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Retrogradation behaviour of high-amylose rice starch prepared by improved extrusion cooking technology

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ABSTRACT

Native rice starch (NRS, amylose/28.9%) was gelatinized by improved extrusion cooking technology (IECT) and retrograded (RRS) after low temperature storage (4 °C). The retrogradation behaviour of RRS was changed to low retrogradation percentage and low retrogradation rate. The retrogradation resulted in a high compact morphology. The melt enthalpy change and percentage of retrogradation of RRS was 3.68 J/g and 37.7%, respectively, compared to those of NRS (9.75 J/g, 100%). The retrogradation percentage for RRS was low during storage as shown as a low retrogradation rate (0.21 d^{-1}) and a high Avrami exponent (0.89). The pattern of rice starch changed from A-type to amorphous and B-type. Both the relative crystallinity of RRS (12.7%) by the X-ray diffractograms and the ratio of the band height (0.63) in the FTIR spectra were low. The analysis of retrogradation structure and short-range molecular order further confirmed the retrogradation behaviour of rice starch after IECT treatment.

1. Introduction

Rice products are staple foods, especially in Asia. Many popular oriental foods, such as rice noodles, rice cakes, and rice pasta are made from rice starch. Now more emphasis is directed towards the improvement of eating and cooking quality of rice all around the world. One of the greatest problems is that rice starch from these foods retrogrades quickly after cooking, which results in the deterioration of desirable attributes (the change of properties and qualities including an increase of hardness and a decline of taste over time). Starch retrogradation is of great interest to food scientists and technologists since it profoundly affects the quality, acceptability and shelf-life of starch-containing foods (Karim, Norziah, & Seow, 2000). The retrogradation of rice starch is influenced by intrinsic and extrinsic factors. Intrinsic factors refer to different botanical sources (Hoover, 2001; Singh, Singh, Kaur, Singh, & Singh, 2003), starch composition (amylose to amylopectin ratio), granule architecture (crystalline to amorphous ratio) and other compounds (lipids) (Singh et al., 2003). Extrinsic factors refer to differences in physical processing technologies and retrogradation conditions during storage (Hoover, 2001).

In order to extend shelf-life, the preparation of rice products requires effective retardation of starch retrogradation. The retrogradation behaviours of starch are affected by processing methods such as hydrothermal treatment (Jacobs & Delcour, 1998; Xu, Xie, Kong, & Bao, 2004; Yu, Ma, & Sun, 2009), annealing (Jacobs & Delcour, 1998), heat-moisture treatment (Jacobs & Delcour, 1998; Khunaea, Tranb, & Sirivongpaisal, 2007), heating–stirring (Wu, Chen, Li, & Wang, 2010), high hydrostatic pressure (Hu et al., 2011), microwave, ultrasonic-microwave (Jiang et al., 2011) and extrusion. Starch processed by extrusion cooking has been widely studied for its retrogradation behaviour. Kadan and Pepperman (2002) studied the physicochemical properties of starch in extruded rice flours by analyzing the changes in melt enthalpy and XRD pattern aspects. Ottenhof, Hill, and Farhat (2005) compared the retrogradation behaviour of waxy maize starch, potato starch and wheat starch after extrusion cooking. Bello-Pérez, Ottenhof, Agama-Acevedo, and Farhat (2005) investigated the retrogradation behaviour of banana starch treated by extrusion cooking during storage. Farhat, Blanshard, and Mitchell (2000) investigated the retrogradation kinetics of waxy maize starch after extrusion.

Conventional extrusion cooking is a continuous high-temperature and short-time process, which physically modifies moistened expansible starchy and proteinaceous material, causing the starchy and proteinaceous material to swell, through the use of the unique

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combination of high temperature, pressure and shear forces. The improved extrusion cooking technology (IECT), a new gelatinization technology, which is reconstituted from traditional single-screw extruders. Compared to the traditional extrusion cooking machines, our transformed single-screw extruder shows the characteristics of a longer screw (1950 cm), longer residence time (40–68 s), higher die pressure (13.356–19.102 MPa), lower temperature (69.8–120.2 °C) and lower screw speed (20.1–32.6 rpm) than traditional extrusion cooking extruders. Furthermore, the new forming mold and rotary cutting knife which are not included in traditional extruders are added (Liu et al., 2011). In our previous study, IECT was applied to prepare texturized rice, in which broken rice and rice bran were used as raw material (Liu et al., 2011). However, the effect of IECT on retrogradation behaviour of high-amylose rice starch is still unknown. Furthermore, the differences between IECT and other physical treatments on retrogradation behaviour of rice starch have not been compared yet.

