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COMBINED EFFECTS OF FREEZING AND STORAGE CONDITIONS ON THE STALING OF COOKED RICE

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ABSTRACT The effects of freezing and storage temperatures on starch retrogradation and textural properties of cooked rice were evaluated. Cooked rice was frozen with different freezing rates and then stored at 4ºC for 14 days or -18 ºC for up to 7 months. Starch retrogradation enthalpy (ΔH_r) of cooked rice was determined by a differential scanning calorimetry, and textural properties were determined by a texture analyser. The results showed that the ΔH_r and hardness values had a negative correlation with freezing rate, however, a positive correlation was found between adhesiveness and freezing rate. On the other hand, the advantages (lower hardness and higher adhesiveness, less starch retrogradaton) of cooked rice gained by rapid freezing, were lost quickly in the first 3 days of storage at 4ºC. However, rapid freezing combined with -18ºC frozen storage can effectively retard starch retrogradation and maintain the textural properties of cooked rice for at least 7 months. Therefore, high quality cooked rice can be produced by combined rapid freezing with frozen storage.

Keywords: Freezing, Storage, Retrogradation, Texture, Cooked rice.

INTRODUCTION In recent years, the ready-meals market has grown significantly in developed or developing countries, and many ready to eat meals including cooked rice have been developed (Zhang & Sun, 2006; Ma & Sun, 2009; Yu et al., 2009; Yu et al., 2010). Freshly cooked rice are soft, pliable and elastic, but when stored they stale within a few hours and become tough and rigid. In less than 3 days the shelf-life of cooked rice presents a major problem and can be costly to the producer, distributor, consumer and the country in general. The short shelf-life of cooked rice, which is mainly due to staling, i.e. starch retrogradation, increased hardness or decreased adhesiveness, is a serious problem. Concerning the preservation technologies applied to ready to eat meals, freezing has been recognized as an excellent method of preserving the quality characteristics of foods (Kock et al., 1995; Reid, 1998) and extending their shelf-life.

Some of the recent studies have reported on the effects of freezing on bread quality and staling properties (Bárcenas et al., 2003; Bárcenas & Rosell, 2006; Yi & Kerr, 2009). Rapid freezing resulted in a less structure changes and less retrogradation of starch or starchy foods than slow freezing (Navarro et al., 1995; Kock et al., 1995; Ferrero & Zaritzky, 2000; Varavinit et al., 2002; Muadklay & Charoenrein, 2008; Olivera & Salvadori, 2009). However, the rate of starch retrogradation is influenced by the cooling rate before storage at temperatures for frozen foods, rapid cooling rate contributed to higher rice starch retrogradation (ΔH_r) than slow cooling rate during storage (Hsu, 1998; Hsu & Heldman, 2005). On the other hand, storage temperature and time also have significant effects on the quality of starchy foods. Kock et al. (1995) reported that the slight advantage of non-cellu1ar starchy product by rapid freezing was lost during storage, and cooked rice hardness increased and stickiness decreased at lower temperatures and longer storage (Perdon et al., 1999). Retrogradation enthalpy of bread increased during frozen storage (Bárcenas et al., 2003; Ribotta et al., 2003), and the hardening rate of bread depended on frozen storage time during aging (Bárcenas & Rosell, 2006). Based on the literatures cited above, freezing rate and storage temperature and time have significant effects on the starch retrogradation and textural properties of starchy foods.

However, the effects of storage temperatures (Perdon et al. 1999), cooling methods (Zhang & Sun, 2006) and cooling rates (Ma & Sun, 2009; Yu et al., 2010) on the quality of cooked rice have been studied, less is known about the effects of freezing rate and storage temperatures on the starch retrogradation and textural properties of cooked rice. Therefore, the objective of the current study was to examine the impacts of freezing rate and storage temperatures on the starch retrogradation and textural properties of cooked rice during storage.

MATERIALS AND METHODS

Materials A Japonica milled rice (medium grains) was used in this study. The rice used for production of cooked rice was analyzed for amylose, amylopectin, protein, lipid and moisture contents by the methods of Yu et al. (2009). The rice had amylose, amylopectin, protein, lipid and moisture contents of 15.78±1.08, 64.12±1.58, 6.93±0.24, 1.44±0.40 and 12.73±0.16 g/100g, respectively.

Rice cooking Cooking of the rice was conducted with an automatic rice cooker (CFXB4003-A1, 4.0L, 700W, 220V, 50Hz, Guangzhou Domestic Appliance Ltd., China). 800g rice was soaked in a pot for 30 min with 1,040 ml of tap water. After the rice cooked for 20 min, the thermostat coupled with micro-switch automatically switched off the cooker. The cooked rice samples were held in the rice cooker for an additional 15min. Finally, about 1,300 g cooked rice was removed from the rice cooker to a stainless steel tray (300*300*20, mm) for freezing to the centre temperature of cooked rice piles to less than -18℃. To avoid the difference of freezing, the cooked rice in the centre layer of the tray was taken out, packaged in polyethylene bags and sealed for experiments.

Freezing system The cooked rice was frozen with two systems: (i) a -20 ℃ refrigerator (KK28E76, Siemens, Germany), and (ii) a freezing system with a cryogenic cabinet (SLX-30, Technical Institute of Physics and Chemistry of CAS, China) as reported in the previous study (Yu et al., 2010), which operates with liquid N_2 creating a cold atmosphere at -30, -40, -60, -100 ℃. The low temperatures were measured by one T type thermocouple (Pt100.0, Baite F&R Technology Co. Ltd, China), and controlled by bursting liquid N_2 at intervals. The low temperature gas was blasted by an electric fan at air velocity of 1.6 m/s. All of the procedures and temperatures were controlled by a computer. In each experimental procedure, sample temperatures were recorded at an interval of 2.0 s using ten T type thermocouples which were connected to a data acquisition program.

