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Differential Scanning Calorimetry Analysis on Effects of Storage Temperature and Water Content on Retrogradation of Concentrated Rice Starches System

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ABSTRACT

The effect of storage temperature and water content on starch retrogradation of RD6 and Supanburi 1 rice starch gels were studied by differential scanning calorimeter and then retrogradation kinetic were evaluated. The storage temperatures were -20, 4, room temperature and 50°C. The water contents were 30-60% (w/w). The melting temperatures of both retrograded starch gels stored at -20, 4°C and room temperature occurred around 50-80°C but the gels stored at 50°C occurred around 70-90°C. However, RD6 starch gels with 60% water content did not retrograde when stored at 50°C. The results on the retrogradation enthalpy were found that the enthalpy increased when storage temperature increased to 4°C, after that they decreased when storage temperature increased to room temperature and 50°C, respectively. In retrogradation kinetic, it was found that Avrami exponent (*n*) values were different from those with excess water. The retrogradation extent and retrogradation rates of starch gels were also highest at 4°C at all water content. Water content in starch gels also affected enthalpy changes and retrogradation rates. The retrogradation properties in Supanburi 1 starch gel were quite similar but in the higher trend than those found in RD6 starch gels.

Keywords: Differential scanning colorimetry/ Retrogradation/ Storage temperature/Water content

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INTRODUCTION

Starch is a major component of cereal-based foods, which are processed in several ways, such as baking, extrusion and puffing. In these processes, the starch granules are gelatinized and/or retrograded. The term retrogradation has been used to describe changes in physical behavior following gelatinization [1]. Atwell proposed that retrogradation be considered “a process that occurs when the molecules comprising gelatinized starch begin to associate in an ordered structure” [2]. They recognized that changes in physical behavior resulted from a process of molecular ordering.

Starch retrogradation is influenced by the botanical source and the fine structure of amylopectin [3, 4, 5, 6]. Amylose content, water content in the starch gel and storage temperature also affected retrogradation of starches. [7-11].

Many researches have been focused on retrogradation of starch in excess water. However, most starch-containing food has been made up from concentrated starch-water systems. Moreover, the previous studies that investigated in concentrated systems have been done in corn [12] and other starches [13, 14]. The purpose of this study was to investigate the effect of storage temperature on starch retrogradation of concentrated rice starch-water systems which containing water 30-60% and then the retrogradation kinetic of those systems were evaluated.

MATERIALS AND METHODS

Rice starch

Whole grains of RD6 glutinous rice (Rice Research Centre, Khonkhan, Thailand) and Supanburi 1 rice (Rice Research Centre, Patumthani, Thailand) were wet milled. Both rice starches were isolated according to the method of Noosuk [15]. The moisture, protein and fat content of RD6 and Supanburi 1 were 9.48, 0.68 and 0.58, and 9.54, 0,75 and 0.56%, respectively [16]. Amylose content RD6 and Supanburi 1 were 8.07 and 39.82%, respectively.

Retrogradation by DSC

Rice starch was weighed accurately into a pre-weighed Differential Scanning Calorimetry (DSC) volatile aluminum sample pan (Kit No. 0219-0062, Perkin-Elmer). Deionized water was added to make starch mixtures with various water contents. The approximate weight of starch and water mixture in the DSC pan was 10 mg. The pan was sealed and equilibrated overnight before heat treatment in the DSC.

Heat treatment of rice starch-water mixtures and the thermal analysis of gelatinization and retrogradation were done using a differential scanning calorimeter (Diamond Pyris, Perkin-Elmer, Norwalk, CT) with data analysis software (Pyris for Windows, Perkin-Elmer). The calorimeter was equipped with an Intracooler 2P (Perkin-Elmer) and nitrogen gas purge.

Calibration was done with indium. An empty volatile sample pan was used as a reference. On completion of the experiment, the sample pan was punctured and dried overnight in an oven at 105^{o}C and then reweighed in order to determine the exact starch weight and water content in the sample.

