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Slowly digestible starch prepared from rice starches by temperature-cycled retrogradation

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ABSTRACT

The temperature-cycled retrogradation of rice starch used to prepare slowly digestible starch was investigated in this study. Our results showed that a maximum slowly digestible starch content of 51.62% was obtained from waxy rice starch at the optimal tested conditions: temperature cycles of 4/25 °C, at intervals of 24 h, and 7 days of storage. The results also indicated that there was a higher onset temperature (T_o), a narrower melting temperature range ($T_c - T_o$), and a higher ratio (1047 cm^{-1}/1022 cm^{-1}) of the slowly digestible starch products prepared under the temperature-cycled condition than that under the isothermal retrogradation. Furthermore, it was evident that the in vitro glycemic index of slowly digestible starch products with temperature-cycled retrogradation was reduced more than that with isothermal storage. These results suggest that the temperature-cycled retrogradation is applicable to prepare the high yield of slowly digestible starch from waxy rice starch.

1. Introduction

Slowly digestible starch has potential applications on human health and it is correlated with a low glycemic index for treatment and prevention of several disease, such as cardiovascular diseases (Ells, Seal, Kettlitz, Bal, & Mathers, 2005), non-insulin diabetes (Shin, Kim, Ha, Lee, & Moon, 2005), and obesity (Wolf, Bauer, George, & Fahey, 1999). It also provides sustained and stable energy for athletes (Eliasson, 2004). Recently, there have been a number of techniques developed to prepare slowly digestible starch. They include, but are not limited to, hydrothermal treatment (Shin et al., 2005), microwave heat treatment (Anderson, Guraya, James, & Salvaggio, 2002), a citric acid modification (Shin et al., 2007), pullulanase debranching (Guraya, James, & Champagne, 2001; Miao, Jiang, & Zhang, 2009), and starch retrogradation (Park, Baik, & Lim, 2009).

Starch retrogradation, including short-term retrogradation and long-term retrogradation, is an unavoidable phenomenon that gelatinized starch changes from an amorphous state to a crystalline area (Tian, Li, Jin, & Xu, 2009; Yuan, Thompson, & Boyer, 1993). The long-term retrogradation mainly related to amylopectin could reduce the digestibility of the starch by amylase (Tian, Li, Manthey, et al., 2009; Wang & Ding, 2005). Park et al. (2009) further reported that temperature-cycled retrogradation could prepare a great amount of resistant starch from waxy maize starch. However, little information is regarding the effect of the temperature-cycled retrogradation on preparing slowly digestible starch from rice starches.

Considering the effect of temperature-cycled storage on starch retrogradation, waxy and normal rice starches were both stored at different temperatures (4 °C, 25 °C, and cycles of 4/25 °C) to perform the aging study. The in vitro digestibility and the glycemic index of slowly digestible starch products were measured. Other crystalline properties of the products were also studied by the DSC and the FT-IR.

2. Experimental

2.1. Materials

Waxy and normal rice starches were obtained from Zhejiang Wufangzhai Agricultural Development Co. Ltd. (Hangzhou, China). Porcine pancreas α-amylase (EC 3.2.1.1) and guar gum were purchased from Sigma–Aldrich Chemical Co. Ltd. (Shanghai, China). Amyloglucosidase (EC 3.2.1.3) was purchased from Wuxi Syder Bioproducts Co. Ltd. (Wuxi, China). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Preparation of slowly digestible starch products

Ten grams of waxy and normal rice starches were dispersed with twofold diluted water and heated in boiling water for 30 min. The

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resultant gels were cooled to 25 °C, hermetically sealed and then stored at different temperatures (4 °C, 25 °C, and cycles of 4/25 °C) for 0, 3, 7, 14, 21 days to prepare the slowly digestible starch products.