Freezing rate Freezing rates (FR) were determined according to Eq. (1), based on the definition given by the International Institute of Refrigeration (1986) and the report (Olivera & Salvadori, 2009):

$$FR = \frac{T_2 - T_1}{t_2 - t_1} \qquad (1)$$

where T_1 is the initial freezing temperature, T_2 is the final freezing point (-18℃), and (t_2 - t_1) is the time elapsed between the beginning and the end of freezing.

Cooked rice storage Both chill storage and frozen storage were used. In chill storage, the cooked rice samples were frozen and then stored in a refrigerator at 4±1 ℃ for 0, 1, 3, 7, 11 and 14 days, while in frozen storage, the samples were stored in a refrigerator at -18±1℃ for 0, 1, 2, 3, 4, 5, 6 and 7 months. For measuring the texture of the stored samples, the sealed bags of cooked rice were taken out at different storage times, and allowed to equilibrate for 1.5~2.0 h at 22±0.2 ℃ in an incubator before texture determination. All the experiments were performed in triplicate.

Textural profile analysis Textural profile analysis (TPA) of the cooked rice was performed using a texture analyser (TA.XT.plus, Texture Technologies Corp., UK) with a 50 kg load cell using a two-cycle compression. The analyser was linked to computer that recorded the data via a software program called Texture Expert Excede Version 1.0 (Stable Micro Systems Software). A two-cycle compression force versus time program was used to compress the samples till 90% of the original cooked grain thickness before returning to the original position and compressing again. A 6-mm diameter ebonite probe was used to compress 3 grains, with pre-test speed of 1.0 mm/s, test speed and post-test speed of 0.5 mm/s. Parameters recorded from the test curves were hardness and adhesiveness. All textural analyses were replicated ten times and results were presented as mean values.

Differential scanning calorimetry Starch retrogradation properties of cooked rice were analyzed by a Perkin Elmer pyris 6 differential scanning calorimeter (DSC) (Perkin Elmer, USA). The DSC was calibrated with indium (melting point =156.6℃, ΔH_f =28.6 J/g) and an empty pan was used as a reference. The cooked rice samples were prepared using the methods of Kim et al. (1997) and Yu et al. (2009, 2010). After textural properties determination, the samples of cooked rice was mixed with 99 % ethanol (1:4, v/v) and dehydrated for 12 h. Then the mixture was passed through a Büchner funnel, and dried at 37 ℃ in an air oven for 24 h. The dried cooked rice was passed through a 100-mesh (0.147 mm) sieve after milling by a universal high-speed smashing machine (FW80-1, Tianjin Taisite Instrument Co. Ltd, China). A total weight of 4.0 mg cooked rice samples (dry basis) and distilled water (1:2, w/w) was placed in pre-weighed aluminum sample pans (PE0219-0062). The pans were sealed hermetically to prevent moisture loss and kept overnight. For all DSC runs, a sealed empty aluminum pan was used as reference. The sample was held isothermally at 20℃ for 1 min before being heated from 20 to 140 ℃ at 10 ℃/min. The peak temperature and the enthalpy (ΔH_r, J/g) associated with the retrograded starch melting peak appearing between 40 and 70 ℃ were calculated. The ΔH_r is used to indicate the enthalpy of amylopectin starch retrogradation. The DSC measurements were performed in triplicate. The results were presented as mean values.

Statistical analysis All tests were performed at least in triplicate. Variance analysis (ANOVA) and Duncan multiple-range test were performed by the procedure of SAS 8.0 (SAS Institute, Cary, NC, USA).

RESULTS AND DISCUSSION

Freezing of cooked rice Cooked rice samples were subjected to different freezing conditions to obtain freezing rates ranging from slow to fast freezing. Fig. 1 showed a typical temperature-time freezing curve obtained experimentally for different freezing rates (0.09, 0.26, 0.33, 0.53 and 1.45℃/min). The characteristic freezing time t_{cf} ranged from 12.79 to 190.00 min, and the freezing rates ranged from 1.45 ℃/min to 0.09 ℃/min, as shown in Table 1.

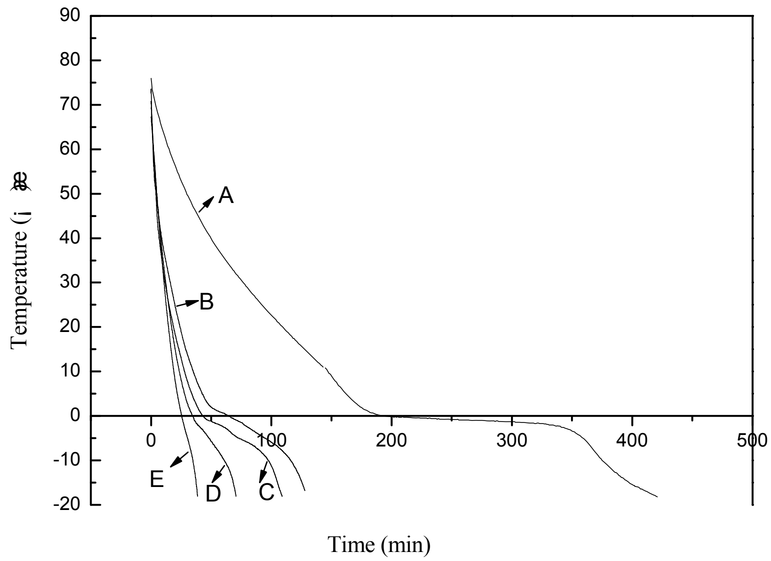

Figure 1. Freezing curve of cooked rice at different freezing conditions A: Freezing in refrigerator (-20□); B: Freezing at -30□; C: Freezing at -40□; D: Freezing at -60□; E: Freezing at -100□.

