et al., 2003). Mechanical force could result in destroying of the starch granule structure, relaxation of the crystalline clusters and appearance of distortion and defects in the crystals. As demonstrated in Fig. 2, the diffraction peaks weakened gradually, in other words, the proportion of crystalline states decreased; the non-crystalline states increased. After 10 h, the crystal structures disappeared basically and the crystallinities did not decrease significantly ($P > 0.05$) (Table 3).

The IRS 6.02% had a higher decreasing rate of crystallinity than IRS 11.05% and IRS 1.05% as the mechanical activation time prolonged. The result suggested that the crystalline structure of rice starch was easily destroyed when the moisture content was 6.02%.

3.3. Molecular weight distributions and VAS of MARS

GPC was utilized to determine the molecular weight distributions of MARS. As shown in Fig. 3, all MARS contained three main fractions which were a larger molecular weight fraction F1 (tube numbers 10–16), an intermediate molecular weight fraction F2 (tube numbers 17–25) and a smaller molecular weight fraction F3 (tube numbers 26–40), respectively. F1 was mostly amylopectin with a larger molecular weight, while F3 was mostly amylose with a smaller molecular weight and fewer branches (Lu, Chen, & Lii, 1996; Madhusudhan, Gowda, & Taranathan, 1996; Mohan, Gopal, Malleshi, & Tharanathan, 2005). The properties of F2, whose molecular structure and molecular weight were between F1 and F3 (Madhusudhan et al., 1996), were seldom reported.

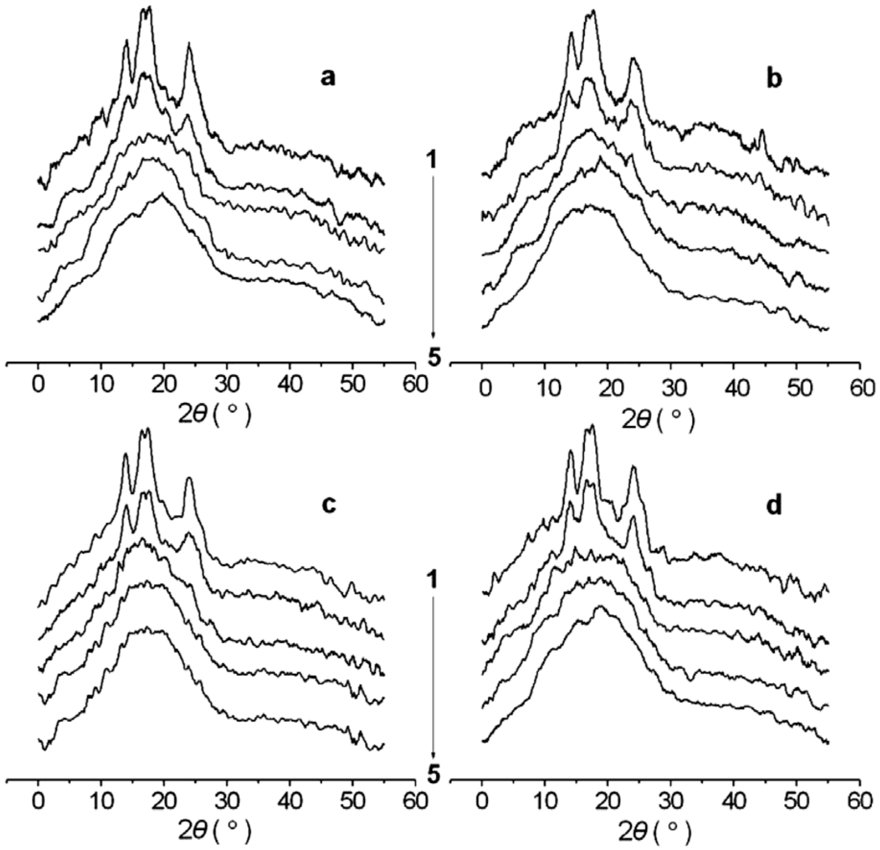

Fig. 2. X-ray diffraction patterns of mechanically activated rice starch (MARS): (a) Indica rice starch (IRS) 6.02%; (b) Glutinous rice starch (GRS) 6.11%; (c) IRS 1.05%; (d) IRS 11.05%; 1–5 mechanical activation time 0, 1, 5, 10 and 25 h.