This research investigates the retrogradation behaviour of high-amylose rice starch after IECT treatment. The morphology of rice starch and percentage of retrogradation were investigated using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The rate of retrogradation was investigated by using DSC and Fourier transform infrared (FTIR) spectroscopy. Besides, the structure of retrograded starch and the ratio of short-range ordered molecule to amorphous phase were investigated using X-ray diffraction (XRD) and FTIR.

2. Materials and methods

2.1. Polished rice flour

Polished rice was purchased from a local food processing factory, Nanchang, Jiangxi province, China. Rice was ground in a hammer mill (Jiangxi Hongxing Machinery Limited Liability Company, Hongxing, China) and passed through a 60-mesh sieve, packed in airtight plastic bags, and stored under room temperature for further use. The rice flour contained starch (88.3 g/100 g), protein (8.66 g/100 g), fat (1.37 g/100 g) on dry basis content (db), moisture (12.2 g/100 g) (AOAC, 2005).

2.2. Extraction of rice starch

Starch was extracted using the method described by Yao, Zhang, and Ding (2002) with some modifications. Rice flour was soaked in 5 equiv (w/w) of 0.4% NaOH solution and deposited at room temperature for 48 h. Then the starch precipitate was repeatedly washed with deionized water to bring the pH to 7. The starch precipitate was vacuum freeze-dried until the moisture content reaches around 9%. The dried starch was ground into powder and was passed through a 100-mesh sieve. The isolated starch had 0.44% protein, 0.61% fat (AOAC, 2005), and 28.9% amylose (Yao et al., 2002). It should be regarded as high amylose rice as far as the eating quality is concerned (Juliano, 1992).

2.3. Sample preparation and treatment by IECT

The independent processing variables for the extrusion (Liu et al., 2011) were moisture content (mass ratio of sample and water 1:1.5 based on sample dry basis content), feed screw rate (30 rpm), screw speed (37.5 rpm). The temperature profiles in the feed, mix, screw conveyor, shearing compression metering, die head zones were kept constant at 50 °C, 65 °C, 85 °C, 100 °C, 95 °C, respectively.

Samples of three groups were prepared: the native rice starch (NRS); rice starch that had been gelatinized via IECT at 51% moisture (GRS) and then freeze-dried; rice starch that had been gelatinized via IECT at 51% moisture, then stored at 4 °C for 7 days, and then freeze-dried (RRS). All of the samples were vacuum freeze-dried to achieve uniform moisture content around 9% according to Wu et al. (2010), Wei et al. (2011), and Zhu, Liu, Wilson, Gu, and Shi (2011). Afterwards, these samples were ground and passed through a 100-mesh sieve before SEM, DSC, XRD, and FTIR analysis.

2.4. SEM analysis

The SEM analysis of three powder samples (NRS, GRS, and RRS) was done using the method of Hu et al. (2011).

2.5. Freeze thaw stability (syneresis %)

Freeze thaw stability of gelatinized starch was measured by the method as used by Yadav, Yadav, and Kumar (2011) with minor modifications. The gel samples after IECT treatment and stored at 4 °C for 7 days, the gel samples were transferred to a standard plastic cup and frozen at −18 °C. Alternately freezing and thawing was performed by freezing for 24 h at −20 °C and thawing for 4 h at 30 °C. The syneresis was calculated as the amount of excluded water as a percentage of the original paste weight up to five freeze thaw cycles.

2.6. DSC analysis

The starch retrogradation behaviour was analyzed by the DSC using Q2000-DSC (TA Corp., New Castle, USA) according to Xu et al. (2004). Samples (2 mg, db) were placed in a high-volume pan and distilled water was added with a microsyringe to achieve a water-sample ratio of 2:1. The sample pan was sealed, equilibrated at room temperature for 24 h, and then heated from 10 to 100 °C at a heating rate of 10 °C/min. An empty pan was used as a reference. The onset temperature T_o, peak temperature T_p, and conclusion temperature T_c were calculated by a Universal Analysis Program, version 4.7A (TA Instruments). Gelatinization enthalpy (ΔH_g) and Retrogradation enthalpy (ΔH_r) were evaluated based on the area of the main endothermic peak by the Universal Analysis Program. The percentage of retrogradation was calculated as $(\Delta H_r)/(\Delta H_g) \times 100$ according to Xu et al. (2004). Analyses were performed in triplicate.