2.3. In vitro digestibility determination

In vitro digestibility of slowly digestible starch products was determined as described by Englyst, Kingman, and Cummings (1992) with a minor modification. G_{20} and G_{120} represent glucose released after 20 and 120 min, respectively. The content of the hydrolyzed starch is calculated by multiplying a factor of 0.9 with the glucose content. The percentage of slowly digestible starch (%) in the products is obtained using Eq. (1)

$$\text{Slowly digestible starch content (\%)} = \left[\frac{(G_{120} - G_{20}) \times 0.9}{200}\right] \times 100 \quad (1)$$

2.4. Differential scanning calorimetry (DSC)

Thermal properties of the slowly digestible starch products were performed using a Pyris 1 DSC (Perkin-Elmer Inc., USA) under ultrahigh-purity nitrogen atmosphere. Two milligrams of anhydrous sample were mixed with 4 μL of deionized water and hermetically sealed in an aluminum pan. All samples were allowed to equilibrate at 25 °C for 6 h and then scanned at a heating rate of 10 °C/min from 25 °C to 90 °C to record the onset temperature (T_o), the peak temperature (T_p), the conclusion temperature (T_c), and the melting enthalpy change (ΔH).

2.5. Fourier transform-infrared spectroscopy (FT-IR)

FT-IR provides information on the structural order of starch chains near the granule surface, since the infrared beam penetrates only to a depth of 2 μm into the granule (Sevenou, Hill, Farhat, & Mitchell, 2002). All infrared spectra were obtained on a Nicolet Nexus 470 spectrometer (Thermo Electron Corporation, Waltham, MA, USA) equipped with a deuterated triglycine sulphate (DTGS) detector using the Digilab attenuated total reflectance (ATR) accessory at 4 cm^{-1} resolution by 64 scans. Each spectrum was recorded against an empty cell as background and was subtracted from the spectrum of air. Spectra were baseline-corrected and deconvoluted by drawing a straight line at 1200 cm^{-1} and 800 cm^{-1} (using Omnic version 6.2 software). The absorbance ratio of 1047 cm^{-1}/1022 cm^{-1} was obtained from the deconvoluted spectra.

2.6. In vitro glycemic index (GI) of slowly digestible starch products

The percentage of total starch was determined according to the procedure described by Englyst et al. (1992) with a minor modification. The rate of the starch digestion was expressed as the percentage of total starch hydrolyzed at intervals of 0, 30, 60, 90, 120, 150, and 180 min. GI of the slowly digestible starch products was obtained with the equation (GI = 39.71 + 0.549 HI) described by Isabel, Alejandra, and Fulgencio (1997).

2.7. Statistical analysis

The data were expressed as means of triplicate determinations. Statistical significance was assessed with one-way analysis of variance (ANOVA) using ORIGIN 7.5 (OriginLab Inc., USA) for windows program. Treatment means were considered significantly different at $P < 0.05$.

