Carbohydrate Polymers 114 (2014) 133–140

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

The effect of moisture content on physicochemical properties of extruded waxy and non-waxy rice flour

Ornpicha Jongsutjarittam, Sanguansri Charoenrein*

Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

ARTICLE INFO

Article history:
Received 20 April 2014
Received in revised form 29 July 2014
Accepted 29 July 2014
Available online 13 August 2014

Keywords:
Extrusion
Water feed rate
Waxy rice flour
Rice flour
Physicochemical properties

ABSTRACT

The properties of waxy rice flour (WRF) and non-waxy rice flour (RF) were modified using an extrusion process with different feeding material moisture contents. WRF was more affected by the thermomechanical stress from extrusion; consequently, it had a lower glass transition temperature but higher water solubility index (WSI) indicating higher molecular degradation than extruded RF. The lower moisture content of the feeding flour caused more severe flour damage (coarser surface of the extruded flour) and lowered relative crystallinity compared to higher moisture content processing. Moreover, low moisture content processing led to complete gelatinization, whereas, partial gelatinization occurred in the higher moisture content extrusion. Consequently, the extruded flours had a lower peak viscosity and gelatinization enthalpy but a higher water absorption index and WSI than native flour. In conclusion, the rice flour type and the moisture content of the extrusion feeding flour affected the physicochemical properties of the extruded flour.

1. Introduction

Rice (*Oryza* sp.) is one of the staple foods consumed worldwide, especially in Asia. The composition of rice granules varies widely depending on the variety. Non-waxy rice has 15–27% amylose, while waxy varieties have almost 100% amylopectin (Guy, 1994) resulting in different properties, such as a higher gelatinization temperature and higher retrogradation of rice flour than for waxy rice flour, and also different functional properties. Similar to other types of flour, the use of native rice flour in foods is limited by its physical and chemical properties. Physical modification not involving any chemical reagents or genetic modification could improve the properties of native starch/flour including its processing, food texture and food stability and achieve maximum overall performance in the process and product (Manson, 2009).

Extrusion is a versatile process that is a highly adaptable, cost effective and energy efficient technology having been applied in the food industry for more than 50 years (Harper, 1989). The extrusion parameters, screw configuration, barrel temperature profile and moisture content, have an effect on the processability and product quality. For starch-based materials, the combination of temperature, moisture and mechanical shear force in the extrusion process causes structural transformations, such as granular disruption, loss of crystalline structure and polymer degradation (Colonna, Tayeb, & Mercier, 1989). Researchers have considered using extrusion to modify the properties of starch and flour, in corn starch (Blanche & Sun, 2004; El-dash, Gonzales, & Ciol, 1983), banana starch (Soto, Escobedo, Sánchez, Rivera, & Pérez, 2007) and barley four (Gill, Vasanthan, Ooraikul, & Rossnagel, 2002). Sompong, Ehn, Berghofer, and Schoenlechner (2011) found that the amylose content of rice flour was correlated with the water absorption index and final viscosity of pregelatinized rice flour produced by extrusion cooking. Guha and Ali (2002) studied the molecular degradation of high, intermediate and waxy amylose rice starches and reported that the degradation of the high molecular weight fraction of rice starch resulted from extrusion cooking and was extended with increasing severity of the extrusion process. The maximum molecular degradation was observed in waxy rice starch.

The glass transition temperature (T_g) defines the transition from a brittle, metastable, amorphous supercooled solid to a rubbery, unstable, amorphous liquid (Kaletunc & Breslauer, 1993). The relationship between the T_g and molecular weight is well described for amorphous and partially crystalline linear homopolymers (Billmeyer, 1984). For a starch polymer, a reduction in the T_g is attributed to molecular fragmentation (Kaletunc & Breslauer, 1993) which could result from the extrusion process.

Many studies have worked on the influence of extrusion on the properties of starch/flour and some have focused on using a response surface methodology to create mathematical models of the relationship between the extrusion parameters and the

* Corresponding author. Tel.: +66 2 562 5025; fax: +66 2 562 5021.
E-mail addresses: fagisscr@ku.ac.th, charoen1234@yahoo.com (S. Charoenrein).

http://dx.doi.org/10.1016/j.carbpol.2014.07.074
0144-8617/

Table 1
Moisture content of waxy rice flour (WRF) and rice flour (RF) with different water feed rates in extrusion process.

Water feed rate (l/h)	Moisture content (%)	
	WRF	RF
Native	12.55	11.88
0.5	20.50	19.89
0.6	21.92	21.32
0.7	23.29	22.70
0.8	24.61	24.03
0.9	25.89	25.32
1.0	27.13	26.57

properties of modified starch/flour. However, information on the change in physicochemical properties, such as the granular structure, pasting and gelatinization properties of starch/flour is still limited. Moreover, most researchers studied the combination effect of the screw speed, temperature and moisture content in extrusion, and did not focus on the effect of each extrusion parameters on the changes in properties of the extruded starch/flour. The amount of water in the extrusion is one of the important parameters that controls the extrusion process because it has an influence on mixing, viscosity and the retention time of the mass in the extruder barrel (Martínez-Bustos, Aguilar-Palazuelos, & Galicia-García, 2012). Therefore, it is of interest to specifically study the influence of the water content in the extrusion process on the physicochemical modification of starch/flour. Furthermore, only Kaletunc and Breslauer (1993) has reported on the T_g of extruded flour in relation to the moisture content in the extrusion process and apart from the crystalline structure, they did not study the changes in other physicochemical properties of extruded corn flour. Therefore, the current work aimed to study the effect of different moisture contents in the feeding material for extrusion on the physicochemical properties including disruption of the granular structure, loss of starch crystallinity, the pasting and gelatinization properties and the water absorption and water solubility of waxy rice flour and rice flour. Moreover, the effect of the moisture content in the extrusion process on the T_g value of extruded rice flour was also investigated.

2. Materials and methods

2.1. Materials

Waxy rice flour (WRF) and rice flour (RF) with moisture content of 12.55 and 11.88%, respectively, (AACC, 2000) were purchased from Cho Heng Rice Vermicelli Factory Co., Ltd. (Nakhon Pathom, Thailand). $Mg(NO_3)_2$ was purchased from Lobachemie, India.