2.7. XRD analysis

Wide-angle X-ray scattering measurements of lyophilized samples (moisture content around 9%) were performed with a Di System X-ray diffractometer (Bede XRD Di System, Durham, United Kingdom) equipped with a copper tube operating at 40 kV and 200 mA, producing CuK_α radiation of 0.154 nm wave length. Diffractograms were obtained by scanning from 4° to 40° (2θ) at a rate of 4°/min, step size of 0.02°, divergence slit width of 1°, receiving slit width of 0.02 mm and scatter slit width of 1°. Each sample was measured in triplicate. Relative crystallinity of starches was calculated as the area ratio of the crystalline sharp peak over the total area using peak-fitting software (Origin-version 8.1, Microcal Inc., Northampton, MA, USA) based on the method of Nara and Komiya (1983).

2.8. FTIR spectroscopy analysis

Middle infrared spectra were acquired using a Nicolet 5700 (Thermo Nicolet Co., Waltham, USA) spectrometer equipped with a deuterated triglycine sulphate detector and temperature controlled single reflectance diamond attenuated total reflectance

accessory with a sealed sapphire anvil according to Ottenhof et al. (2005). For each spectrum, 128 scans acquired at a resolution of 4 cm^{-1} were co-added, recorded against an empty cell as background. At least triplicate measurements were carried out for each sample at each storage time. Data analysis was carried out using the OMNIC 6.2 software (Thermo Electron Corporation, Madison, WI, USA). Spectra were baseline-corrected at 1200 and 800 cm^{-1} by drawing a straight line. All spectra were deconvoluted. A half-bandwidth of 26 cm^{-1} and an enhancement factor of 2.4 with triangular apodization were employed. Intensity measurements were performed on the deconvoluted spectra by recording the height of the absorbance bands from the baseline. The ratios of absorbance height 1045 cm^{-1}/1151 cm^{-1} and 1047 cm^{-1}/1022 cm^{-1} were obtained for the deconvoluted spectra.

2.9. Retrogradation behaviour of the tested rice starch samples

The gelatinized rice starches prepared by IECT were sealed in a container and stored at 4 °C for 0, 1, 3, 5, 7, 14, 21, 28, and 35 days to perform the retrogradation study. Each sample was vacuum freeze-dried until the moisture content reaches 9.02 ± 0.89% before DSC and FTIR test. The Avrami equation has been widely applied to investigate the behaviour of starch retrogradation (Hu et al., 2011; Mua & Jackson, 1998; Tian et al., 2009; Yao et al., 2002). The Avrami equation and its rearranged forms in this work were expressed as follows:

$$1-\theta=\exp(-kt^n) \tag{1}$$

$$\theta=X(t) \tag{2}$$

$$X(t)=\frac{x(t)-x_0}{x_\infty-x_0} \tag{3}$$

$$\ln[-\ln(1-X(t))]=\ln k+n\ln t \tag{4}$$

where $X(t)$, $x(t)$ represented relative changes and the measured parameter (e.g., enthalpy or IR absorbance ratio) at time t, respectively, x_0 is the value of x for $t = 0$, and x_∞ is the value of x for $t = \infty$ (35 days for all samples). 'n' was Avrami exponent determined from the slope of $\ln[-\ln(1-X(t))]$ versus $\ln t$ plot, and k was the rate constant determined from the intercept of the plot.

2.10. Statistical analysis

The mean, standard deviations and significant differences of the data collected were calculated and reported using SPSS 12.0.1 (SPSS Inc., Chicago, Illinois, US). Whenever differences were reported as significant, a confidence level of 95% was considered. The data reported in all of the tables were the average of triplicate observations.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) and percentage of retrogradation

As shown in SEM results (Fig. 1a), the granules of the native rice starch were small and showed the angular, polyhedral shapes, and were 6–8 μm in size. This result was similar with Yadav et al. (2011). NRS was gelatinized and formed GRS when it was IECT treated at low temperature and high pressure. This represented the gelatinization process. GRS showed continuous and porous aggregates (Fig. 1b). Gelatinized NRS recrystallized and large amounts of water were lost from the aggregates (syneresis) due to the starch chain association during storage at 4 °C for 7 days.