Moisture content The moisture of cooked rice frozen with different freezing rates was shown in Table 1. The moisture content of cooked rice was 58.61 to 62.36 g/100g. There was significant difference between the slow freezing (0.09 □/min) and rapid freezing (1.45□/min) (P<0.05). These values confirm the influence of freezing rate on the quality of the product: the moisture content of cooked rice frozen with fast freezing (1.45 □/min) does not differ from the initial value (fresh cooked rice); the moisture content of the samples frozen in slow freezing rate (0.09 □/min) are significantly lower than their initial value. This weight loss is probably due to water evaporation, much more water evaporated with low freezing rate, because of longer freezing time. Another possible explanation for this is that during the slow freezing, cellular structures are damaged, and therefore more water is able to migrate to the outside of the product during thawing. Rapid freezing produces a large number of very small ice crystals, with less damage to the cellular structure, however, slow freezing promoted large ice crystals, and more damage occurs to the cellular structure. The results were very similar to those of cooked organic pasta frozen with slow and rapid freezing rates (Olivera & Salvadori, 2009).

Table 1. Freezing time, freezing rate and moisture content of cooked rice at different freezing conditions.

Freezing conditions	Freezing time (min)	Freezing rate (℃/min)	Moisture (%, w.b.[z])
-20℃	190.00±3.25[a]	0.09±0.02[e]	58.61±0.33[d]
-30℃	70.50±0.73[b]	0.26±0.0 1[d]	60.10±0.35[c]
-40℃	60.40±3.30[c]	0.33±0.01[c]	60.41±0.42[c]
-60℃	35.00±2.50[d]	0.53±0.02[b]	61.27±0.22[b]
-100℃	12.79±2.10[e]	1.45±0.01[a]	62.36±0.35[a]
	Fresh cooked rice		62.98±0.21[a]

[a,b,c,d,e] Means in the same column followed by the same lowercase superscript letters are not different (P>0.05). [z] Means: w.b.= Wet basis.

Effects of freezing rates on starch retrogradation and texture of cooked rice during chill storage Frozen samples were stored for 0~14 days in order to analyze starch retrogradation during chill storage at 4 ℃. Retrogradation properties were studied by analyzing the melting endotherm of recrystallized amylopectin by DSC and results were shown in Fig. 2 and Fig. 3. There were no significant differences in onset, peak and conclusion temperatures for different rates at the same storage time except with freezing rate of 0.09 ℃/min (P>0.05). The mean melting onset, peak and conclusion temperatures of frozen cooked rice decreased within 3 days storage (P<0.05), and they were not significantly different during the last 11 days of storage (P>0.05). However, the value of onset, peak and conclusion temperature of cooked rice frozen with 0.09 ℃/min were lower than other freezing rates (0.26, 0.33, 0.53 and 1.45 ℃/min, respectively) within 3 days of storage, there were not significant differences of all freezing rates during the last 11 days of storage. These results indicated that the onset, peak and conclusion temperatures were not significantly affected by freezing rates except the rate of 0.09 ℃/min. However, the onset, peak and conclusion temperatures of cooked rice were higher than the results of Yu et al. (2009) without freezing. An explanation is that the differences may be caused by rice varieties, or by the freezing process which formed ice crystals in frozen cooked rice, possibly leading to the damage of the gel structure of cooked rice grains when thawing at 4 ℃, thus resulting in the onset, peak and conclusion temperature differences between freezing and cooling cooked rice.

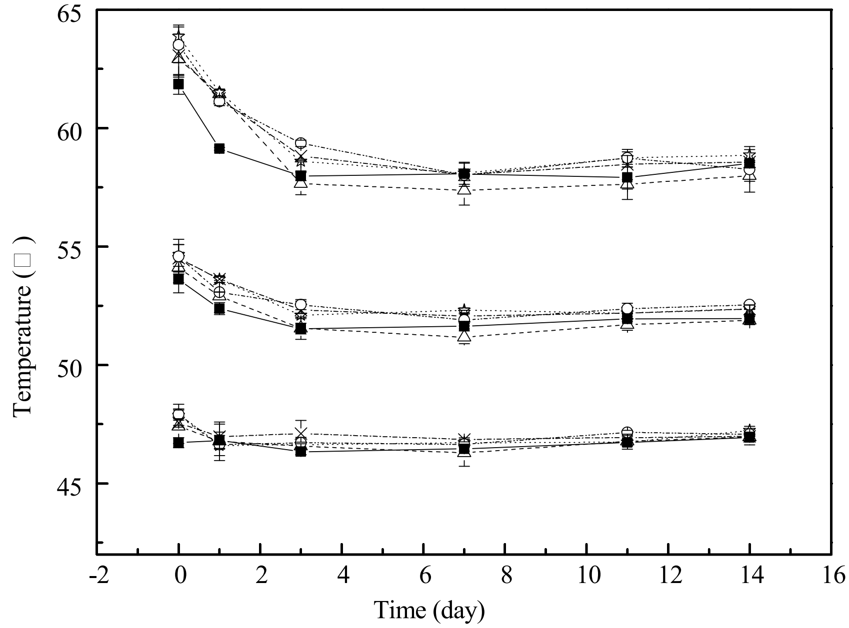

Figure 2. Onset (lower), peak (middle) and conclusion (upper) temperatures of retrogradation melting endotherm of cooked rice freezing with different freezing rates when chill storage at 4 □. (—■—) 0.09 □/min, (…Δ…) 0.26□/min, (…□…) 0.33□/min, (…□…) 0.53 □/min and (…○…) 1.45□/min.

Amylopectin retrogradation enthalpy (ΔH_r) of cooked rice was shown in Fig. 3. Most recrystallization of cooked rice occurred during the first 3 days of storage. The retrogradation process continued up to 7 days and then slowed down during the last 7 days of storage, and the retrogradation process finished within 14 days. The ΔH_r of cooked rice increased with decrease of freezing rate within 3 days of storage. This results suggested that frozen cooked rice retrograded much more slowly with fast freezing than slow freezing (0.09 □/min) when chill storage for less than 3 days. Fast freezing probably took the starchy food through the temperature zone of maximum staling faster than slow freezing, so the slow freezing had higher retrogradation enthalpy than fast freezing (Kock et al. 1995). And fast freezing produced a large number of very small ice crystals (Olivera & Salvadori, 2009), these small ice crystals produced faster thawing, therefore, the frozen cooked rice which contained small ice crystals will thaw quicker and pass through the zone of maximum retrogradation faster than slow frozen cooked rice, thereby minimizing starch retrogradation during less than 3 days chill storage. Results of this study suggested that freezing rates have significant effects on starch retrogradation in a short period of chill storage, but have no significant effects during a long period of chill storage at 4□.