Rice starch mixtures with water content ranging from 30-60% (w/w) were held at 30^{o}C for 1 min, heated from 30^{o}C to the target heating temperature (depending on water content) to complete gelatinization with a rate of 10^{o}C/min. and then held at that temperature for 1 min. The samples were then cooled to 30^{o}C and stored at temperature -20, 4, ambient temperature and 50^{O}C. After 1, 3, 5, 7 and 14 days, stored samples were heated from 30^{o}C to 98^{o}C at a rate of 10^{o}C/min. All measurements were done in triplicate.

The temperature of the transition, onset (T_o), peak (T_p) and conclusion (T_c) were obtained from the DSC thermograms and the enthalpy (ΔH) of the transition was measured and expressed as J/g on a dry weight basis.

Retrogradation kinetic

The enthalpy change (ΔH) during starch retrogradation can be described with the Avrami equation [11, 17].

$$\theta = (\Delta H_{\infty} - \Delta H_{t}) / (\Delta H_{\infty} - \Delta H_{0}) = \exp(-k\, t^{n}) \quad (1)$$

$$\log(-\ln \theta) = n \log t + \log k \quad (2)$$

where θ is the fraction of crystallization resting to take place; ΔH_0 and ΔH_t are the retrogradation enthalpy (J/g dry starch) at storage times 0 and t days, respectively; ΔH_{∞} is the limiting ΔH at infinite time ($t \rightarrow \infty$) and obtained from the intercept of $1/\Delta H_t$ vs. $1/t$ plot; n and k are the Avrami exponent and rate constant (day^{-1}) derived from the slope and intercept of log (-ln θ) vs. log t plot. Retrogradation rate (G) can be calculated from

$$G = k^{1/n} \quad (3)$$

Statistical Analysis

Analysis of variance (ANOVA) and Duncan's multiple range tests of the obtained data was analyzed SPSS software (version 11, SPSS Inc., Chicago, USA).

RESULTS AND DISCUSSION

Effect of storage temperature and water content on transition temperature and retrogradation enthalpy

Retrogradation has been used to describe changes in physical behavior following gelatinization of starch chains as double helices, and variably ordered semi-crystalline arrays of these helices, as monitored by DSC to observe endothermic changes when these structures are lost on heating.

Table 1: Transition temperature of RD6 and Supanburi 1 rice starch gels containing 30-60% water content stored at -20, 4, 30 and 50°C for 14 days.

	Water	Tp (°C)			
	(%)	-20	4	RT	50
RD6	30	62.62±2.52bc	61.39±1.98ab	69.27±2.20gh	79.84±2.10i
	40	63.62±1.71bcd	61.24±0.75ab	66.26±0.53def	80.72±0.66ij
	50	61.19±1.94ab	61.23±0.46ab	66.03±1.53def	82.56±1.74ij
	60	58.67±3.79a	61.73±0.62bc	66.32±2.56def	nd
Supanburi 1	30	63.82±2.27bcd	62.99±0.97bc	69.94±1.11gh	82.91±1.40j
	40	66.71±0.56efg	62.43±0.52bc	67.31±1.24efg	80.70±0.38ij
	50	67.32±1.63efg	62.55±1.21bc	67.94±0.77fgh	79.94±1.68i
	60	64.52±0.92cde	61.63±0.70bc	68.25±0.45fgh	80.73±1.58ij

nd : not determined because retrogradation peak was not observed.