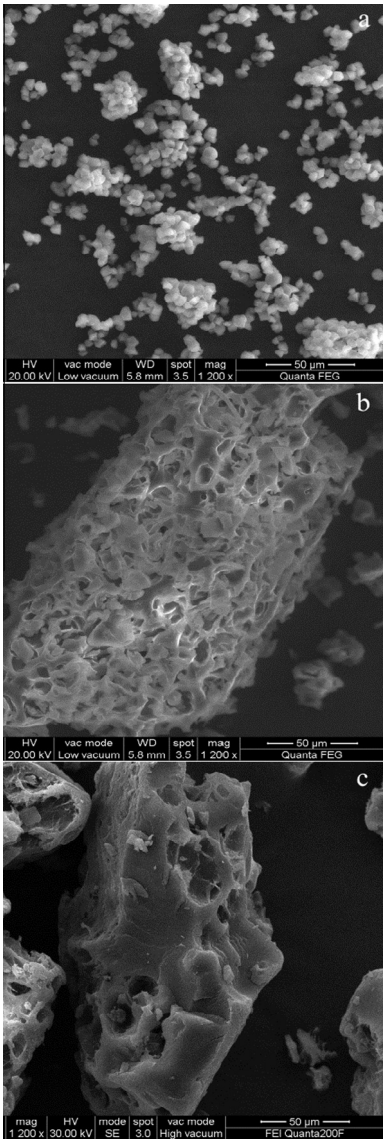

Fig. 1. SEM microstructure of three samples: (a) NRS, (b) GRS, and (c) RRS.

After low temperature storage RRS was formed. This exhibited the phenomenon of retrogradation. RRS had a high compact morphology and a few holes were observed on the surface as shown in Fig. 1c. According to Karim et al. (2000), the amount of syneresis could be used as an indicator for the tendency of starch to retrograde. Wu et al. (2010) reported similar results that the effect of syneresis during retrogradation process resulted in starch chain association, forming compact structure for rice starch. Our results showed that the freeze–thaw stability, measured as % syneresis, of the GRS and RRS samples were 3.23% and 10.2%, respectively. The syneresis of rice starch was obvious during retrogradation, which indicated that rice starch gelatinized after IECT started to retrograde. Although rice starch started to retrograde after IECT, it was still unknown how the percentage and rate of retrogradation for rice starch would be.

DSC was used to measure temperature parameters, the enthalpy and the percentage of retrogradation associated with starch retrogradation by monitoring the progressive increase of endotherm due to recrystallization of amylopectin molecules with storage time (Karim et al., 2000; Tian et al., 2009; Xu et al., 2004). Fig. 2 showed the melting thermograms of NRS, GRS and RRS. The corresponding transition temperatures (T_o, T_p, T_c) and the enthalpy

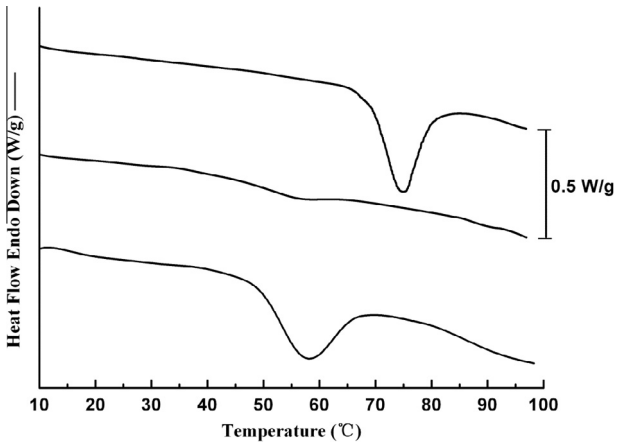

Fig. 2. The DSC curves of NGS, GRS and RRS, the curves were NGS, GRS and RRS from top to below.

change of NRS, GRS and RRS are listed in Table 1. The melting temperatures (T_o, T_p, T_c) and enthalpy change of NRS were higher compared to those of GRS and RRS. The results indicated that the melting temperatures (T_o, T_p, T_c) and enthalpy change decreased after IECT treatment. According to Banchathanakij and Suphantharika (2009), the T_0 of the retrogradation endotherm coincides with the temperature where the least stable amylopectin crystallites formed during storage. Therefore, the marked decrease in T_0 or even T_p means that there was a large amount of new and less stable amylopectin crystallites formed during storage. These results suggested that retrogradation after IECT treatment resulted in the reassociation of the gelatinised starch molecules, but in less order and hence less perfect or stable forms and more heterogeneous in stability than those exist in the native starch granules (Table 1).