2.2. Extrusion process

Extrusion was performed in a co-rotating twin screw extruder (EV25-A120, Clextral, France). The extruder barrel was segmented into 6 zones with the controlled temperature profile as follows: 30–30–45–45–60–75 °C. The feed rate of flour and the screw speed were set at a constant 5 kg/h and 350 rpm, respectively. The water feed rate was varied from 0.5 to 1.0 l/h which resulted in different moisture contents of the feeding material as shown in Table 1. A single circular die with 3.2 mm diameter was used. The extruded products were cut into about 1 cm lengths before drying in a hot air oven (ULE500, Memmert, Germany) at 40 °C for 24 h. The dried extruded products were ground using a blender (Turbora TRK-01, Napat Inter Ltd., Thailand) and passed through a 100-mesh sieve screen.

2.3. Characteristics of native and extruded WRF and RF

2.3.1. Microstructure

For sample dehydration, the native and extruded WRF and RF were dried in hot air oven at 40 °C for 3 d. After that, they were fixed on a stub and coated with gold. The samples were observed using scanning electron microscopy (SEM; JSM-5600LV, JEOL, Japan) with the magnifications and accelerating voltages as shown on the SEM images.

2.3.2. Crystallinity

The flour samples were equilibrated for 3 d in a desiccator containing saturated K_2SO_4 solution in order to prepare flour samples containing 20% H_2O (wet basis) according to the method of Phothiset and Charoenrein (2007). The crystallinity of native and extruded WRF and RF was determined by X-ray diffractometry (JDX-3530, JEOL, Japan) with Cu-$K\alpha$ radiation (wavelength = 1.5406 Å) and a Ni filter. The scanning diffraction angle (2θ) ranged from 5 to 40° and the X-ray generator was operated at 45 kV and 45 mA. The relative crystallinity (%) of the samples was calculated according to the method of Cheetam and Tao (1998).

2.3.3. Water absorption index (WAI) and water solubility index (WSI)

The WAI and WSI of native and extruded samples were measured according to the method of Anderson, Conway, Pfeifer, and Griffin (1969). The samples (2 g dry basis) were dispersed in water at 30 °C for 30 min with gentle stirring every 5 min. Then, they were separated using a centrifuge (Z206A, Hermle, Germany) at 3000 × g for 15 min. The supernatant was placed into an aluminum can and dried in the hot air oven at 90 °C for 6 h. The WAI and WSI were determined as follows:

$$\mathrm{WAI}\,(\mathrm{g/g}) = \frac{\text{weight of wet sediment}}{\text{dry weight of sample}}$$

$$\mathrm{WSI}(\%) = \frac{\text{weight of dry solid in supernatant}}{\text{dry weight of sample}} \times 100$$

2.3.4. Glass transition temperature

Each extruded flour sample (6 mg on a dry basis) was weighed and placed in an aluminum pan and equilibrated for 24 h to a relative humidity of 52.9% at 25 °C using saturated $Mg(NO_3)_2$. After that, the pan was immediately sealed and accurately weighed before analysis with a differential scanning calorimeter (DSC; Pyris-1, Perkin Elmer, USA) using nitrogen as the purge gas. The pans were cooled from 25 °C to 5 °C, held at this temperature for 1 min and then heated to 170 °C at a rate of 10 °C/min. Then, they were cooled to 5 °C and re-heated to 170 °C at the same rate. No shift in the heat capacity could be observed in the second scan; therefore, the T_g values were determined from the onset of the heat capacity change over the glass transition. All measurements were performed in triplicate.

2.3.5. Pasting properties

Suspensions of native and extruded flour were prepared at 8% (w/w) in distilled water. The pasting properties of each suspension were measured using a rapid visco analyzer (RVA; RVA3D, Newport Scientific Instrument and Engineering, Australia). The paste was held at 50 °C for 1 min before heating to 95 °C at a constant rate of 12 °C/min, and then it was held at 95 °C for 2.5 min. After that, it was cooled to 50 °C at the same constant rate and held at 50 °C for 2 min. All measurements were performed in triplicate.

2.3.6. Gelatinization properties

Each sample was weighed to provide 6 mg (dry basis) into a stainless steel pan, and then distilled water was added to obtain 70% moisture content. After that, the pan was hermetically sealed and kept at the room temperature (25 ± 2 °C) for 24 h. The gelatinization properties of the samples were analyzed using the DSC. The samples were placed and held isothermally at 25 °C for 1 min in the DSC before heating from 25 °C to 130 °C at a rate of 10 °C/min. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were calculated. The data were reported as the average of triplicate measurements.

2.4. Experimental design and statistical analysis

The properties of the native and extruded WRF and RF were analyzed using analysis of variance followed by Duncan's test ($p \leq 0.05$) using the SPSS program (SPSS 17.0, SPSS Inc., USA). Each experiment was repeated twice.

3. Results and discussion

3.1. Characteristic of extruded products

The appearance of the extruded products of rice flour could be affected by the amylose and amylopectin content of the flour and the moisture of feeding materials which can be adjusted by the water feed rate in the extrusion process. Table 1 shows that the extrusion with the lowest water feed rate (0.5 l/h) resulted in the lowest moisture content in the feeding flours (20.50% for WRF and 19.89% for RF), and the extruded WRF products expanded and then collapsed immediately after emerging from the die (Fig. 1a), whereas extruded RF did not show any obvious collapse (Fig. 1g). The expansion and collapse of products were reduced when a higher moisture content in the feeding materials was used (Fig. 1b–f and h–l) which agreed with the results of Singh, Sekhon, & Singh (2007) who reported extrusion with a higher water feed level decreased the expansion of the extruded product. In the current study, the extrusion process with a lower moisture content in the feeding materials resulted in dry and hard extruded products with a lower moisture content (Table 2); however, sticky and soft extruded flour with a higher moisture content was produced using an extrusion process with a higher moisture content. At the same moisture content of feeding materials (as clearly seen at a water feed rate 0.7 l/h, Fig. 1c and i), the expansion of extruded products