RD6 and Supanburi 1 rice starch gels with water 30-60% were stored to retrograde at -20 4, room temperature and 50°C. The melting temperature of the recrystallites were presented in Table 1. Retrogradation peaks of both RD6 and Supanburi 1 were quite similar; however, the transition temperatures (T_p) of Supanburi 1 starch gels were occurred at higher temperature than RD6. Rice starch gels containing 30-60% water content stored at -20°C and 4°C had T_p lower than those stored at room temperature and 50°C. T_p of RD6 and Supanburi 1 rice starch gels with 30-60% water content is the highest when the gels were stored at 50°C. The reason for this is that at higher storage temperatures, the occurred crystallites had more symmetrically perfect crystalline structure while at low storage temperature (4-5°C), they form less perfect and had a lower melting temperature than those formed at higher storage temperature [18, 19]. Moreover, starch gels stored at 50°C had T_p at ~ 80°C, which were closed to the melting temperature of A-type crystalline structure. This is consistent with March who showed that the shift in the crystalline pattern from A- to B-type crystal depended strongly on water content and storage temperature [20]. A-type crystal was observed at high temperature and/or low water contents, while B-type crystal was observed at low temperature and/or high water contents. The comparison of transition temperature in starch gels with water 30-60% was performed. It was shown that at -20°C, starch gels with high water content had low T_p due to the effect of water plasticization in reducing T_g. However, at the other storage temperature, there was no effect of water content on T_p of rice starch gels.

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a)
b)
c)
d)