In addition, it was hypothesized that NRS should be completely gelatinized after IECT, but the ΔH_r (0.49 J/g) was observed for GRS in this study. According to Kadan and Pepperman (2002), the rice starch could be completely gelatinized between 90 °C and 100 °C. Ottenhof et al. (2005) stated that the ΔH_r was not believed to be related to residual native starch crystallinity but to a crystalline amylose–lipid complex after extrusion cooking. However, compared to the above results, different results were obtained in this study. The ΔH_r of GRS (0.49 J/g) represented the melting of the retrograded starch molecules during the drying processes when the melting temperatures T_0, T_p, and T_c were 45.76 °C, 55.91 °C and 65.54 °C, respectively, (Table 1).

The ΔH_g was 9.75 J/g for NRS (amylose content, 28.9%) while the melting enthalpies for the retrograded starch molecules were 0.49 and 3.68 J/g for GRS and RRS, respectively. The remarkable change in ΔH_r indicated that more energy was required for melting a large amount of amylopectin crystallites that are formed during the storage of RRS as compared to GRS, which could be the result of the formation of partially recrystallized amylopectin after IECT treatment and 7 days storage, compared to the GRS. The increased ΔH_r and percentage of retrogradation were 3.19 J/g and 27.4% from GRS to RRS, respectively. Although RRS retrograded, its ΔH_r and percentage of retrogradation were only 3.68 J/g and 37.7%, respectively.

Starch retrogradation is a non-equilibrium thermoreversible recrystallisation process which is governed by a consecutive three-step mechanism of nucleation, propagation, and maturation (Banchathanakij & Suphantharika, 2009). In the retrogradation process, amylose is responsible for the short-term development of gel structure via crystallization, while amylopectin is responsible for the long-term reordering and relatively slower process. For common starches containing amylose and amylopectin, a composite gel network forms, consisting of swollen amylopectin-enriched granules filling an interpenetrating amylose gel matrix which was used as crystal nuclei (Karim et al., 2000). Therefore, the higher the amylose contents of rice starch, the higher the percentage of retrogradation and the rate of retrogradation. This would result in a change of rice food properties and qualities including reduced stickiness, undesirable firming of bread and other starch-based products.

The retrogradation behaviour of starches with various amylose contents was investigated by other researchers. Xu et al. (2004) clearly stated that the retrograded rice starch (amylose content, 25.4%) showed its ΔH_r and percentage of retrogradation were 5.40 J/g and 63.5%, respectively. According to Yu et al. (2009), high amylose rice (27.6%) showed its ΔH_r with 9.76 J/g. Compared to the above results based on different amylose contents, ΔH_r (3.68 J/g) and percentage of retrogradation (37.7%) for RRS were relatively lower when the amylose content was 28.9% in this study.

Many researchers used physical methods to study the retrogradation behaviour of rice starch or starches of other botany sources. Wu et al. (2010) demonstrated that the retrograded rice starch samples showed ΔH_r with 5.14 J/g (stirring), 5.34 J/g (heating–stirring), and 5.13 J/g (no treatment). Jiang et al. (2011) indicated that the ΔH_r of retrograded non-waxy rice starch was 3.90 J/g, 4.00 J/g, and 4.80 J/g corresponding to microwave, ultrasonic-microwave synergistic and conventional heat treated, respectively. Furthermore, Kadan and Pepperman (2002) reported the retrograded rice showed ΔH_r with 4.50 J/g by 2 peaks after extrusion cooking. Ottenhof et al. (2005) indicated the ΔH_r and percentage of retrogradation were 11.6 J/g amylopectin and 50.0%, 9.00 J/g amylopectin and 56.9%, 6.10 J/g amylopectin and 37.7% for waxy maize starch, wheat starch, potato starch, respectively, after extrusion treatment. Bello-Pérez et al. (2005) reported the ΔH_r of banana starch was 5.00 J/g after extrusion treatment. Compared to the above results of retrogradation based on different physical methods, the ΔH_r and percentage of retrogradation were lower in this study.

3.2. The rate of rice starch retrogradation

The ΔH_r from DSC could be used to calculate the rate of retrogradation (Mua & Jackson, 1998). The ΔH_r of gelatinized starches after IECT being stored at 4 °C for different storage time were shown in Table 2. The rate of rice starch retrogradation (k) and Avrami exponent (n) were 0.21 ± 0.01 d^{-1} and 0.89 ± 0.06,

Table 1
Retrogradation temperatures and enthalpy of samples (NRS, GRS, and RRS).