Table 3
Crystallinity of mechanically activated IRS[A] and GRS[B] (%).

	0 h	1 h	5 h	10 h	25 h
IRS 6.02%	17.18 ± 0.24[a]	9.44 ± 0.25[b]	2.20 ± 0.17[c]	1.27 ± 0.13[d]	1.05 ± 0.17[d]
GRS 6.11%	14.57 ± 0.28[a]	9.07 ± 0.07[b]	2.84 ± 0.18[c]	1.41 ± 0.07[d]	1.06 ± 0.06[d]
IRS 1.05%	15.74 ± 0.02[a]	11.59 ± 0.44[b]	4.97 ± 0.24[c]	2.21 ± 0.25[d]	1.93 ± 0.09[d]
IRS 11.05%	17.17 ± 0.17[a]	9.47 ± 0.29[b]	3.50 ± 0.05[c]	2.14 ± 0.08[d]	2.14 ± 0.10[d]

[A] IRS, Indica rice starch.
[B] GRS, Glutinous rice starch.
[a–d] Each value is the mean ± SD over three measurements. Different lowercase letters in the same row indicate significant difference ($P \leqslant 0.05$) using Duncan's test.

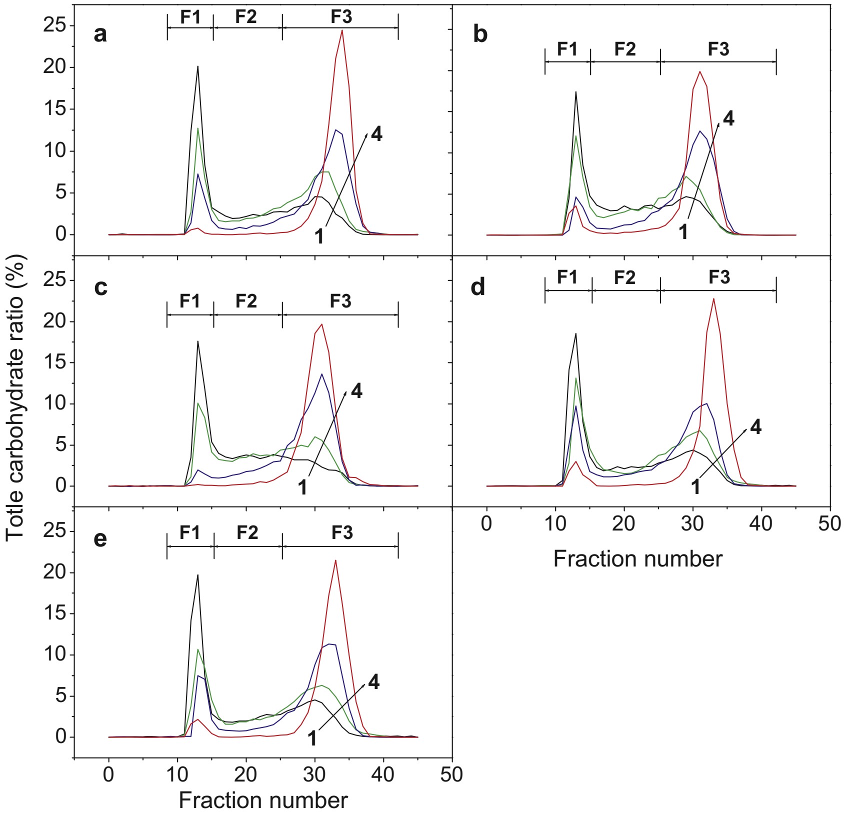

Fig. 3. Molecular weight distribution of mechanically activated rice starch (MARS): (a) Indica rice starch (IRS) 6.02%; (b) Japonica rice starch (JRS) 6.16%; (c) Glutinous rice starch (GRS) 6.11%; (d) IRS1.05%; (e) IRS 11.05%; F1 larger molecular weight fraction; F2 intermediate molecular weight fraction; F3 smaller molecular weight fraction; 1–4 mechanical activation time 0, 10, 50 and 100 h.

As demonstrated in Fig. 3, the peak value fraction numbers of F1 with various mechanical activation times remained the same at 13, and the peak value fraction numbers of F3 became larger (IRS 6.02% from 30 to 34, JRS 6.16% from 29 to 31, GRS 6.11% from 30 to 31, IRS 1.05% from 30 to 33, IRS 11.05% from 30 to 33). When the mechanical activation time increased, F1 and the area percent became smaller whereas F3 and the area percent became larger, gradually (Fig. 3 and Table 4).

The results indicated that when the mechanical activation time prolonged, amylopectin was decomposed and converted to a smaller molecular weight fraction, which was similar to the results of Morrison and Tester (1994). Tamaki et al. (1998) found that when the ball milling time was prolonged, both amylopectin and amylose of cassava starch were possibly decomposed. However, it was uncertain in the present study whether the amylose was decomposed. In order to explore if the amylose was also decomposed, the fractions of peak value numbers of F1 and F3 (F3 of GRS 6.11% 0 h had no peak value point, so the fraction of number 31 was used) were used to react with iodine and determine VAS whose maximum absorption wavelengths (λ_{max}) are shown in Table 5.