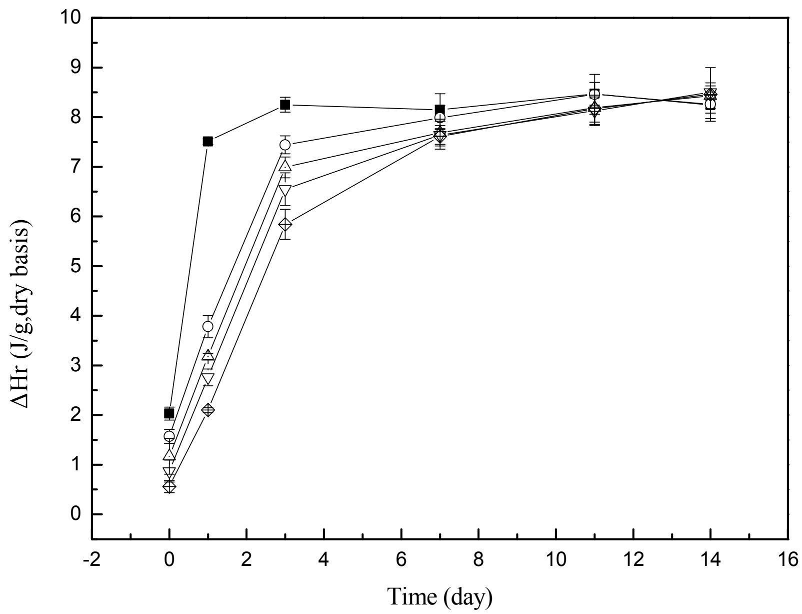

Figure 3. Retrogradation enthalpy of cooked rice freezing with different freezing rate when chill storage at 4 □. (—■—) 0.09 □/min, (—○—) 0.26 □/min, (—Δ—) 0.33 □/min, (—□—) 0.53□/min and (—◊—) 1.45□/min. ΔH_r: Amylopectin retrogradation enthalpy.

Cooked rice, which was frozen with different freezing rates and stored at 4 □ for 0 ~14 days, was evaluated for textural properties using a texture analyser. Results of two major textural parameters (hardness and adhesiveness) were shown in Table 2 and Table 3.

Table 2. Hardness (N) of cooked rice freezing at different freezing rates and storage at 4□ for 0, 1, 3, 7, 11 and 14 days.

Freezing rate (□/min)	Storage time (day)					
	0	1	3	7	11	14
0.09	68.61 ±1.16^{a,C}	74.57 ±2.16^{a,B}	94.06 ±3.13^{ab,A}	95.67 ±2.33^{a,A}	95.47 ±3.62^{a,A}	95.58 ±1.94^{a,A}
0.26	65.24 ±1.27^{b,D}	71.96 ±1.76^{a,C}	92.85 ±2.08^{b,B}	96.40 ±1.74^{a,A}	95.65 ±1.64^{a,A}	95.22 ±1.15^{a,A}
0.33	61.93 ±1.59^{b,D}	70.22 ±2.58^{a,C}	92.03 ±2.41^{b,B}	94.73 ±2.32^{a,A}	95.14 ±3.74^{a,A}	96.31 ±2.32^{a,A}
0.53	60.55 ±1.02^{bc,D}	66.33 ±1.81^{b,C}	90.60 ±2.28^{b,B}	94.73 ±1.67^{a,A}	96.00 ±2.26^{a,A}	96.50 ±2.07^{a,A}
1.45	58.72 ±1.97^{c,D}	63.73 ±1.87^{c,C}	85.81 ±2.48^{c,B}	93.43 ±2.64^{a,A}	95.44 ±1.93^{a,A}	96.80 ±2.91^{a,A}

^{A,B,C,D} Numbers followed by the same uppercase superscript letters in the same row are not different (P>0.05); ^{a,b,c} Means in the same column followed by the same lowercase superscript letters are not different (P>0.05).

The hardness of cooked rice increased rapidly within 3 days storage (*P*<0.05), and the increase slowed down from 3 to 14 days (*P*>0.05). Most of the loss of texture occurred during the first 7 days of storage, and there was no significant difference in the last 7 days of storage. Cooked rice frozen with slow rate (0.09 □/min) had a higher hardness of 68.61 N than frozen with fast rate (1.45□/min) of 58.72 N. Results of these indicated that freezing rate determined the hardness of frozen cooked rice for less than 7 days chill storage. Furthermore, the hardness of cooked rice increased continually with the amylopectin retrogradation during storage. This finding was in agreement with the research of Perdon et al. (1999) and Yu et al. (2009), who reported that starch retrogradation resulted in an increased hardness of cooked rice during storage. On the other hand, it seemed that rapid freezing retarded starch retrogradation and decreased the hardness of cooked rice during less than 3 days storage.

Table 3. Adhesiveness (N.s) of cooked rice freezing at different freezing rates and storage at 4 ℃ for 0, 1, 3, 7, 11 and 14 days.