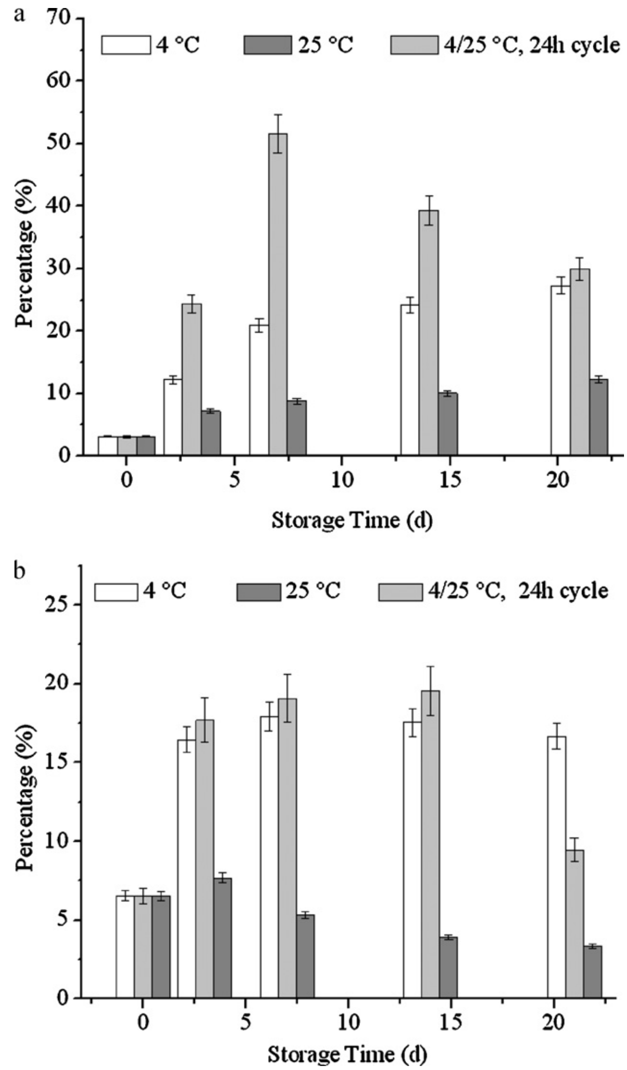

Fig. 1. Percentage of slowly digestibility starch in (a) waxy rice starch and (b) normal rice starch stored at 4 °C, 25 °C, and cycles of 4/25 °C (24 h each) for up to 21 days.

3. Results and discussion

3.1. In vitro digestibility of slowly digestible starch products

The digestibility of the slowly digestible starch products is significantly affected by the storage conditions (Fig. 1). The results showed that a maximum slowly digestible starch content of 51.62% was obtained from waxy rice starch, but not from normal rice starch, with 7 days of storage at cycles of 4/25 °C. This high content was attributed to the recrystallization of amylopectin and the increased imperfect crystallites under the temperature-cycled conditions (Park et al., 2009; Wang & Ding, 2005). Furthermore, it is evident that the yield of slowly digestible starch was related to the temperature-cycled storage, but not linearly correlated the retrogradation time. This indicated that the type and the percentage of the crystallites formed during the temperature-cycled storage could be the main factors for the slowly digestible starch preparation.

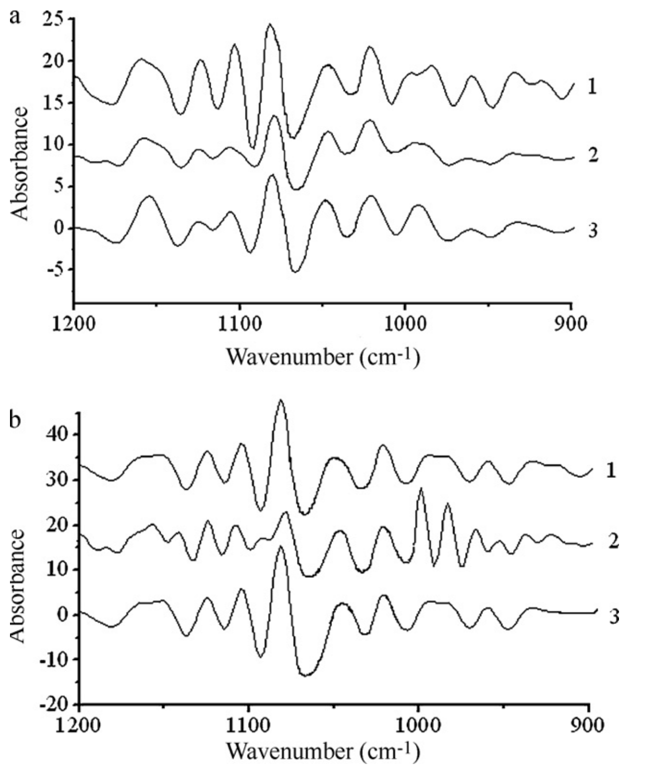

Fig. 2. Typical deconvoluted FT-IR spectra of the peaks at 1047 cm^{-1} and 1022 cm^{-1} for the gelatinized (a) waxy rice starch and (b) normal rice starch stored at (1) 25 °C for 7 days, (2) 4 °C for 7 days, and (3) cycles of 4/25 °C (24 h each) for 7 days.