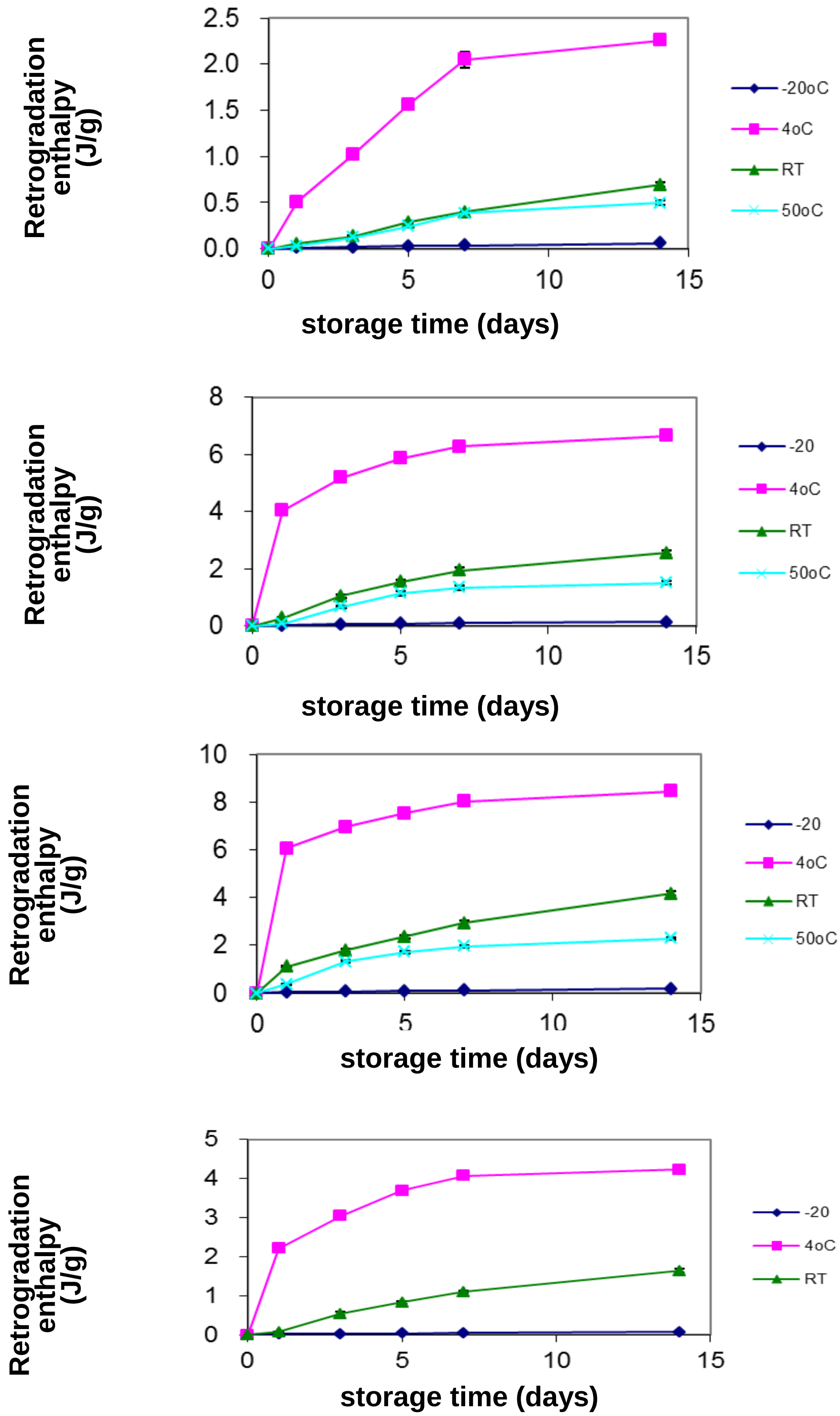


Figure 1: Retrogradation enthalpy of RD6 rice starch gels containing 30-60% water content stored at various temperatures, gel containing water 30% (a), 40% (b), 50% (c) and 60% (d), respectively.