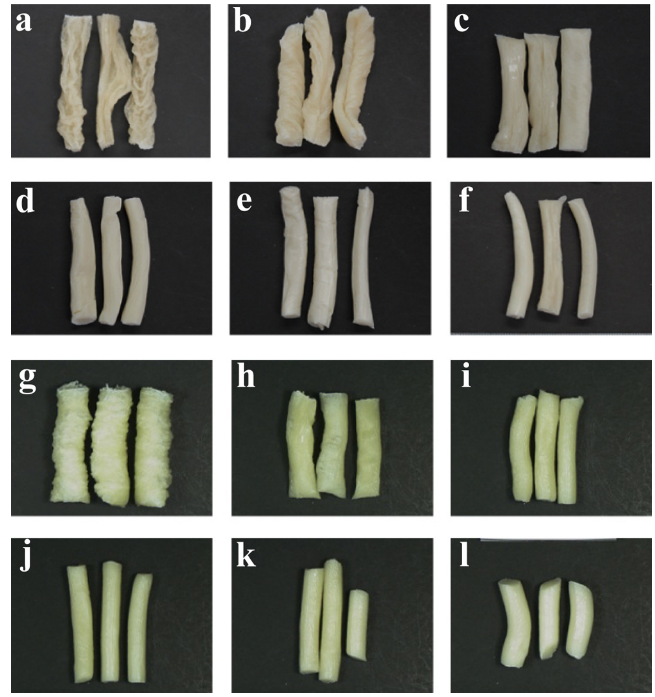

Fig. 1. Products of waxy rice flour ((a)–(f)) and rice flour ((g)–(l)) modified by extrusion process with water feed rate at 0.5 l/h ((a) and (g)), 0.6 l/h ((b) and (h)), 0.7 l/h ((c) and (I)), 0.8 l/h ((d) and (j)), 0.9 l/h ((e) and (k)) and 1.0 l/h ((f) and (l)).

was lower in the extruded RF than for the extruded WRF because of the higher amylose content of the RF compared to that of the WRF. The linear amylose chains were difficult to pull apart during expansion because they aligned themselves in the shear field of extrusion (Martínez-Bustos et al., 2012) leading to lower expansion of the extruded RF; however, amylopectin starches were not as hard as amylose starches which also favored expansion (Valle, Colonna, & Patria, 1996).

3.2. Microstructure of native and extruded WRF and RF

SEM micrographs showed that the starch granules of the native WRF and RF were polygonal (Figs. 2(a and f) and 3(a and f)) but the starch granules were bound together and appeared as large particles as a result of extrusion (Fig. 2b–e and g–j). After the product emerged from the extrusion die, a sudden disequilibrium between

Table 2
Moisture content and characteristics of native and extruded waxy rice flour (WRF) and rice flour (RF).

Flour	Water feed rate (l/h)	Moisture content (%) of extruded product	WAI (g/g)	WSI (%)	Gelatinization properties			
					T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g dry flour)
WRF	Native	12.55 ± 0.59^{a}	2.16 ± 0.15^{d}	0.69 ± 0.02^{a}	62.3 ± 0.93^{a}	69.7 ± 1.62^{a}	77.1 ± 3.64^{a}	8.9 ± 3.67^{b}
	0.5	20.08 ± 0.05^{b}	0.55 ± 0.03^{a}	82.45 ± 0.65^{g}	n.d.	n.d.	n.d.	n.d.
	0.6	22.15 ± 0.84^{c}	1.00 ± 0.04^{b}	73.00 ± 1.96^{f}	66.1 ± 0.03^{b}	72.1 ± 0.47^{b}	76.8 ± 2.21^{a}	0.2 ± 0.12^{a}
	0.7	22.90 ± 0.58^{c}	1.85 ± 0.07^{c}	59.83 ± 0.62^{e}	65.8 ± 0.97^{b}	72.0 ± 0.35^{b}	77.3 ± 0.75^{a}	0.7 ± 0.14^{a}
	0.8	24.13 ± 0.25^{cd}	3.04 ± 0.06^{f}	39.04 ± 0.62^{d}	66.5 ± 0.13^{b}	72.5 ± 0.12^{b}	77.8 ± 0.03^{a}	1.1 ± 0.08^{a}
	0.9	25.37 ± 1.24^{d}	3.07 ± 0.08^{f}	25.94 ± 0.21^{c}	66.2 ± 0.73^{b}	72.0 ± 0.35^{b}	77.6 ± 0.20^{a}	1.6 ± 0.29^{a}
	1.0	29.37 ± 1.44^{e}	2.72 ± 0.01^{e}	12.25 ± 0.06^{b}	65.3 ± 0.07^{b}	71.6 ± 0.12^{b}	77.1 ± 0.36^{a}	2.5 ± 0.05^{a}
RF	Native	11.88 ± 0.68^{a}	2.05 ± 0.07^{a}	0.34 ± 0.01^{a}	76.1 ± 0.07^{a}	79.3 ± 0.10^{a}	83.3 ± 0.57^{a}	6.9 ± 0.10^{b}
	0.5	16.89 ± 0.57^{b}	6.01 ± 0.12^{b}	25.90 ± 0.23^{g}	n.d.	n.d.	n.d.	n.d.
	0.6	18.67 ± 0.31^{c}	8.78 ± 0.06^{f}	9.32 ± 0.10^{f}	n.d.	n.d.	n.d.	n.d.
	0.7	20.89 ± 0.45^{d}	8.17 ± 0.04^{e}	6.70 ± 0.05^{e}	n.d.	n.d.	n.d.	n.d.
	0.8	22.59 ± 0.04^{e}	7.47 ± 0.04^{d}	4.92 ± 0.02^{d}	78.2 ± 0.18^{c}	81.1 ± 0.47^{b}	84.0 ± 0.58^{a}	0.1 ± 0.02^{a}
	0.9	23.89 ± 0.37^{f}	6.87 ± 0.05^{c}	3.85 ± 0.03^{c}	77.2 ± 0.68^{b}	80.6 ± 0.35^{b}	84.0 ± 0.79^{a}	0.2 ± 0.10^{a}
	1.0	25.59 ± 0.49^{g}	6.03 ± 0.03^{b}	2.84 ± 0.02^{b}	75.4 ± 0.06^{a}	80.2 ± 0.23^{b}	84.8 ± 0.08^{a}	0.3 ± 0.02^{a}

Data are mean ± standard deviation. WAI = water absorption ability, WSI = water solubility index. $^{a-g}$: Means with different superscripts in the same column for each rice flour are significantly ($p \leq 0.05$) different. n.d. = not detectable. T_o = onset temperature, T_p = peak temperature, T_c = conclusion temperature, ΔH_{gel} = enthalpy of gelatinization.