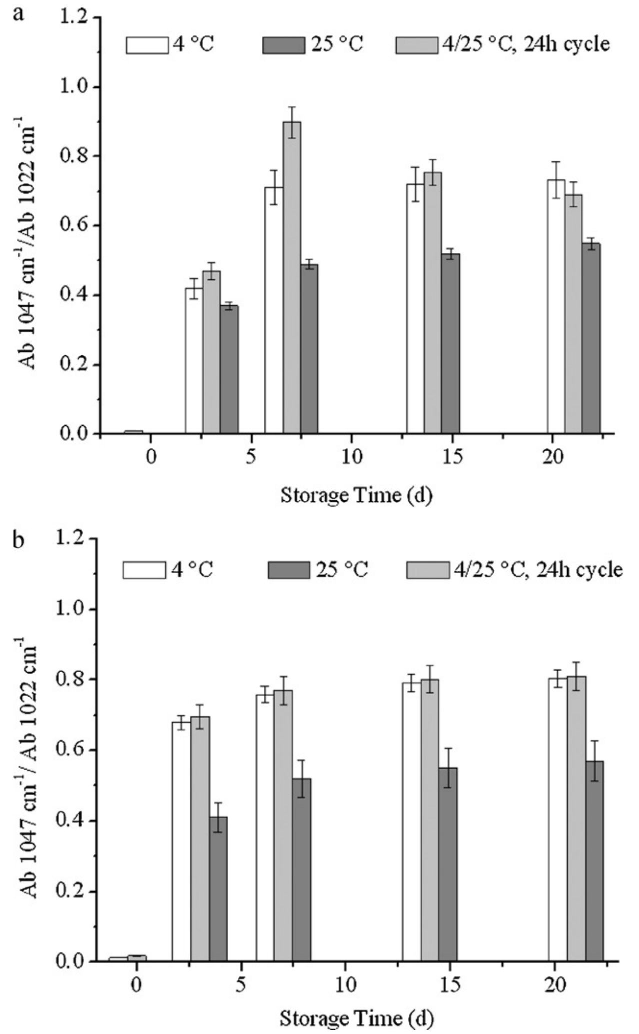

Fig. 3. The absorbance ratio 1047 cm^{-1}/1022 cm^{-1} of (a) waxy rice starch and (b) normal rice starch stored at 4 °C, 25 °C, and cycles of 4/25 °C (24 h each) for up to 21 days.

3.2. Thermal properties of the slowly digestible starch products

The DSC data showed that waxy and normal rice starches stored under the cycled temperature exhibited higher onset temperature (T_o) and narrower melting temperature range ($T_c - T_o$) than that treated under the isothermal storage (Tables 1 and 2). This indicated that the crystallites of the slowly digestible starch products prepared under the cycled retrogradation were more homogenous. Furthermore, it was found that there was a mediate melting enthalpy change (ΔH) for the waxy and normal rice starches treated by the temperature-cycled retrogradation. This result suggests that more imperfect crystallites were formed in the slowly digestible starch products with the cycled treatment.

3.3. Fourier transform-infrared spectroscopy (FT-IR)

The absorbance ratio of 1047/1022 cm^{-1}obtained from the deconvoluted FT-IR spectra is illustrated in Figs. 2 and 3. The results showed that the absorbance ratio for waxy rice starch stored at

Table 1
DSC parameters[a] of waxy rice starch stored at 4 °C, 25 °C, and cycles of 4/25 °C (24 h each) for up to 21 days.