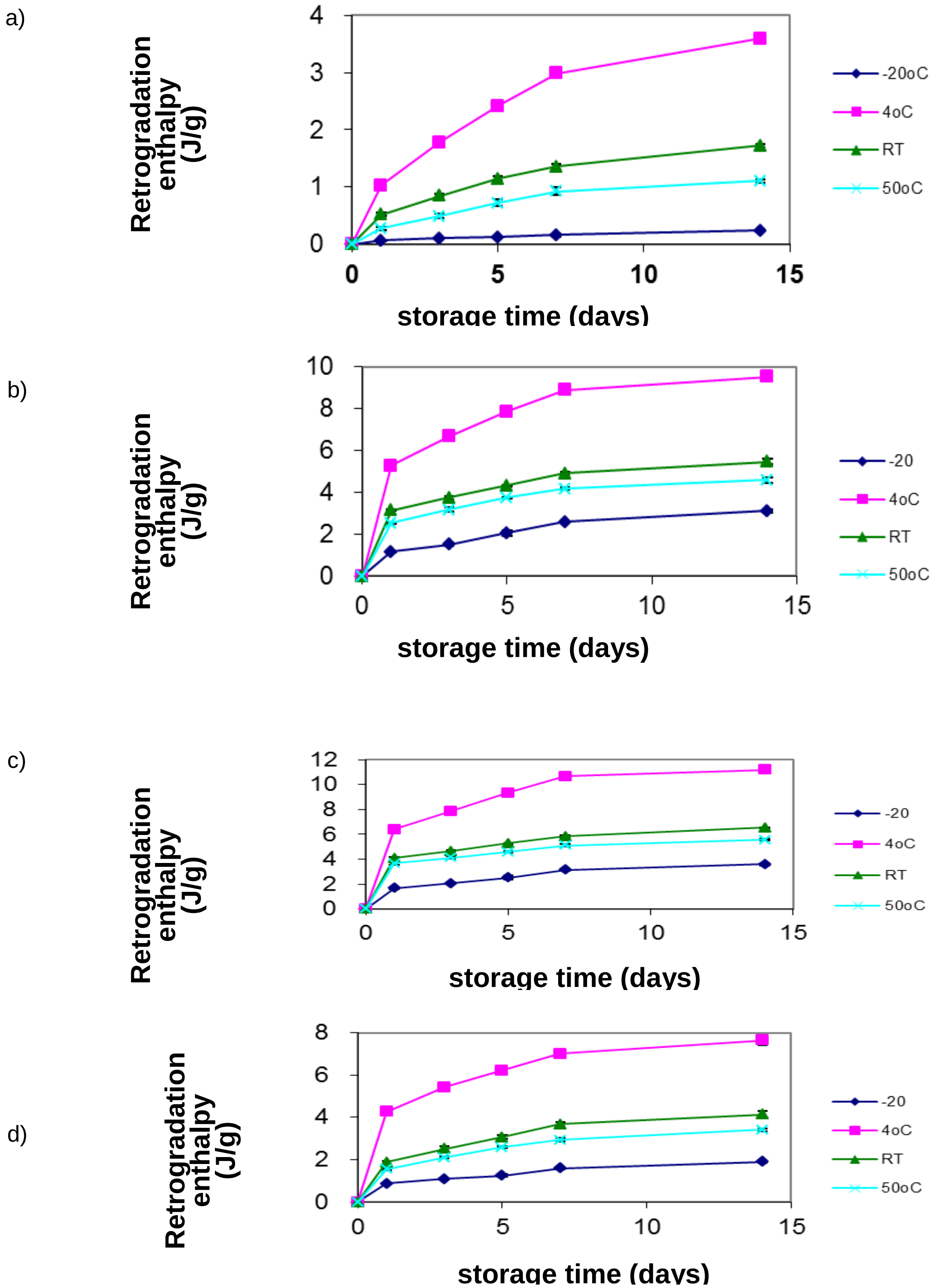


Figure 2: Retrogradation enthalpy of RD6 rice starch gels containing 30-60% water content stored at various temperature, gel containing water 30% (a), 40% (b), 50% (c) and 60% (d), respectively.

Retrogradation change was observed in terms of retrogradation enthalpy. Figure 1 and 2 showed retrogradation enthalpy of RD6 and Supanburi 1 starch gels containing 30-60% water content stored at -20^{o}C, 4^{o}C, room temperature and 50^{o}C, respectively. It was found that retrogradation enthalpy increased with storage time. The maximum retrogadation occurred in starch gels stored at 4^{o}C, whereas retrogradation extent was very little at -20^{o}C storage temperature.

RD6 starch gel with 60% water content stored at 50^{o}C did not retrograde. This result also agrees with Baik [21] that no recrystallization was found when storage temperature was below -20 or above 30^{o}C. This might be the less mobility due to frozen state and the close of storage temperature and melting temperature.

Retrogradation of both RD6 and Supanburi1 rice starch gels occurred maximum at 50% water content at all storage temperatures. These results were consistent with that of Longton and LeGrys: maximum crystallization in a wheat starch gel occurred at 40-50% moisture [22]. Because at very low water content, the amorphous gel is in a highly viscous glassy state that effectively hinders molecular mobility. Recrystallization increases with increasing water content, because of progressively more effective plasticization and increase molecular mobility [19].

Retrogradation change in term of retrogradation index (RI) was calculated from retrogradation enthalpy divided by gelatinization enthalpy in order to compare the reorder structure with the loss order structure. Figure 3 showed that the relationship between RI and $T - T_g$ of rice starch was parabolic. At storage temperature -20 ^{o}C or low $T - T_g$ conditions, recrystallization occurred to a lower extent because starch gels were stored at temperature lower than T_g. T_g data of rice starches with water 30-60% in this study was in the range of -8 to -2^{o}C, which was consistent with that of Baik [20]. Thus, the molecular mobility was low and the crystal growth was kinetically restricted and slow. Moreover, the crystal formed at the beginning of storage at low $T - T_g$ conditions act as barriers for molecular rearrangements [23]. In addition, the degree of perfection of the recrystallites may become fairly low if storage at temperatures close to the glass transition are employed. At higher T-T_g, 4^{o}C storage temperature, retrogradation occurred rapidly because the higher in the difference of storage temperature and T_g caused higher in crystallite nucleation and recrystallization occurred much at temperature above T_g. Starch gels stored at room temperature, T ~ 30^{o}C, decreased retrogradation because higher storage temperature favor in more propagation step of crystallites than nucleation step. Thus, new crystallites formed in fewer extents. At 50^{o}C, decreasing in retrogradation was observed. This might be that storage temperatures were higher and closed to melting temperature of the recrystallites.