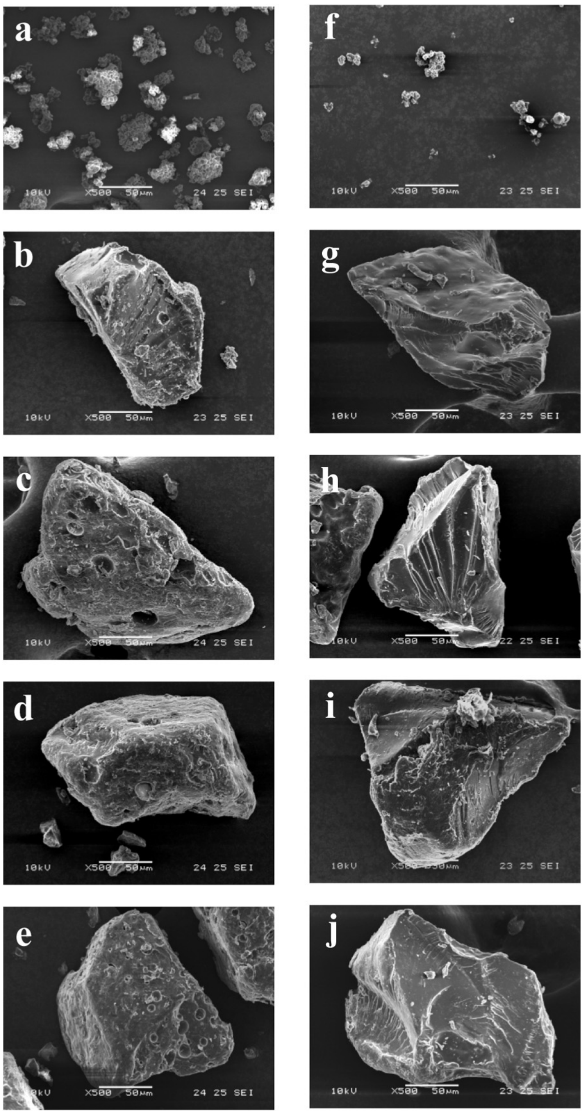

Fig. 2. Scanning electron micrographs (500×) of native waxy rice flour (a) and rice flour (f). Waxy rice flour ((b)–(e)) and rice flour ((g)–(j)) were modified by extrusion process with water feed rate at 0.5 l/h ((b) and (g)), 0.6 l/h ((c) and (h)), 0.7 l/h ((d) and (i)), and 1.0 l/h ((e) and (j)).

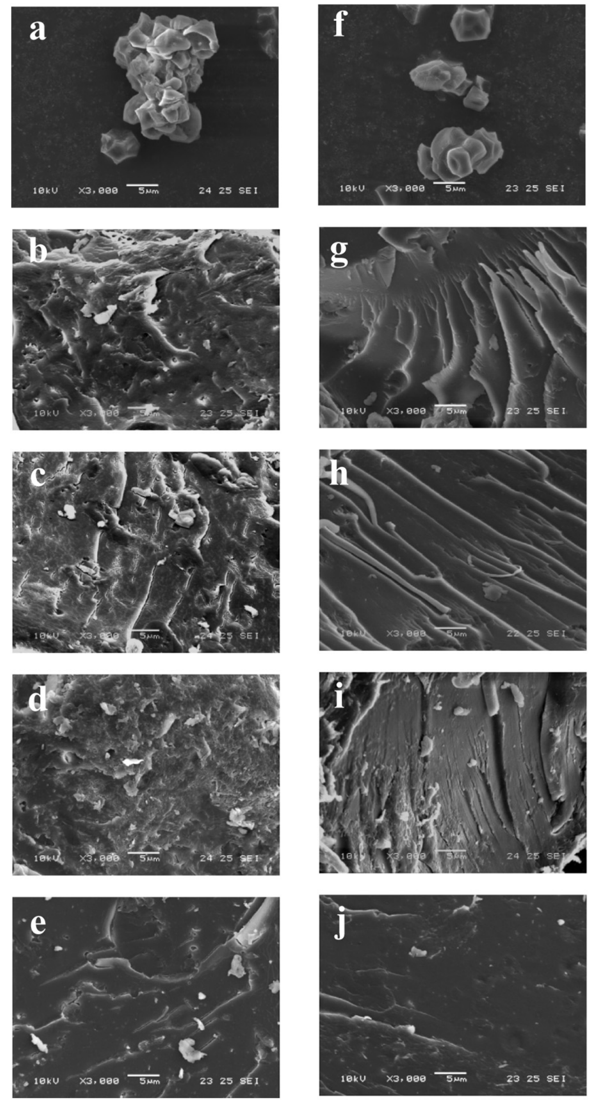

Fig. 3. Scanning electron micrographs (3000×) of native waxy rice flour (a) and rice flour (f). Waxy rice flour ((b)–(e)) and rice flour ((g)–(j)) were modified by extrusion process with water feed rate at 0.5 l/h ((b) and (g)), 0.6 l/h ((c) and (h)), 0.7 l/h ((d) and (i)), and 1.0 l/h ((e) and (j)).

the extruded product and the atmosphere caused steam generation within the product (Miller, 1994); consequently pores, on the extruded WRF particles could be observed (Fig. 2b–e). However, no pores were visible on the extruded RF particles (Fig. 2g–j). The higher peak and final viscosity of the extruded RF (Fig. 6b) made it difficult for the RF extrudate to form pores. Moreover, the smoother surfaces of the extruded RF compared to those of the extruded WRF may have resulted from the presence of amylose which could leach out of the starch granules during the extrusion cooking and bind to the surface of the extruded RF particles (Gill et al., 2002). At 3000× magnification (Fig. 3), the formation of the coarse structure could be seen in the extruded flour of both the WRF and RF which may have been produced by an alignment of starch molecules during shear stress in the extrusion process (Soto et al., 2007). Sample with a higher moisture content in the extrusion process had smoother surfaces which represented less severe conditions during the extrusion process because the moisture acted as a plasticizer during extrusion and lowered the extent of shear degradation (Lai & Kokini, 1991) leading to less damage in the extruded flour compared to samples with coarser surfaces resulted from using a lower moisture content.