Freezing rate (℃/min)	Storage time (day)					
	0	1	3	7	11	14
0.09	5.60 $\pm 0.54^{d,A}$	0.08 $\pm 0.02^{c,B}$	0.03 $\pm 0.01^{c,C}$	0.03 $\pm 0.01^{d,C}$	0.02 $\pm 0.01^{c,C}$	0.02 $\pm 0.01^{b,C}$
0.26	6.70 $\pm 0.20^{c,A}$	3.47 $\pm 0.54^{b,B}$	0.05 $\pm 0.02^{c,C}$	0.02 $\pm 0.01^{d,D}$	0.02 $\pm 0.01^{c,D}$	0.02 $\pm 0.01^{b,D}$
0.33	6.95 $\pm 0.44^{bc,A}$	3.88 $\pm 0.79^{ab,B}$	0.24 $\pm 0.07^{b,C}$	0.10 $\pm 0.01^{c,D}$	0.07 $\pm 0.02^{b,DE}$	0.06 $\pm 0.02^{a,E}$
0.53	7.29 $\pm 0.19^{b,A}$	3.89 $\pm 0.40^{ab,B}$	0.30 $\pm 0.06^{ab,C}$	0.15 $\pm 0.04^{b,D}$	0.06 $\pm 0.02^{b,E}$	0.06 $\pm 0.02^{a,E}$
1.45	7.84 $\pm 0.59^{a,A}$	4.41 $\pm 0.20^{a,B}$	0.58 $\pm 0.17^{a,C}$	0.22 $\pm 0.03^{a,D}$	0.10 $\pm 0.02^{a,E}$	0.07 $\pm 0.02^{a,E}$

^{A,B,C,D,E} Numbers followed by the same uppercase superscript letters in the same row are not different (P>0.05); ^{a,b,c,d} Means in the same column followed by the same lowercase superscript letters are not different (P>0.05).

As shown in Table 3, the adhesiveness values of cooked rice ranged from 0.02 N.s to 7.84 N.s with different freezing rates during chill storage for 0~14 days. Fresh cooked rice (storage 0 day) frozen with a rapid freezing rate (1.45 ℃/min) was observed to have higher adhesiveness (7.84 N.s) than other freezing rates. Most decrease in adhesiveness values occurred within 3 days storage. The adhesiveness decrease continued up to 7 days and then slowed down during the last 7 days. Amylose retrogradation and amylopectin retrogradation contributed to the adhesiveness decreased during storage (Yu et al., 2009). The faster the freezing rates, the less freezing time and starch retrogradation. Therefore, the cooked rice frozen with fast freezing rates showed higher adhesiveness values than that with slow freezing rates. These results indicated that freezing rate affect the texture of cooked rice. Two possibilities exist which can explain the differences of hardness between slow and fast freezing rates. Firstly, starch retrogradation contributes to the hardness differences. Fast freezing took the starchy foods through the temperature zone of maximum staling faster than slow freezing (Kock et al. 1995), so much more starch retrogradation occurs during slow freezing process with higher hardness and lower adhesiveness values of cooked rice. Secondly, the hardness differences can be caused by structure damage due to the formation of ice crystals. Fast freezing produces a large number of very small ice crystals (Olivera & Salvadori, 2009), these small ice crystals permit faster thawing, therefore, the frozen cooked rice which contain small ice crystals will thaw quicker and pass through the maximum retrogradation zone faster than slow frozen cooked rice, thereby minimizing starch retrogradation. The adhesiveness differences maybe attribute to amylose and amylopectin retrograation, which had reported in the previous study (Yu et al., 2009). Furthermore, rice retrogradation maby be caused by glass-trasition temperature (T_g), molecular molility above T_g is higher and caused higher rates of water diffusion and accelerated starch retrogradation during storage (Hsu & Heldman, 2005). However, freezing rates had no effects on the finally starch retrogradation enthalpy and the texture of cooked rice during storage 4 for a long storage time.

Effects of freezing rates on starch retrogradation of cooked rice during frozen storage The retrogradation enthalpy (ΔH_r) of the amylopectin was measured in the cooked rice after 0~7 months of frozen storage at -18 . Results of mean melting onset, peak, conclusion temperatures and ΔH_r were shown in Fig. 4 and Fig. 5. The onset, peak and conclusion temperatures of cooked rice were not significantly different among different freezing rates after 0~7 months of frozen storage at -18 ($P>0.05$). The amylopectin retrogradation enthalpy of cooked rice increased gradually from 0 to 7 months of frozen storage (Fig. 5). These results were different from those with bread during frozen storage (Bárcenas et al., 2003; Bárcenas & Rosell, 2006), who reported that there were no amylopectin retrogradation in bread during frozen storage. However, Perdon et al. (1999) found that starch retrogradation enthalpy of cooked rice increased with storage time when stored at -13 . The differences of starch retrogradation of bread and cooked rice may be due to the different compositions and starch structures and processing methods between bread and cooked rice.