Samples	T_0	T_p	T_c	ΔH_g (ΔH_r)	R (%)
NRS	69.32 ± 0.33[a]	74.73 ± 0.12[a]	85.90 ± 0.55[a]	9.75 ± 0.22[a] (13.71)	100
GRS	45.76 ± 0.25[c]	55.91 ± 0.51[b]	65.54 ± 0.39[c]	0.49 ± 0.11[c] (0.69)	10.36
RRS	46.44 ± 0.27[b]	56.38 ± 0.19[b]	70.86 ± 0.21[b]	3.68 ± 0.32[b] (5.18)	37.74

T_0, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_g (ΔH_r), enthalpy of gelatinization and retrogradation (J/g dry starch); brackets, J/g amylopectin; R (%), percentage of retrogradation. Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

Table 2
Retrogradation rate of rice starch by IECT during different storage days.

Periods (days)	ΔH_r (J/g)[a]	(1045 cm^{-1}:1151 cm^{-1})[b]
0	0.49 ± 0.05	0.36 ± 0.01
1	1.38 ± 0.11	0.43 ± 0.02
3	2.76 ± 0.12	0.58 ± 0.04
5	3.23 ± 0.14	0.63 ± 0.05
7	3.68 ± 0.10	0.69 ± 0.05
14	4.51 ± 0.18	0.81 ± 0.04
21	5.14 ± 0.16	0.86 ± 0.02
28	5.52 ± 0.11	0.89 ± 0.03
35	5.71 ± 0.14	0.90 ± 0.04

[a] Data were from ΔH_r of DSC.
[b] Data were based on the ratio of the absorbencies 1045 cm^{-1}:1151 cm^{-1} from FTIR.

respectively. The increases of ΔH_r were only 3.19 J/g, 4.02 J/g and 4.65 J/g from 0 to 7 days, from 0 to 14 days and from 0 to 21 days, respectively. Recrystallization kinetics data obtained from rice starch samples fitted well with the Avrami equation with the correlation coefficient R^2 values close to 1 (0.9903). This indicates a low rate of retrogradation after IECT and storage. It was found that the rate of retrogradation of rice starch after IECT in this study was lower than that of the hydrothermal treatment as found by Yao et al. (2002) who reported that the k value of 0.87 d^{-1} for high-amylose rice starch (30.0%), or heat treatment by Hu et al. (2011) who showed k value of 0.54 ± 0.01 d^{-1}. Retrogradation rate was slightly faster than that of high hydrostatic pressure treatment by Hu et al. (2011) who showed k value of 0.18 ± 0.01 d^{-1}. Meanwhile, the ⟨DELTA⟩ H_r values were lower than those of Yu et al. (2009) who reported that cooked rice showed 3.11 ± 0.02, 7.87 ± 0.08, 9.44 ± 0.07, 9.76 ± 0.11, 10.19 ± 0.03, 10.63 ± 0.20 J/g corresponding to 0, 1, 3, 7, 11, 14 days, respectively. Furthermore, these values were also lower than those of Jiang et al. (2011) who indicated that the ΔH_r of non-waxy rice starch were 0, 3.7 ± 0.2, 4.8 ± 0.1, 6.5 ± 0.2, 7.7 ± 0.1 J/g; 0, 2.7 ± 0.1, 3.9 ± 0.1, 5.5 ± 0.0, 6.1 ± 0.1 J/g; 0, 3.0 ± 0.1, 4.0 ± 0.2, 6.0 ± 0.1, 6.4 ± 0.1 J/g corresponding to 0, 3, 7, 14, 21 days for conventional heat, microwave, ultrasonic-microwave, respectively. This indicated that the rate of retrogradation of rice starch during storage was low after IECT. Avrami exponent 'n' of rice starch after IECT was higher than the corresponding values (0.57, 0.47 ± 0.02, 0.70 ± 0.02) of Yao et al. (2002), Hu et al. (2011), Yu et al. (2009), and Jiang et al. (2011), respectively. According to Mua and Jackson (1998), it was indicated that the higher Avrami exponent 'n' related to a lower percentage of retrogradation. In this study, the higher Avrami exponent 'n' indicated that IECT resulted in a low percentage of retrogradation of rice starch.