3.3. Starch crystallinity of native and extruded WRF and RF

The X-ray diffractograms of the native WRF and RF showed an A-type pattern with 29.13 and 23.34% relative crystallinity, respectively (Fig. 4). For the extruded WRF, the lower the feeding moisture content applied, the lower the crystallinity of the extruded WRF. Fig. 4a with extruded WRF with the lowest moisture content of feeding flour at 20.50% shows an amorphous peak which represents the complete destruction of starch crystallinity during extrusion by the mechanical disruption of the molecular bonds due to the intense shear fields within the extruder (Wen, Rodis, & Wasserman, 1990) at a low moisture content. Similarly, the relative crystallinity of the extruded RF reduced with a lowering of the moisture content from 26.57 to 24.03%. However, the extrusion process with the moisture content at 22.70% resulted in a change in the X-ray diffraction pattern of the extruded RF from the A-type to the V-type pattern with additional peaks at 12.7 and 19.8° (2θ) (Fig. 4b), which indicated the formation of complexes between starches and native lipids (Zobel, 1964). The peak heights for the V-type pattern and the percentage of crystallinity increased when the moisture content of the feeding flour was lower than 22.70%. This confirmed the

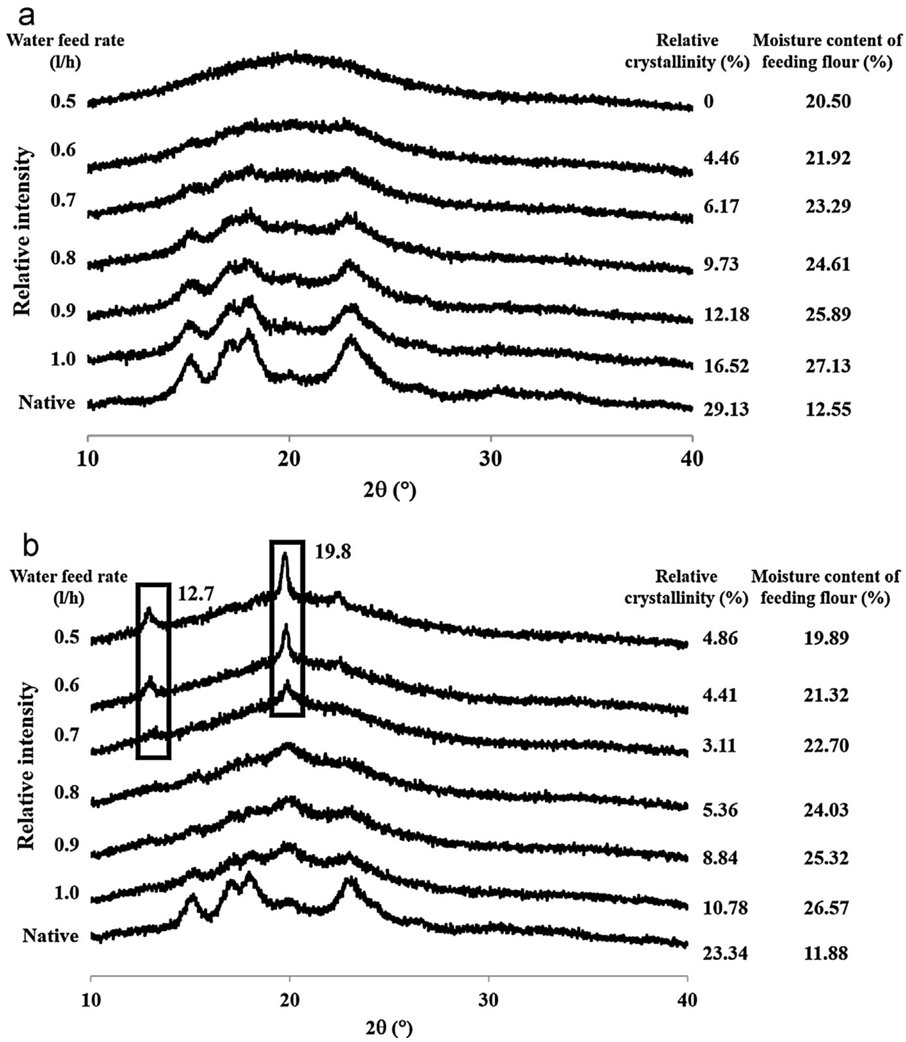

Fig. 4. X-ray diffraction patterns and relative crystallinity of native and extruded waxy rice flour (a) and rice flour (b) by extrusion process with water feed rate at 0.5–1.0 l/h. The extruded rice flour shows additional peaks at 12.7° and 19.8° indicating a change in crystallinity pattern from A-type to V-type.

formation of amylose-lipid complexes caused by the severity of the process. At low moisture content, the increasing shear force of the process could increase the availability of amylose chains, together with, the high temperature during the extrusion process that could promote molecular movement (Blanche & Sun, 2004); therefore, amylose-lipid complexes were produced when using the lower moisture content in extrusion. Additionally, the intense shear field of the extrusion could cause molecular bond disruption (Wen et al., 1990), and the complexes between starches and lipids resulted from the ability of amylose to bind to lipids (Bhatnagar & Hanna, 1994); therefore, it could be possible that, during severe extrusion (moisture content lower than 22.70%), the double helix structure of amylose was disrupted and unfolded which could favor forming the complexes with native lipids. Our results were consistent with the results from Bhatnagar and Hanna (1994) who found that the formation of complexes increased with a higher amylose content in corn starch but no V-type pattern was observed in extruded waxy corn starch.