Storage conditions	T_o (°C)	T_p (°C)	T_c (°C)	$T_c - T_o$ (°C)	ΔH (J/g)
0 d	–	–	–	–	–
4 °C – 3 d[b]	43.0 ± 1.2	50.9 ± 2.7	60.1 ± 3.3	17.1 ± 0.7	1.8 ± 0.0
4 °C – 7 d[b]	43.2 ± 1.2	51.0 ± 1.9	59.3 ± 2.7	16.1 ± 0.0	3.9 ± 0.1
4 °C – 14 d[b]	43.5 ± 0.9	53.8 ± 2.1	59.4 ± 2.2	15.8 ± 0.1	4.7 ± 0.1
4 °C – 21 d[b]	44.8 ± 0.7	54.0 ± 1.9	59.5 ± 2.5	14.6 ± 0.2	6.1 ± 0.1
25 °C – 3 d[c]	43.0 ± 2.1	51.9 ± 1.4	58.7 ± 1.5	15.6 ± 0.1	0.4 ± 0.1
25 °C – 7 d[c]	43.8 ± 1.3	52.6 ± 0.3	59.4 ± 1.9	15.6 ± 0.1	0.5 ± 0.2
25 °C – 14 d[c]	43.6 ± 1.2	52.3 ± 0.6	58.3 ± 1.7	14.7 ± 0.3	0.9 ± 0.2
25 °C – 21 d[c]	44.0 ± 0.4	52.9 ± 1.0	58.3 ± 0.9	14.3 ± 0.2	1.0 ± 0.2
4/25 °C – 3 d[d]	45.1 ± 0.5	52.2 ± 1.2	60.0 ± 1.8	14.9 ± 0.3	1.6 ± 0.1
4/25 °C – 7 d[d]	45.2 ± 0.4	51.9 ± 1.1	59.4 ± 1.9	14.2 ± 0.0	1.8 ± 0.2
4/25 °C – 14 d[d]	45.4 ± 0.7	52.8 ± 0.9	59.4 ± 1.9	13.9 ± 0.2	2.7 ± 0.3
4/25 °C – 21 d[d]	46.1 ± 1.0	52.6 ± 0.7	59.3 ± 2.3	13.3 ± 0.4	3.7 ± 0.1

[a] T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; $T_c - T_o$, melting temperature range; ΔH, melting enthalpy change.
[b] Samples stored at isothermal 4 °C for 3, 7, 14, and 21 days.
[c] Samples stored at isothermal 25 °C for 3, 7, 14, and 21 days.
[d] Samples stored at cycles of 4/25 °C for 3, 7, 14, and 21 days.

Table 2
DSC parameters[a] of normal rice starch stored at 4 °C, 25 °C, and cycles of 4/25 °C (24 h each) for up to 21 days.

Storage conditions	T_o (°C)	T_p (°C)	T_c (°C)	$T_c - T_o$ (°C)	ΔH (J/g)
0 d	–	–	–	–	–
4 °C – 3 d[b]	47.0 ± 0.4	58.0 ± 0.1	63.2 ± 0.3	16.2 ± 0.1	4.4 ± 0.0
4 °C – 7 d[b]	46.5 ± 0.7	54.4 ± 0.3	62.4 ± 0.6	15.9 ± 0.1	4.5 ± 0.1
4 °C – 14 d[b]	46.6 ± 1.3	55.1 ± 0.9	62.1 ± 0.5	15.5 ± 0.2	4.9 ± 0.2
4 °C – 21 d[b]	46.7 ± 0.8	55.3 ± 0.6	62.2 ± 0.7	15.5 ± 0.1	5.0 ± 0.2
25 °C – 3 d[c]	46.3 ± 3.4	53.5 ± 3.1	61.1 ± 2.3	14.7 ± 0.9	2.1 ± 0.3
25 °C – 7 d[c]	46.3 ± 2.4	53.0 ± 2.5	61.0 ± 2.3	14.7 ± 0.0	2.5 ± 0.3
25 °C – 14 d[c]	46.4 ± 0.9	53.0 ± 0.9	60.0 ± 0.6	13.6 ± 0.6	2.8 ± 0.2
25 °C – 21 d[c]	46.4 ± 2.1	53.3 ± 2.0	60.0 ± 0.7	13.5 ± 0.3	2.8 ± 0.2
4/25 °C – 3 d[d]	48.6 ± 0.9	57.8 ± 0.7	63.1 ± 0.4	14.5 ± 0.7	2.8 ± 0.2
4/25 °C – 7 d[d]	48.8 ± 0.3	57.6 ± 0.1	63.1 ± 0.9	14.3 ± 0.2	3.5 ± 0.1
4/25 °C – 14 d[d]	49.9 ± 0.1	57.8 ± 0.1	63.3 ± 1.2	13.4 ± 0.2	3.7 ± 0.1
4/25 °C – 21 d[d]	50.3 ± 0.1	58.2 ± 0.1	63.6 ± 1.7	13.3 ± 2.0	3.8 ± 0.4