It can be seen from Table 5 that λ_{max} of F1–I_2 of native and MARS were basically the same. However λ_{max} of F3–I_2 became smaller when the mechanical activation time was 50 h. When the mechanical activation time was 100 h, λ_{max} of F3 was smaller than 550 nm, while the range of λ_{max} of native amylose was from 575 to 630 nm (Cornell & Rix, 2006; Edwards et al., 2002; Zeeman et al., 1998). It could be concluded that the native amylose of rice starch was also decomposed gradually with prolonging mechanical activation time.

Interestingly, the area percent of F3 of the native GRS 6.11% (0 h) was 21.85% (Table 4), but the λ_{max} was 523 nm. According to the above analysis, the native GRS molecule of F3 was amylopectin with small molecular weight instead of amylose.

For the effect of moisture content on molecular weight distribution, the area percent of F1 of IRS 6.02% was the smallest, followed by those of IRS 11.05% and IRS 1.05% at the same mechanical activation time (except 0 h), while the area percent of F3 followed the reverse rule (Table 4). The result suggested that the starch molecule was easily decomposed by mechanical force when the moisture content of starch was 6.02%, which was similar to the effect of moisture content on crystalline structure. However, there was no obvious effect on the λ_{max} of F1 and F3 (Table 5).

3.4. Cold-water solubility, reducing power and BV of MARS

Fig. 4a shows the effect of mechanical activation on the cold-water solubility of MARS. The data indicated that the longer the mechanical activation time, the higher the cold-water solubility. As revealed in Fig. 4a, the cold-water solubilities of the native IRS 6.02%, JRS 6.16%, GRS 6.11%, IRS 1.05% and IRS 11.05% were 0.54%, 0.56%, 0.33%, 0.57% and 0.58%, respectively. However, the cold-water solubilities of the starches activated for 100 h were 91.00%, 77.95%, 94.34%, 74.12% and 78.92%, respectively. Among the three rice cultivars, GRS 6.11% had the highest increasing rate of cold-water solubility, whereas JRS 6.16% had the smallest one. The observed increase in cold-water solubility of starch with increased duration of activation time was consistent with the model that mechanical agitation was capable of degrading the crystalline regions (Huang et al., 2007) and decomposing the molecule of the starch and allowing the molecule of starch dissolving into cold-water. With three levels of moisture content, IRS 6.02% had the smallest crystallinity and area percent of F1 and the largest area percent of F3 at the same mechanical activation time (except 0 h), thus causing the highest cold-water solubility.