3.4. Water absorption index and water solubility index of native and extruded WRF and RF

The WAI values of the extruded WRF and RF were significantly higher than those of native flour samples, with the exception of the extrusion process using the WRF with a moisture content lower than 23.29% that had a lower WAI than the native WRF (Table 2). The WAI could be increased by the degree of starch damage which was caused by starch gelatinization and extrusion-induced gelatinization (Colonna et al., 1989). At room temperature, the gelatinized starch had a higher ability to absorb water than did the native starch granules. Thus, the WAI of the extruded flours was higher than that of the native flours. The WAI of the extruded flours increased with an increase in the moisture content in feeding flour and reached a maximum when the moisture content was 25.89 and 21.32% for WRF and RF, respectively. The WAI reduced with a higher moisture content, due to the less severe conditions in the extrusion process leading to less damage of the extruded flour (Figs. 2 and 3). However, the extrusion process at high temperature with a low amount of water could cause melting crystalline of amylopectin molecules (Colonna et al., 1989) or severe damage to the extruded flour which can be seen in the SEM images (Figs. 2 and 3). As a result, the damaged particles lost their ability to absorb water; consequently, the WAI of the extruded WRF with moisture content lower than 23.29% was lower than for the native WRF.

The WSI measures the degree of starch degradation in the extrusion process (Ding, Ainsworth, Tucker, & Marson, 2005). Similarly to the WAI, the WSI values of the extruded WRF and RF were significantly higher than those of native flour samples with maxima obtained when using the lowest moisture content in the feeding flour because of dextrinization in the extrusion system at

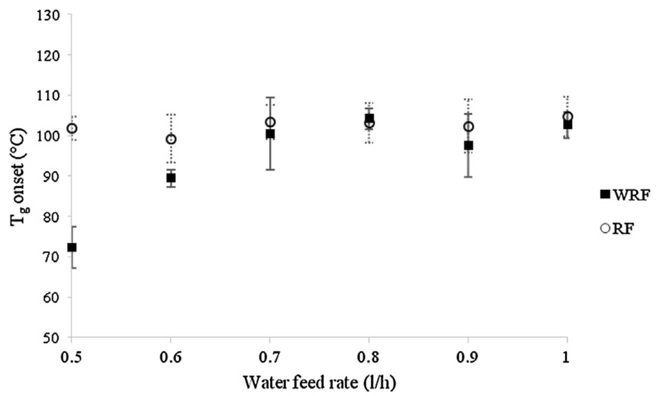

Fig. 5. Glass transition temperature (T_g) of extruded waxy rice flour (WRF) and rice flour (RF) by extrusion process with water feed rate at 0.5–1.0 l/h. T_g onset values were determined at relative humidity 52.9%, 25 °C.

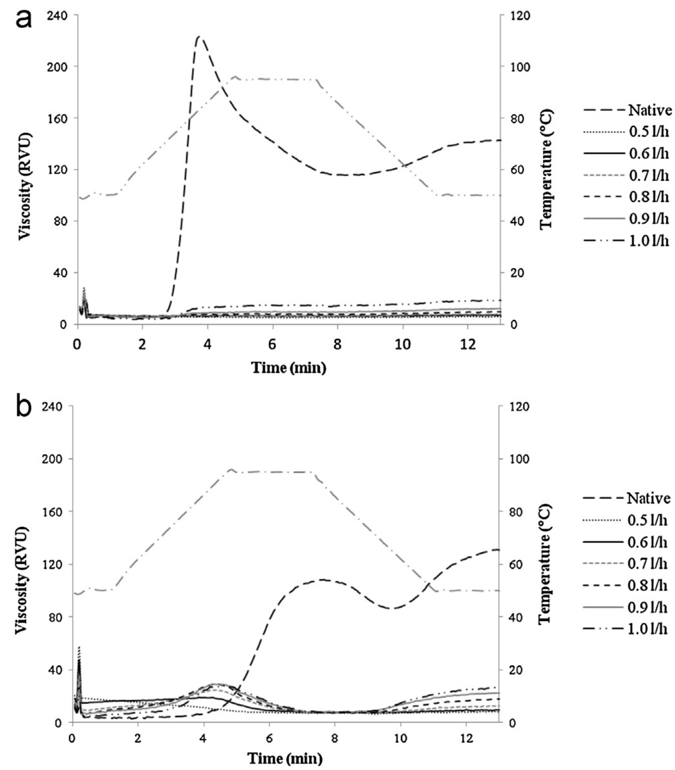

Fig. 6. Pasting profile of native and extruded waxy rice flour (a) and rice flour (b) by extrusion process with water feed rate at 0.5–1.0 l/h.

high temperature but with low water or shear fragmentation of the starch during extrusion at low moisture content which led to an increase in the number of water-soluble carbohydrate molecules (Colonna et al., 1989) resulting in the higher WSI. An increase in the moisture content reduced the process severity; consequently, the WSI was lowered and continued to decrease and was close to the WSI of the native flour samples.

The extruded WRF had a higher WSI than the extruded RF which was in line with the results of Sompong et al. (2011) and Guha, Ali, and Bhattacharya (2003). They concluded that glutinous rice flour (high amylopectin content) was more degraded during extrusion than rice flour with higher amylose content.