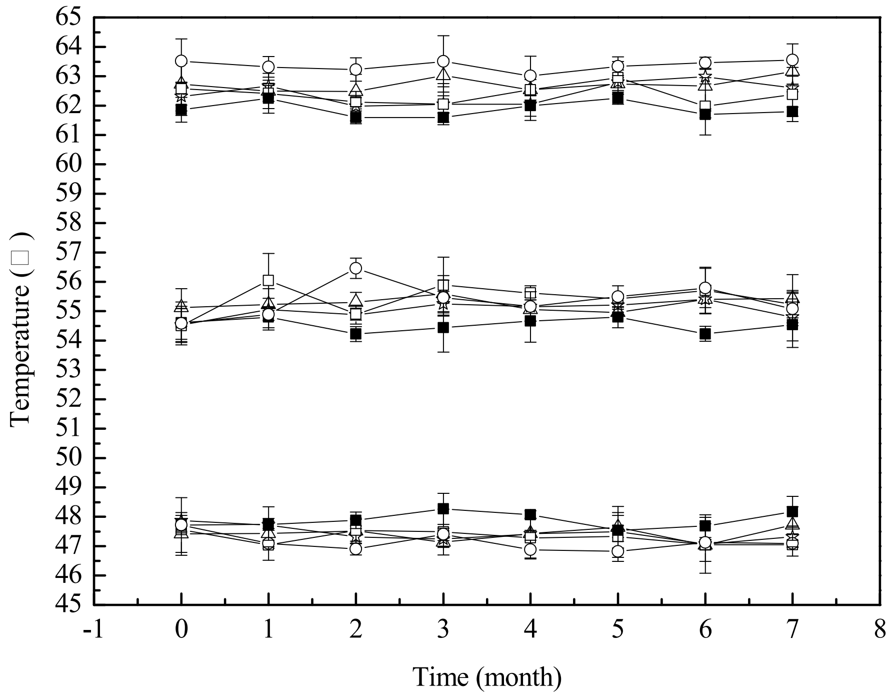

Figure 4. Onset (lower), peak (middle) and conclusion (upper) temperatures of retrogradation melting endotherm of cooked rice freezing with different freezing rate when frozen storage at -18 □. (—■—) 0.09 □/min, (—Δ—) 0.26 □/min, (—□—) 0.33 □/min, (—□—) 0.53□/min and (—○—) 1.45□/min.

The ΔH_r value was the highest when frozen with the freezing rate of 0.09 □/min, because a longer freezing time was needed and more starch retrograded during the freezing process. However, the ΔH_r value was the lowest when cooked rice frozen with freezing rate of 1.45 □/min, because of shorter freezing time and less starch retrogradation. Moreover, the ΔH_r values were not significantly different between freezing rate of 0.26 and 0.53 □/min after 5 months of frozen storage. These results suggested that slow freezing rates (0.09 □/min) increased the starch retrogradation and higher freezing rates (1.45 □/min) retarded starch retrogradation during frozen storage. These results were in agreement with the research (Varavinit et al., 2002) who reported that quick freezing retard retrogradation of starch gel, because the freezing rate was too fast for the starch molecules to reorient to form the precipitate or the hard gel.

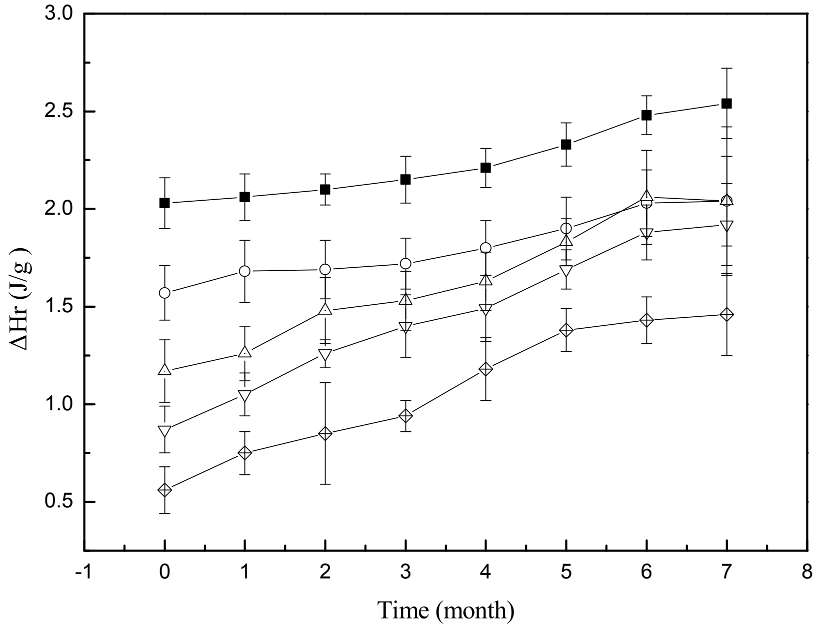

Figure 5. Retrogradation enthalpy of cooked rice freezing with different freezing rate when frozen storage at -18 □. (—■—) 0.09 □/min, (—○—) 0.26 □/min, (—Δ—) 0.33 □/min, (—□—) 0.53□/min and (—◊—) 1.45□/min. ΔH_r: Amylopectin retrogradation enthalpy.

Cooked rice frozen and stored for 0~7 months was evaluated at intervals for textural properties using a texture analyzer. Results of two major textural parameters (hardness and adhesiveness) were shown in Table 4 and Table 5. The hardness values were not significantly different between the cooked rice processed with freezing rates of 0.26 and 0.53 □/min after 5 months frozen storage (*P*>0.05). The hardness of cooked rice increased continually with the amylopectin retrogradation during frozen storage. The amylopectin retrogradation contributed to the hardness increase during storage. This was in agreement with the research of Perdon et al. (1999) and Yu et al. (2009). On the other hand, it seemed that rapid freezing (1.45 □/min) retarded starch retrogradation and decreased the hardness of cooked rice during storage. Higher freezing rates resulted in lower starch retrogradation enthalpy and hardness values.

Table 4. Hardness (N) of cooked rice freezing at different freezing rates and frozen storage at -18 ℃ for 0, 1, 2, 3, 4, 5, 6 and 7 months.

Freezing rate	Storage time (months)							
(℃/min)	0	1	2	3	4	5	6	7
0.09	$68.61\pm 1.16^{a,B}$	$70.30\pm 1.74^{a,A}$	$71.26 \pm 1.62^{a,A}$	$71.76\pm 1.64^{a,A}$	$72.03\pm 1.52^{a,A}$	$71.94\pm 1.94^{a,A}$	$73.22\pm 1.62^{a,A}$	$73.04\pm 1.74^{a,A}$
0.26	$65.24\pm 1.27^{b,B}$	$67.72\pm 1.94^{b,A}$	$68.06\pm 1.89^{a,A}$	$68.52\pm 1.19^{ab,A}$	$68.53\pm 1.21^{ab,A}$	$68.60\pm 1.31^{ab,A}$	$69.79\pm 1.59^{bc,A}$	$69.61\pm 1.33^{bc,A}$
0.33	$61.93\pm 1.59^{b,C}$	$63.93\pm 1.77^{c,BC}$	$64.12\pm 1.57^{b,BC}$	$66.21\pm 1.81^{b,B}$	$66.85\pm 1.56^{ab,B}$	$67.83\pm 1.56^{b,B}$	$69.50\pm 1.62^{bc,A}$	$69.60\pm 1.41^{bc,A}$
0.53	$60.55\pm 1.02^{bc,D}$	$62.76\pm 1.12^{c,CD}$	$63.11\pm 1.86^{b,C}$	$63.59\pm 1.46^{b,C}$	$64.32\pm 1.61^{b,BC}$	$65.30\pm 1.81^{b,B}$	$66.45\pm 2.38^{c,B}$	$67.87\pm 2.72^{c,AB}$
1.45	$58.72\pm 1.97^{c,B}$	$59.28\pm 1.42^{d,B}$	$59.84\pm 2.57^{c,B}$	$60.01\pm 1.39^{c,B}$	$60.64\pm 1.89^{c,B}$	$60.76\pm 1.68^{c,B}$	$59.83\pm 2.94^{d,B}$	$61.30\pm 2.19^{d,AB}$