It can be seen from Fig. 4b that the reducing power of MARS increased linearly (R^2 of IRS 6.02%, JRS 6.16%, GRS 6.11%, IRS 1.05% and IRS 11.05% were 0.994, 0.998, 0.995, 0.997 and 0.997, respectively.) when the mechanical activation time increased from 0 to100 h. One starch molecule has one reducing end group (semi-acetal hydroxyl) which can react with DNS. During mechanical activation, the starch molecule was decomposed continuously and the reducing end groups were produced continuously, which resulted in the increase of reducing power.

BV can be used to reflect the interaction of starch and iodine, which is one of the most useful and characteristic reactions of polysaccharide. The blue color of the stain is due to the amylose component of starch. The other component, amylopectin, gives a red–purple color which is much less intense than the amylose stain (Bailey & Whelan, 1961). The native GRS 6.11% (0 h) had a smaller BV than IRS 6.02% and JRS 6.16% (Fig. 4c) due to the lack of amylose. During mechanical activation, the starch molecules were gradually decomposed and weakened the capacity to stain with iodine, which resulted in the linear decrease of BV (R^2 of IRS 6.02%, JRS 6.16%, GRS 6.11%, IRS 1.05% and IRS 11.05% were 0.997, 0.982, 0.823, 0.993 and 0.998, respectively. R^2 of GRS 6.11% was 0.969 when the mechanical activation time increased from 0 to 50 h).

From Fig. 4b and c, the straight-line slope of reducing power increase of IRS 1.05%, IRS 6.02% and IRS 11.05% were 0.0246, 0.0283 and 0.0194, respectively, while the straight-line slope of BV decrease of IRS 1.05%, IRS 6.02% and IRS 11.05% were −0.0031, −0.0038 and −0.0030, respectively. These data suggested that IRS 6.02% had higher increasing rate of reducing power and decreasing rate of BV than IRS 1.05% and IRS 11.05%. This result agreed well with the effect of moisture content on molecular weight distributions. However, IRS 1.05% had larger increasing rate of reducing power and decreasing rate of BV than IRS 11.05%, which was different from the effects of moisture content on the other physicochemical properties possibly due to the different molecular structures when starch was mechanically activated with different moisture contents.

3.5. Pasting properties of MARS

The RVA viscographs and parameters of mechanically activated IRS are shown in Fig. 5 and Table 6, respectively. When the mechanical activation time increased, PT, PV, FV, BD and SB decreased, which was similar to the results of Chen et al. (2003) and Devi et al. (2009).

Table 4
Area percent of main fractions of MARS[a] (%).

Mechanical activation time (h)	IRS[b] 6.02%		JRS[c] 6.16%		GRS[d] 6.11%		IRS 1.05%		IRS 11.05%	
	F1[e]	F3[f]	F1	F3	F1	F3	F1	F3	F1	F3
0	47.51	31.94	38.89	31.7	42.35	21.85	47.12	31.95	47.44	31.98
10	27.37	52.58	30.76	42.15	27.32	35.50	32.41	47.92	30.48	50.11
50	11.09	82.23	11.06	74.85	6.13	70.68	22.01	64.89	18.35	71.37
100	1.81	97.16	8.2	87.93	0.75	93.51	7.13	91.69	5.74	93.24

[a] MARS, mechanically activated rice starch.
[b] IRS, Indica rice starch.
[c] JRS, Japonica rice starch.
[d] GRS, Glutinous rice starch.
[e] F1, larger molecular weight fraction.
[f] F3, smaller molecular weight fraction.