To compare the effect of IECT on the rate of retrogradation of rice starch with those of conventional extrusion cooking, FTIR measurements were carried out to determine the degree of short-range molecular order (helical order) developed in rice starch samples after IECT during storage. According to Ottenhof et al. (2005), the ratios of heights (1045 cm^{-1}/1151 cm^{-1}) for gelatinized starches after IECT being stored at 4 °C for different storage times were shown in Table 2. It was observed that the ratio increased with increasing storage times, reaching 0.69 after 7 days. The results showed that the k and n were 0.23 d^{-1} and 0.78, respectively. Recrystallization kinetics data of the rice starch samples fitted well with Avrami equation with the correlation coefficient R^2 values is 0.9938. This indicated that the rate of retrogradation of rice starch was lower after IECT when compared to other reports. Ottenhof et al. (2005) and Bello-Pérez et al. (2005) reported the retrogradation plateau reached 0.66, 0.70, 0.60, 0.84 (the ratios of heights) corresponding to 5 h, 10 h, 20 h, and 8 h for potato starch, waxy maize starch, wheat starch and banana starch after extrusion cooking, respectively. However, the time taken to reach the same FTIR absorbance ratio was 7 days after IECT. Furthermore, a good relationship existed between FTIR and DSC results based on the Avrami equation in this study.

3.3. Retrogradation structure and short-range molecular order of retrograded starch

As shown in Fig. 3a (II), the XRD diffractograms acquired for GRS showed an essentially diffused pattern for amorphous materials, as compared to a clear crystallization structure for NRS. The diffractograms of GRS contained a small peak at a Bragg's angle value of 20° superimposed on the diffuse background. This peak was identifiable with the main diffraction peak of the V_h polymorph of crystalline amylose–lipid complex (Kadan & Pepperman, 2002; Wu et al., 2010). As shown in Fig. 3a (I, III), the typical pattern of NRS was an A-pattern whereas the diffraction pattern of RRS was a B-pattern with peaks at 17°, 20° as described by Wu et al. (2010) and Kadan and Pepperman (2002). This indicated that native rice starch crystalline structures had been disrupted during the IECT process. This corresponded with the results of enthalpy change in this study.

The relative crystallinity of retrograded rice starch could be used to reflect the percentage of retrogradation as well. In this study, the relative crystallinity observed from NRS, GRS, and RRS were shown in Table 3. The relative crystallinity of GRS increased from 4.22% to 12.7% for RRS, compared to 31.6% for NRS. The low relative crystallinity of RRS by the X-ray diffractograms agreed well

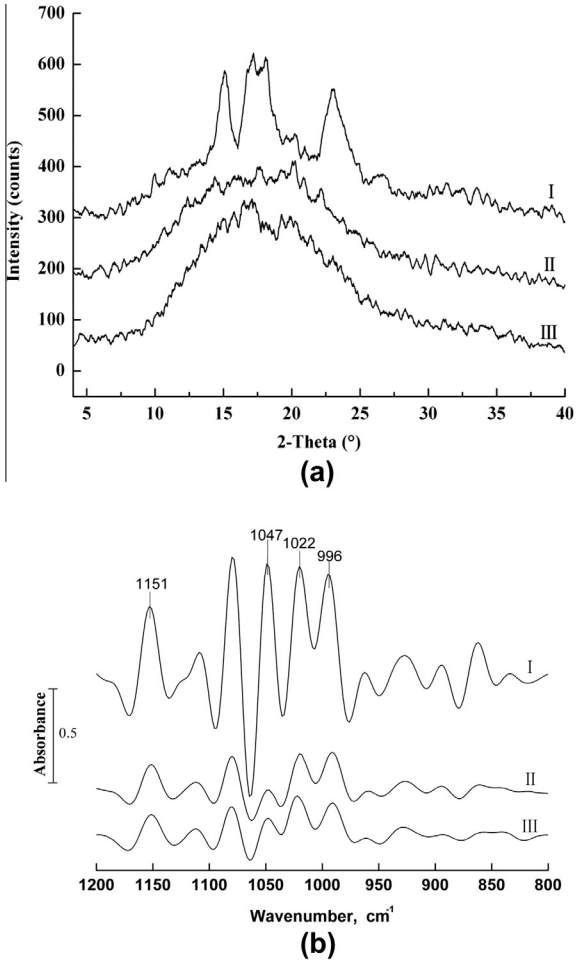

Fig. 3. (a) X-ray diffraction patterns of three samples: NRS (I), GRS (II), RRS (III); (b) FTIR deconvoluted spectra of three samples: (I) NRS (II) GRS (III) RRS.

Table 3
The relative crystallinity and the ordered short-range molecule to amorphous phase.