[a] T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; $T_c - T_o$, melting temperature range of slowly digestible starch products; ΔH, melting enthalpy change of slowly digestible starch products.
[b] Samples stored at isothermal 4 °C for 3, 7, 14, and 21 days.
[c] Samples stored at isothermal 25 °C for 3, 7, 14, and 21 days.
[d] Samples stored at cycles of 4/25 °C for 3, 7, 14, and 21 days.

cycles of 4/25 °C was increased to a maximum (0.899) with the storage time up to 7 days and then decreased with storage time from 7 to 21 days. On the other hand, the absorbance ratio for normal rice starch stored under the temperature-cycled condition rapidly increased at the first 3 days, and then kept in a stable level. These results indicated that the surface of the slowly digestible starch crystallites was ordered by the temperature-cycled retrogradation and only was slowly digested by amylase.

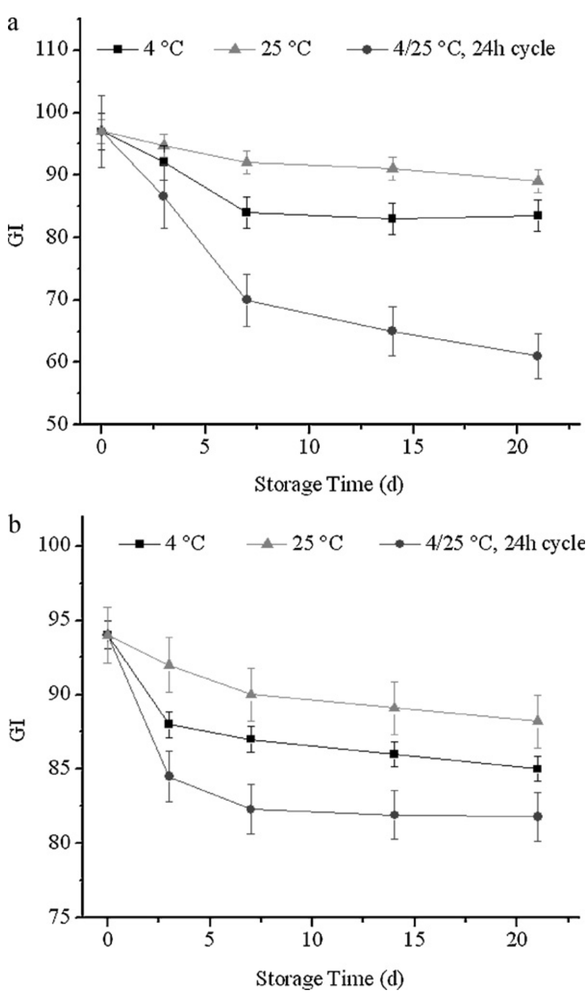

Fig. 4. GI of (a) waxy rice starch and (b) normal rice starch stored at 4 °C, 25 °C, and cycles of 4/25 °C (24 h each) for up to 21 days.

3.4. *In vitro glycemic index (GI) of slowly digestible starch products*

The results showed that in vitro GI of slowly digestible starch from both of waxy and normal rice starch was decreased with the increasing of storage time, and that the waxy rice starch stored at cycles of 4/25 °C had a lowest value in in vitro GI (Fig. 4). This result was in a good agreement with the previous study that GI of waxy maize starch gel was significantly decreased when it was treated under a cycled temperature (Park et al., 2009). The reason for the lowest GI was probably attributed to the higher extent of imperfect crystallites and the ordered external region formed under the temperature-cycled storage.

4. Conclusions

This work clarified that there was no positive correlation existing between the yield of slowly digestible starch and the retrogradation time, and that the moderate temperature-cycled retrogradation was favorable for preparing the slowly digestible starch products from waxy rice starch. The mechanism behind was attributed to the large amount of imperfect crystallites and more ordered external region of starch granules formed during the temperature-cycled storage. Therefore, the cycled retrogradation of waxy rice starch is applicable as a new technique for preparing the slowly digestible starch product in food industry.

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