Table 5
λ_{max}[a] of fraction–iodine complex.

Mechanical activation time (h)	λ_{max} of F1 (nm)					λ_{max} of F3 (nm)				
	IRS[b] 6.02%	JRS[c] 6.16%	GRS[d] 6.11%	IRS 1.05%	IRS 11.05%	IRS 6.02%	JRS 6.16%	GRS 6.11%	IRS 1.05%	IRS 11.05%
0	568	573	532	572	569	600	604	523	605	602
5	562	571	537	574	564	598	602	524	600	599
10	569	579	538	569	572	599	596	516	601	601
50	572	581	540	573	571	576	578	506	582	575
100	–	584	–	574	573	546	522	501	549	552

[a] λ_{max}, maximum absorption wavelengths.
[b] IRS, Indica rice starch.
[c] JRS, Japonica rice starch.
[d] GRS, Glutinous rice starch.

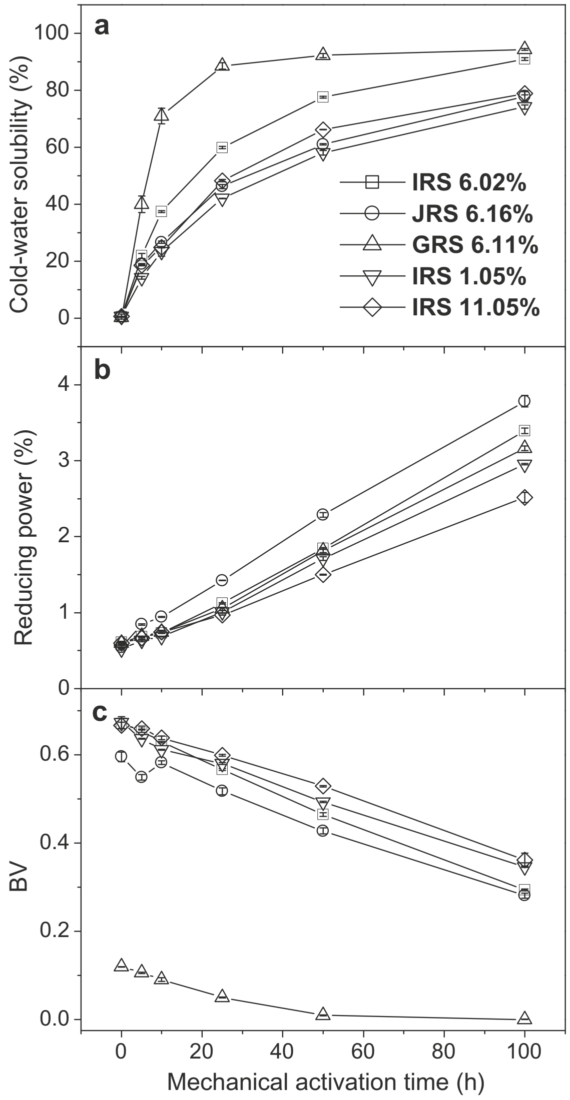

Fig. 4. Cold-water solubility, reducing power and BV (blue value) of mechanically activated rice starch (MARS): (a) cold-water solubility; (b) reducing power; (c) BV (blue value); IRS, Indica rice starch; JRS, Japonica rice starch; GRS, Glutinous rice starch. Values represented are the means (±SD) of three determinations.

Mechanical activation can convert crystal structures to amorphous ones which absorb water easily, even at a low temperature. When activated for 10, 25, 50 and 100 h, the MARS could be disrupted in water at a temperature (PT) below 50 °C, which was lower than that of native starch (78.8 °C).

As the mechanical activation time prolonged, the damage of starch granules was more noticeable. The drop of PV was due to the decrease of the number of swollen but still intact starch granules (Copeland, Blazek, Salman, & Tang, 2009). During mechanical activation, the molecules were decomposed to smaller ones which can be dispersed into water and intermolecular interactions were smaller than those of the native starch, which caused the decrease of FV and SB.