The transition temperature and extent of recrystallization of Supanburi1 rice starch gels were higher than those of RD6 at all levels of water content and storage temperatures. This a)

b)

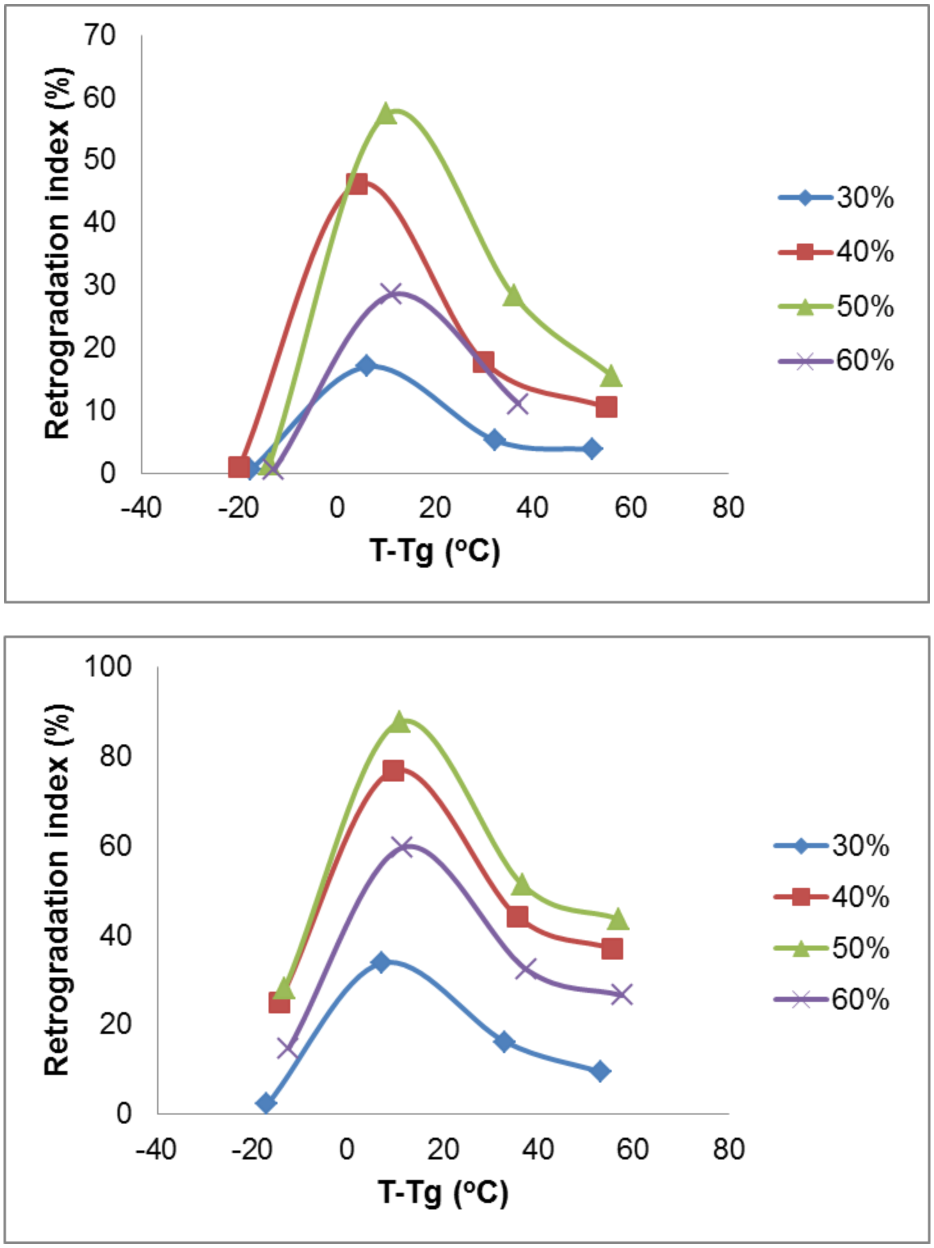


Figure 3 Retrogrdation index of rice starch gels with 30-60% water stored at -20, 4, 30 and 50°C for 7 days, RD6, a) and Supanburi 1, b).

can be explain that amylopectin of Supanburi1 rice starch were L-type amylopectin because it had higher ratio of long chains (DP 12-24) to short chains (DP 3-11). It was suggested that the minimum chain length for rice starch amylopectin retrogradation was DP 12 [24]. The short rice amylopectin chains most probably (1) did not form double helices or (2) at the very most co-crystallized with amylose and/or longer amylopectin chains and hence (1) inhibited retrogradation or (2) lower the recrystallization perfection during retrogradation. On the contrary, longer amylopectin chains possibly formed double helices more easily and quickly and thus favored retrogradation.