3.5. Glass transition temperature of native and extruded WRF and RF

Feeding WRF and RF with a lower moisture content in the extrusion process led to higher molecular degradation in the starch resulting in a lower T_g in the extruded products (Fig. 5). It is well established that the T_g of a polymer is related to its molecular weight (Kaletunc & Breslauer, 1993). The extrusion-induced fragmentation into smaller molecules represented the primary cause of changes in the T_g and the extent of the fragmentation reduced the T_g of the extruded corn flour (Kaletunc & Breslauer, 1993). Wen et al. (1990) reported that at each screw speed and temperature tested, a decrease in the moisture content from 30 to 20% resulted in an increase in the fragmentation and a decrease in the high molecular weight of the corn starch. Molecular degradation could be the result of thermomechanical stress from the extruder that could produce a low molecular weight in the extruded flour, but it was considered to be the result of mechanical rather than thermal degradation (Kaletunc & Breslauer, 1993). The effect of the moisture content in the feeding flour on molecular degradation was more significant in the extruded WRF than the extruded RF which could be seen in the bigger change in the T_g of the extruded WRF (Fig. 5). Chung and Lim (2003) reported that the lower T_g of waxy rice starch could be a result of the presence of branching in waxy rice starch which may obstruct the chain association, whereas the linear amylose molecule facilitates rapid chain association causing a more rigid amorphous structure resulting in higher T_g values. It was clearly observed that the T_g values of the extruded WRF with a lower moisture content were lower than those with a higher moisture content, while this was not clearly seen in the extruded RF. This T_g result was in line with the result from the WSI where a lower moisture content in the feeding flour caused higher molecular degradation resulting in more water-soluble molecules; moreover, the WSI was higher in the extruded WRF than in the extruded RF. Therefore, it could be concluded that extrusion had a stronger effect on the molecular fragmentation of WRF than of RF, which also agreed with the suggestion of Wen et al. (1990) that extrusion-induced molecular fragmentation of starch occurred preferentially at the branching point (α 1–6) of the amylopectin fraction, while the amylose polymer passed through extrusion process without significant molecular degradation.

3.6. Pasting properties of native and extruded WRF and RF

The pasting times of native and extruded RF were longer than that of WRF (Fig. 6) because the higher amylose content in the RF restricted swelling of the rice granules; therefore, they required a longer time to reach maximum viscosity than did the native and extruded WRF, respectively. The viscosity of a paste depends on the degree of gelatinization and molecular breakdown (El-Dash et al., 1983). The initial viscosities of the extruded flours were higher than those of the native flour sample which confirmed that the properties of pre-gelatinized extruded WRF and RF could absorb water and be viscous at room temperature (Wurzburg, 1995). The peak and final viscosity values of the extruded WRF and RF were far lower than that those of the native flours (Fig. 6), which were characteristics of the extruded samples (Menegassi, Pilosof, & Arêas, 2011). Since the extruded WRF and RF were pre-gelatinized by thermal gelatinization and mechanically damaged during the extrusion process (Colonna et al., 1989), they lost the ability to swell upon heating resulting in a lower viscosity compared with native flours. No gelatinization peaks were observed in the viscogram of the extruded WRF (Fig. 6a) but they could be observed in the extruded RF (Fig. 6b). This could imply that under the same conditions of extrusion, increased gelatinization took place during the extrusion of the WRF than of the RF possibly because the higher amylose content in the RF restricted the swelling and gelatinization of the starch granules, as mentioned before. Moreover, the peak viscosity of the extruded RF increased with an increased moisture content in the feeding RF because, with a high moisture content, partial gelatinization occurred and some ungelatinized-starch was still presented in the extruded flour causing an increase in the viscosity during heating in the RVA. This indicated that a high moisture content in the feeding material decreased the stress on granule disruption during extrusion. The native and extruded RF had higher setback from the trough compared to the native and extruded WRF, respectively, which showed higher retrogradation of native and extruded RF due to the reassociation of amylose molecules during cooling. Our result was in line with that of Sompong et al. (2011).

3.7. Gelatinization properties of native and extruded WRF and RF

Native flours had lower T_o and T_p values than the extruded flours; however, there was no significant difference in the T_c values (Table 2). The higher values of T_o and T_p in the extruded flour samples could have been because starch was partially gelatinized by the extrusion process and more heat-stable granules remained in the extruded products causing higher T_o and T_p levels in the extruded flour, compared to those of the native flour samples. The enthalpy of gelatinization or enthalpy of melting endotherm (ΔH_{gel}) values of the native and extruded WRF were higher than those of the native and extruded RF for all levels of moisture content in the feeding flour because the native and extruded WRF had higher relative crystallinity than did the RF (Fig. 4). ΔH_{gel} reflects the loss of molecular order (Cooke & Gidley, 1992). Since amylopectin plays a major role in starch granule crystallinity, the presence of amylose lowers the energy for gelatinization (Flipse, Keetels, Jacobson, & Visser, 1996). The extrusion process of WRF and RF with the lowest moisture contents did not show melting endotherms of crystalline portion which could have been due to complete starch conversion during extrusion. An increase in the moisture content in the feeding flour tended to increase the enthalpy of melting endotherm of the extruded flour which confirmed that partial conversion had occurred when using high moisture content, which agreed with the result from the RVA. Indeed, these melting enthalpy values corresponded to the results for % crystallinity as the extrusion process with the higher moisture content resulted in a higher % crystallinity causing a higher enthalpy of melting endotherm than the process with the lower moisture content. We also found that the extruded RF with a moisture content lower than 22.70% had an endotherm at a high temperature (T_p = 114 °C) representing an amylose-lipid complex (data not shown). This result was consistent with the result from the X-ray diffractogram that indicated that the crystallinity pattern of the extruded RF changed from the A-type to the V-type (Fig. 4).

4. Conclusion

The structure and physicochemical properties of extruded rice flour were influenced by the amylose and amylopectin content and the moisture content of the feeding material. Extrusion had a stronger effect on the WRF due to the higher amylopectin content of the WRF than in the RF; thus, the extruded WRF showed higher molecular degradation, exhibited an amorphous pattern in the X-ray diffractometry and significant changes in the T_g, compared to the extruded RF. The extrusion process with a lower moisture content in the feeding flour increased the thermomechanical stress which resulted in a change in the microstructure, destruction of the crystalline structure, degradation of the starch molecules, lowering of T_g values and complete starch gelatinization. In contrast, a higher moisture content in the feeding flour caused partial gelatinization and less mechanical damage to the extruded flour. The WAI of flour samples increased after the extrusion process which could potentially be useful in food products, such as frozen bakery products, where a flour is required with high water absorption ability and moisture loss reduction.

Acknowledgements

Financial support from Kasetsart University and the Faculty of Agro-Industry, Kasetsart University is gratefully acknowledged.