When mechanically activated for 5 h, the IRS 6.02% had the smallest PT, PV, FV, BD and SB, followed by IRS 11.05% and IRS 1.05% (Table 6), which was in accord with the effect of moisture content on crystallinity.

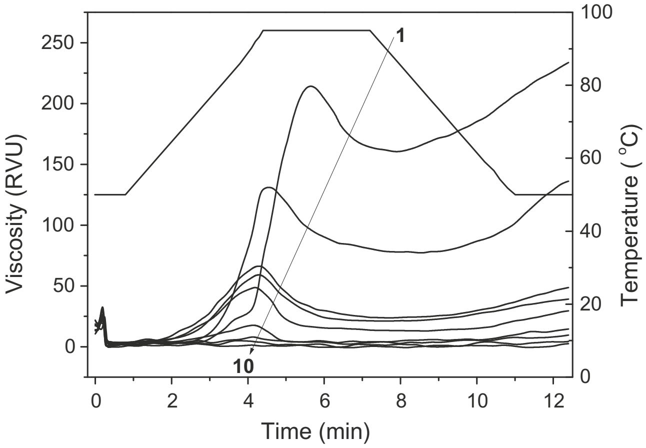

Fig. 5. RVA curves of mechanically activated Indica rice starch (MAIRS): 1 temperature; 2 MAIRS 6.02% 0 h; 3 MAIRS 6.02% 1 h; 4 MAIRS 1.05% 5 h; 5 MAIRS 11.05% 5 h; 6–10 MAIRS 6.02% 5, 10, 25, 50 and 100 h.

Table 6
RVA[a] parameters of mechanically activated IRS.[b]

Samples	PT[c] (°C)	PV[d] (RVU)	FV[e] (RVU)	BD[f] (RVU)	SB[g] (RVU)
IRS 6.02% 0 h	78.8	215.5	233.8	51.5	69.8
IRS 6.02% 1 h	71.6	131.6	136.1	51.0	56.3
IRS 6.02% 5 h	66.8	49.2	29.5	35.6	15.9
IRS 6.02% 10 h	⩽50	17.8	14.6	13.6	10.3
IRS 6.02% 25 h	⩽50	8.3	9.5	4.9	6.2
IRS 6.02% 50 h	⩽50	5.0	4.3	4.7	3.9
IRS 6.02% 100 h	⩽50	3.5	2.4	3.1	2.0
IRS 1.05% 5 h	69.2	66.3	48.6	42.5	24.8
IRS 11.05% 5 h	68.1	59.2	39.2	37.8	17.8

[a] RVA, Rapid Visco Analysis.
[b] IRS, Indica rice starch.
[c] PT, pasting temperature.
[d] PV, peak viscosity.
[e] FV, final viscosity.
[f] BD, breakdown viscosity.
[g] SB, setback viscosity.

The effects of moisture content on the physicochemical properties of MARS indicated that the starch with 6.02% moisture content was more easily mechanically activated than those with 1.05% and 11.05% moisture content. Moisture content may affect the mechanical properties of starch granules. Too high or too low moisture content would make negative effect on mechanical activation of starch. This required further study.

4. Conclusions

As the mechanical activation time prolonged, rice starch granule shape and the average granule size were changed. The moisture content of rice starch had serious effect on the agglomeration of MARS granules. Mechanical force resulted in destroying of starch crystal structure and decomposing of the amylopectin and amylose of rice starch, thus causing the increase of the cold-water solubility and reducing power and the decrease of BV. Meanwhile, the PT, PV, FV, BD and SB of MARS decreased when the mechanical activation time prolonged. It was suggested that the starch with 6.02% moisture content was more easily mechanically activated than those with 1.05% and 11.05% moisture content.

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