^{A,B,C,D} Numbers followed by the same uppercase superscript letters in the same row are not different (P>0.05); ^{a,b,c,d} Means in the same column followed by the same lowercase superscript letters are not different (P>0.05).

As shown in Table 5, the adhesiveness values of cooked rice ranged from 3.26 to 7.84 N.s with different freezing rates during frozen storage for 0~7 months. Most adhesiveness values decrease occurred within 1 month storage. The adhesiveness decrease slowly continued up to 7 month. Cooked rice frozen with rapid freezing rate (1.45 ℃/min) showed higher adhesiveness values than that with slow freezing rate (0.09 ℃/min). These results indicated that most adhesiveness decreased within 1 month, this is caused by amylose retrogradation, it is confirmed by the report of Yu et al. (2009). And the adhesiveness continue decreased slowly up to 7 months, which are mainly caused by amylopectin retrogradation, these conclusions are accordance with the results of Fig. 5.

Table 5. Adhesiveness (N.s) of cooked rice freezing at different freezing rates and frozen storage at -18 ℃ for 0, 1, 2, 3, 4, 5, 6 and 7 months.

FR	Storage time (months)							
℃/min	0	1	2	3	4	5	6	7
0.09	5.60± $0.54^{d,A}$	3.94± $0.36^{d,B}$	3.51± $0.46^{d,BC}$	3.36± $0.47^{c,C}$	3.40± $0.40^{c,C}$	3.36± $0.36^{c,C}$	3.31± $0.45^{c,C}$	3.26± $0.40^{c,C}$
0.26	6.70± $0.20^{c,A}$	5.98± $0.38^{c,B}$	5.96± $0.22^{c,B}$	5.93± $0.39^{b,B}$	5.92± $0.40^{b,B}$	5.94± $0.30^{b,B}$	5.91± $0.43^{b,B}$	5.95± $0.38^{b,B}$
0.33	6.95± $0.44^{bc,A}$	6.27± $0.20^{bc,B}$	6.35± $0.36^{bc,B}$	6.13± $0.34^{b,B}$	6.10± $0.50^{bc,B}$	6.12± $0.43^{b,B}$	6.11± $0.25^{b,B}$	6.12± $0.42^{b,B}$
0.53	7.29± $0.19^{ab,A}$	6.53± $0.44^{ab,B}$	6.54± $0.25^{ab,B}$	6.53± $0.21^{ab,B}$	6.45± $0.41^{ab,B}$	6.50± $0.35^{ab,B}$	6.40± $0.37^{ab,B}$	6.44± $0.26^{ab,B}$
1.45	7.84± $0.59^{a,A}$	6.82± $0.46^{a,B}$	6.77± $0.34^{a,B}$	6.73± $0.17^{a,B}$	6.70± $0.38^{a,B}$	6.67± $0.27^{a,B}$	6.74± $0.49^{a,B}$	6.75± $0.43^{a,B}$

^{A,B,C} Numbers followed by the same uppercase superscript letters in the same row are not different (P>0.05); ^{a,b,c,d} Means in the same column followed by the same lowercase superscript letters are not different (P>0.05).

CONCLUSION Freezing rates and storage temperatures significantly affected the starch retrogradation and textural properties of cooked rice. The textural properties (hardness and adhesiveness) of cooked rice correlated with freezing rates and starch retrogradation. The cooked rice processed with higher freezing rates was observed to have a lower hardness and higher adhesiveness. Slow freezing rate (0.09 ℃/min) processing increased cooked rice staling during freezing, and rapid freezing rate (1.45 ℃/min) processing can produce a better quality of cooked rice during freezing process. Rapid freezing (1.45 ℃/min) combined with frozen storage at -18℃ can effectively retard starch retrogradation and maintain the texture properties of cooked rice for at least 7 months. However, if the freezing rates of frozen cooked rice were 0.26~0.53 ℃/min, the initial advantage (lower hardness and higher adhesiveness value) gained by rapid freezing were lost during long time frozen storage. Furthermore, the slight advantages (lower hardness and higher adhesiveness value) gained by rapid freezing of the cooked rice, is lost very quickly during chill storage at 4 ℃. Therefore, rapid freezing combined with frozen storage at -18℃ can produce a high quality of cooked rice for at least 7 months. These findings, if generally applicable to cooked rice products, could have important quality and economic implications for the convenience of the food industry.

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REFERENCES

Bárcenas, M. E., M. Haros, C. Benedito, and C. M. Rosell. 2003. Effect of freezing and frozen storage on the staling of part-baked bread. Food Research International 36: 863-869.

Bárcenas, M. E., and C. M. Rosell. 2006. Effect of frozen storage time on the bread crumb and aging of par-baked bread. Food Chemistry 95:438-445.

Brown, M. H. 1991. Microbiological aspects of frozen foods. In W.B Bald (Ed.), Food Freezing: Today and Tomorrow (pp. 15-25). London: Springer.