Samples	Relative crystallinity (%)[a]	(The ordered short-range molecule to amorphous phase)[b]
NRS	31.63 ± 0.24[a]	1.42 ± 0.01[a]
GRS	4.22 ± 0.11[c]	0.32 ± 0.01[c]
RRS	12.68 ± 0.21[b]	0.63 ± 0.02[b]

Values in the same column are considered significantly different at $P < 0.05$.
[a] Data were from X-ray.
[b] Data were based on the ratio of the absorbencies 1047 cm^{-1} and 1022 cm^{-1} from FTIR.

with the low percentage of retrogradation based on DSC data. Meanwhile, the crystallinity of RRS (12.7%) was lower than that of some reports based on different treatment. Khunaea et al. (2007) reported that Chiang rice starch showed 30.3% of relative crystallinity after heat-moisture treatment. Wu et al. (2010) indicated the relative crystallinity of retrograded rice starch was 94.44%, 100.21% and 100% for stirring, heating–stirring and no treatment, respectively. In addition, Ottenhof et al. (2005) reported that the relative crystallinity of retrograded potato starch, waxy maize starch and wheat starch were 36.0%, 24.0%, and 32.0%, respectively, after extrusion cooking.

FTIR had been suggested to be sensitive to the changes of structure on a short-range molecular level. The absorbencies at 1047 cm^{-1} and 1022 cm^{-1} were assigned to the ordered short-range molecule to amorphous phase. The ratio of the heights of the bands at 1047 and 1022 cm^{-1} could be used to express the amount of ordered starch to amorphous starch (Sevenou, Hill, Farhat, & Mitchell, 2002).

The ratios of the band height in the FTIR spectra and the deconvoluted spectra in the range 800–1200 cm^{-1} were showed in Table 3 and Fig. 3b, respectively. Results showed that the heights ratio of NRS was 1.42, which was changed to 0.32 for GRS after IECT. As shown in Fig. 3b (II), when rice starch was gelatinized after IECT, it was initially in a disordered state. The polymer had a spread conformation. According to Wilson et al. (1991), as retrogradation proceeded, the system became more ordered and the range of conformations would be reduced, resulting in a smaller distribution of bond energies compared with the initial state. Hence, as shown in Fig. 3b (III), the band-narrowing was observed for RRS after 7 days of retrogradation. The ratio of the band height for RRS (0.63) was significantly lower than that of NRS (1.42). It was indicated that IECT destroyed the crystalline structure of NRS, leading to lower amounts of ordered starch, even though retrogradation took place in the case of RRS. Those results were in accordance with the DSC data obtained. Meanwhile, RRS (0.63) was lower than that of some results. For example, Ji, Zhu, Zhou, and Qian (2010) indicated that the retrogradation ratio of the heights of rice starch was from 0.87 to 0.90 corresponding 1 day to 5 days. Khunaea et al. (2007) showed that the ratio of the heights of rice starch was from 0.67 to 0.69 after heat moisture treatment. The change of ordered to amorphous starch explains the DSC results that rice starch showed a low percentage of retrogradation during storage after IECT.

In this work the reason why the IECT can improve the retrogradation character of starch efficiently is probably that the structure of rice starch was changed. The character of starch depends on its structure. First, the rice starch that with high moisture contents during IECT would soften the amylopectin molecular structure. Second, the big shear stress in IECT probably induced the breakdown of the starch molecules. These structure changes may destroy the native rice starch crystalline structures, which resulted in the pattern of rice starch changed from A-type to amorphous and B-type from XRD diffractograms, respectively, and the relative crystallinity was low after the IECT process. In addition, these structure changes may destroy the ordered structure of rice starch, leading to lower amounts of ordered starch. We will further study the effect of IECT on the properties of the starch based on structure changes including degree of polymerization and molecular weight distribution of starch in details.

4. Conclusion

The retrogradation behaviour of rice starch containing high amylose treated by IECT was investigated by morphology, retrogradation enthalpy, percentage of retrogradation, relative crystallinity and FTIR absorbance ratio. The results indicated that rice starch with high amylose retrogrades during storage after IECT gelatinization. The percentage of retrogradation turned out to be low. During storage, the rate of retrogradation of rice starch was low whereas Avrami exponent was found to be high. Furthermore, the pattern of rice starch changed from A-type to amorphous and B-type after IECT and the retrogradation process, respectively. The results of XRD and FTIR confirmed this retrogradation behaviour. The retrogradation behaviour after IECT treatment has been compared to literature data of other physical methods. These results demonstrates that IECT is an applicable and promising technique for preparing rice starch products with low percentage of retrogradation and low rate of retrogradation in the food industry.

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