References

AACC. (2000). *Approved methods of the American association of cereal chemists* (10th ed.). St. Paul, MN: American Association of Cereal Chemists.
Anderson, R. A., Conway, H. F., Pfeifer, V. F., & Griffin, E. L. (1969). Gelatinization of corn grits by roll and extrusion-cooking. *Cereal Science Today*, *14*, 4–12.
Bhatnagar, S., & Hanna, M. A. (1994). Extrusion processing conditions for amylase-lipid complexing. *Cereal Chemistry*, *71*, 587–593.
Billmeyer, F. W. (1984). *Textbook of polymer science*. New York, NY: A Wiley-Interscience Publication (Chapter 12).
Blanche, S., & Sun, X. (2004). Physical characterization of starch extrudates as a function of melting transition and extrusion condition. *Advances in Polymer Technology*, *23*, 277–290.
Cheetam, N. W. H., & Tao, L. (1998). Variation in crystalline type with amylose content in maize starch granules: An X-ray powder diffraction study. *Carbohydrate Polymers*, *36*, 277–284.
Chung, H. J., & Lim, S. T. (2003). Physical aging of glassy normal and waxy rice starches: Effect of aging temperature on glass transition and enthalpy relaxation. *Carbohydrate Polymers*, *53*, 205–211.
Colonna, P., Tayeb, J., & Mercier, C. (1989). Extrusion cooking of starch and starchy products. In C. Mercier, P. Linko, & J. M. Harper (Eds.), *Extrusion cooking* (pp. 247–319). Saint Paul, MN: American Association of Cereal Chemists.
Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinization: Origin of the enthalpic transition. *Carbohydrate Research*, *227*, 103–112.
Ding, Q. B., Ainsworth, P., Tucker, G., & Marson, H. (2005). The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-based expanded snacks. *Journal of Food Engineering*, *66*, 283–289.
El-Dash, A. A., Gonzales, R., & Ciol, M. (1983). Response surface methodology in the control of thermoplastic extrusion of starch. *Journal of Food Engineering*, *2*, 129–152.
Flipse, E., Keetels, C. J. A. M., Jacobson, E., & Visser, R. G. F. (1996). The dosage effect of the wildtype GBSS allele is linear for GBSS activity but not for amylose content: Absence of amylose has a distinct influence on the physic-chemical properties of starch. *Theoretical and Applied Genetics*, *92*, 121–127.
Gill, S., Vasanthan, T., Ooraikul, B., & Rossnagel, B. (2002). Wheat bread quality as influenced by the substitution of waxy and regular barley flours in their native and extruded forms. *Journal of Cereal Science*, *36*, 219–237.
Guha, M., & Ali, S. Z. (2002). Molecular degradation of starch during extrusion cooking of rice. *International Journal of Food Properties*, *5*, 509–521.
Guha, M., Ali, S. Z., & Bhattacharya, S. (2003). Screening of variables for extrusion of rice flour employing a Plackett–Burman design. *Journal of Food Engineering*, *57*, 135–144.
Guy, R. C. E. (1994). Raw materials for extrusion cooking process. In N. D. Frame (Ed.), *The technology of extrusion cooking* (pp. 52–72). London: Blackie Academic & Professional.
Harper, J. M. (1989). Food extruders and their applications. In C. Mercier, P. Linko, & J. M. Harper (Eds.), *Extrusion cooking* (pp. 1–16). Saint Paul, MN: American Association of Cereal Chemists.
Kaletunc, G., & Breslauer, K. J. (1993). Glass transition of extrudates: Relationship with processing-induced fragmentation and end-product attributes. *Cereal Chemistry*, *70*, 548–552.
Lai, L. S., & Kokini, J. L. (1991). Phyicochemical changes and rheological properties of starch during extrusion. *Biotechnology Progress*, *7*, 251–266.
Manson, W. R. (2009). Starch used in food. In J. BeMiller, & R. Whistler (Eds.), *Starch chemistry and technology* (pp. 762–788). Oxford: Elsevier.
Martínez-Bustos, F., Aguilar-Palazuelos, E., & Galicia-García, T. (2012). Thermoplastic behaviour of biopolymers during extrusion. In V. R. N. Telis (Ed.), *Biopolymer engineering in food proccessing* (pp. 245–278). Tallahassee, FL: CRC Press.
Menegassi, B., Pilosof, A. M. R., & Arêas, J. A. G. (2011). Comparison of properties of native and extruded amaranth (*Amaranthus cruentus* L.-BRS Alegria) flour. *LWT—Food Science and Technology*, *44*, 1915–1921.
Miller, R. C. (1994). Breakfast and cereal extrusion technology. In N. D. Frame (Ed.), *The technology of extrusion cooking* (pp. 73–109). London: Blackie Academic & Professional.
Phothiset, S., & Charoenrein, S. (2007). Morphology and physicochemical changes in rice flour during rice paper production. *Food Research International*, *40*, 266–272.
Singh, B., Sekhon, K. S., & Singh, N. (2007). Effects of moisture, temperature and level of pea grits on extrusion behavior and product characteristics of rice. *Food Chemistry*, *100*, 198–202.

Sompong, R., Ehn, S. S., Berghofer, E., & Schoenlechner, R. (2011). Extrusion cooking properties of white and colored rice varieties with different amylose content. *Starch-Stärke*, *63*, 55–63.
Soto, R. A. G., Escobedo, R. M., Sánchez, H. H., Rivera, M. S., & Pérez, L. A. B. (2007). Extrusion of banana starch: Characterization of the extrudates. *Journal of the Science of Food and Agriculture*, *87*, 348–356.
Valle, G. D., Colonna, P., & Patria, A. (1996). Influence of amylose content on the viscous behavior of low hydrated molten starches. *Journal of Rheology*, *40*, 347–362.
Wen, L. F., Rodis, P., & Wasserman, B. P. (1990). Starch fragmentation and protein insolubilization during twin-screw extrusion of corn meal. *Cereal Chemistry*, *67*, 268–275.
Wurzburg, O. B. (1995). Modified starch. In A. M. Stephen (Ed.), *Food polysaccharides and their applications* (pp. 67–98). New York, NY: Marcel Dekker.
Zobel, H. F. (1964). X-ray analysis of starch granules. In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (pp. 109–113). Tallahassee, FL: Academic Press.