Ferrero, C., and N. E. Zaritzky. 2000. Effect of freezing rate and frozen storage onstarch–sucrose–hydrocolloid systems. Journal of the Science of Food and Agriculture 80: 2149-2158.

Hsu, C.-L. 1998. Influence of cooling rate on glass transition temperature and starch retrogradation during low temperature storage. University of Missouri-Columbia, Doctoral paper, pp. 102-112.

Hsu, C.-L., and D. R. Heldman. 2005. Influence of glass transition temperature on rate of rice starch retrogradation during low-temperature storage. Journal of Food Process Engineering 28: 506-525.

International Institute of Refrigeration. Recommendations for the processing andhandling of frozen foods, third ed. IIR, Paris. pp. 32-39.

Kim, J.-O., W.-S. Kim, M.-S. Shin and Kwangiu. 1997. A comparative study on retrogradation of rice starch gels by DSC, X-ray and α-amylase methods. Starch/Stärke 49: 71-75.

Kock, S., D. A. Minnaar, D. Berry, and J. R. N. Talor. 1995. The effect of freezing rate on the quality of cellular and non-cellular par-cooked starchy convenience foods. Lebensmittel-Wissenschaft und-Technologie 28: 87-95.

Ma, Y., and D.-W. Sun. 2009. Hardness of cooked rice as affected by varieties, cooling methods and chill storage. Journal of Food Process Engineering 32: 161-176.

Muadklay, J., and S. Charoenrein. 2008. Effects of hydrocolloids and freezing rates on freeze–thaw stability of tapioca starch gels. Food Hydrocolloids 22: 1268-1272.

Navarro, A. S., M. N. Martino, and N. E. Zaritzky. 1995. Effect of freezing rate on the rheological behaviour of systems based on starch and lipid phase. Journal of Food Engineering 26: 481-495.

Olivera, D. F., and V. O. Salvadori. 2009. Effect of freezing rate in textural and rheological characteristics of frozen cooked organic pasta. Journal of Food Engineering 90: 271-276.

Perdon, A. A., T. J. Siebenmorgen, R. W. Buescher, and E. E. Gbur. 1999. Starch retrogradation and texture of cooked milled rice during storage. Journal of Food Science 64 (5): 828-832.

Reid, D. S. 1998. Over view of physical/chemical aspect of freezing. In: Erickson, M.C., Hung, Y.-C. (Eds.), Quality of Frozen Foods. Chapman Hall, London, pp. 10-28.

Ribotta, P. D., A. E. León, and M. C. Añón. 2003. Effect of freezing and frozen storage on the gelatinization and retrogradation of amylopectin in dough baked in a differential scanning calorimeter. Food Research International 36, 357-363.

Varavinit, S., S. J. Shobsngob, W. Varanyanond, P. Chinachoti, and O. Naivikul. 2002. Freezing and thawing conditions affect the gel stability of different varieties of rice flour. Starch/Stärke 54: 31-36.

Yi, J., and W. L. Kerr. 2009. Combined effects of freezing rate, storage temperature and time on bread dough and baking properties. LWT - Food Science and Technology 42: 1474-1483.
Yu, S. F., Y. Ma, and D.-W. Sun. 2009. Impact of amylose content on starch retrogradation and texture of cooked milled rice during storage. Journal of Cereal Science 50: 139-144.
Yu, S. F., Y. Ma, T.Y. Liu, L. Menager, and D.-W. Sun. 2010. Impact of cooling rates on the staling behaviour of cooked rice during storage. Journal of Food Engineering 96: 412-420.
Zhang, Z. H., and D.-W. Sun. 2006. Effects of cooling methods on the cooling efficiency and quality of cooked rice. Journal of Food Engineering 77: 269-274.

APPENDIX A

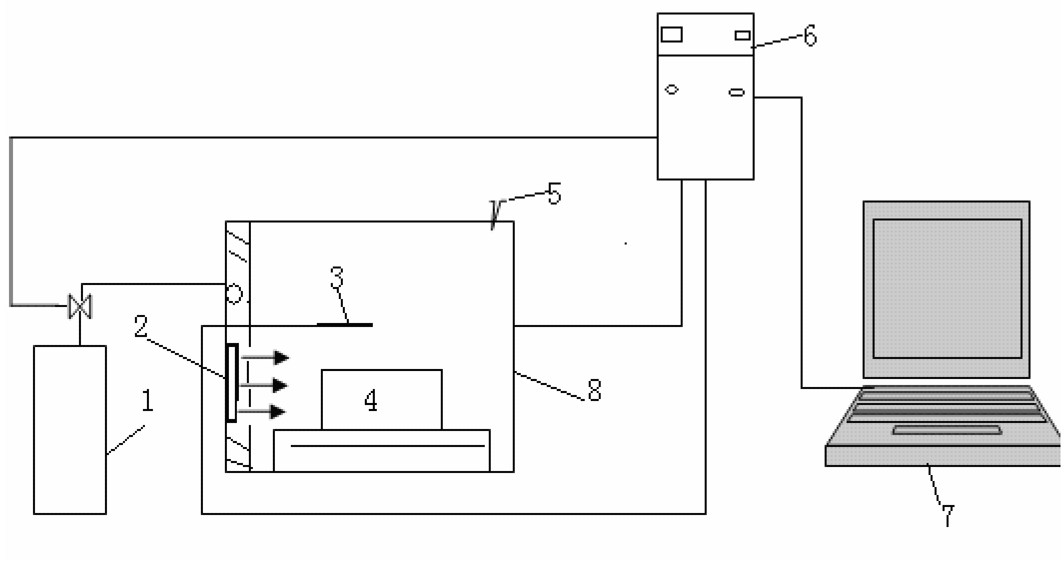

Figure 6 Schematic figure of freezing system (Yu et al. 2010). 1. Liquid nitrogen tank; 2. electric Fan; 3.T-Thermocouple; 4. Stainless steel tray; 5. Gas exiting hole; 6. Program controlling box; 7. Computer; 8. Cryogenic cabinet.