Retrogradation kinetic

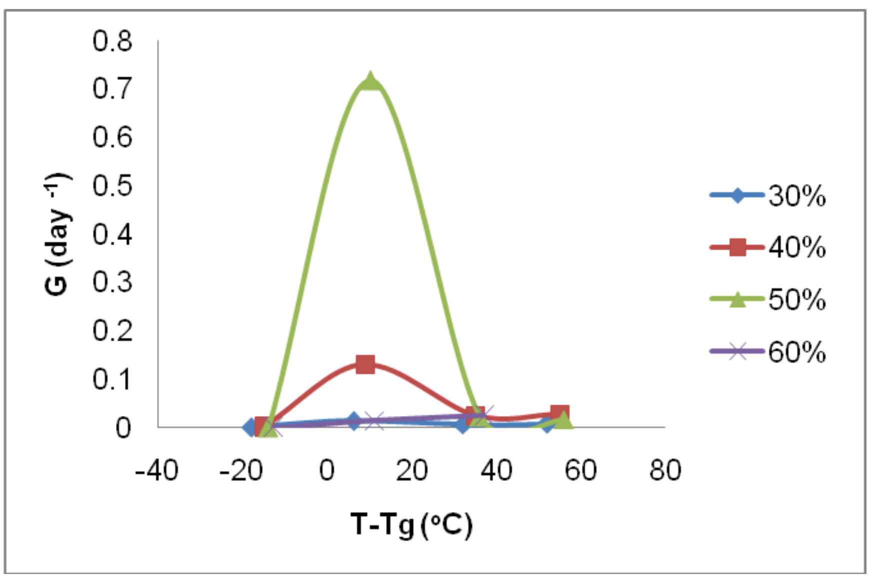
Table 2 Avrami exponent, *n* and rate constant,*k*, of RD6 and Supanburi1 rice starches.

			RD6			Supanburi 1			
		30%	40%	50%	60%	30%	40%	50%	60%
n	-20	0.718	0.705	0.733	0.544	0.515	0.440	0.341	0.320
	4	0.649	0.300	0.270	0.319	0.556	0.428	0.503	0.335
	30	1.010	0.913	0.581	1.259	0.491	0.280	0.249	0.363
	50	1.122	1.246	0.734	nd	0.535	0.284	0.213	0.347
k	-20	0.0010	0.0021	0.0027	0.0016	0.0065	0.1012	0.1496	0.0736
	4	0.0612	0.5433	0.9141	0.2564	0.1148	0.6166	0.8630	0.4508
	30	0.0058	0.0343	0.1104	0.0091	0.0558	0.3162	0.4188	0.1726
	50	0.0039	0.0110	0.0488	nd	0.0308	0.2529	0.3690	0.1416

nd : not determined because retrogradation peak was not observed.

Retrogradation kinetics of RD6 and Supanburi 1 starch gels with water content 30-60% were determined. The data of Avrami exponent (*n*) and rate constant (*k*) were obtained from Avrami plot and then time constant (*1/k*) were calculated and presented in Table 2. It was shown that *n, k* and *1/k* were depended on storage temperature and water content in both rice starch gels. The *n* values were 0.270 < *n* < 1.246 and 0.213 < *n* < 0.556 for RD6 and Supanburi 1 gels, respectively. Based on many researches, the experimentally obtained *n* were quite equal 1 [20, 25, 26]. However, these *n* values in this study were agreed with some studies which was found that *n* would be <1 ([12, 24]. The value of *1/k* of both RD6 and Supanburi 1 rice starch gels were found to be lowest at storage temperature 4^{o}C at all levels of water content. This data were agreed with the data of retrogradation extent of both rice starches.

a)



b)

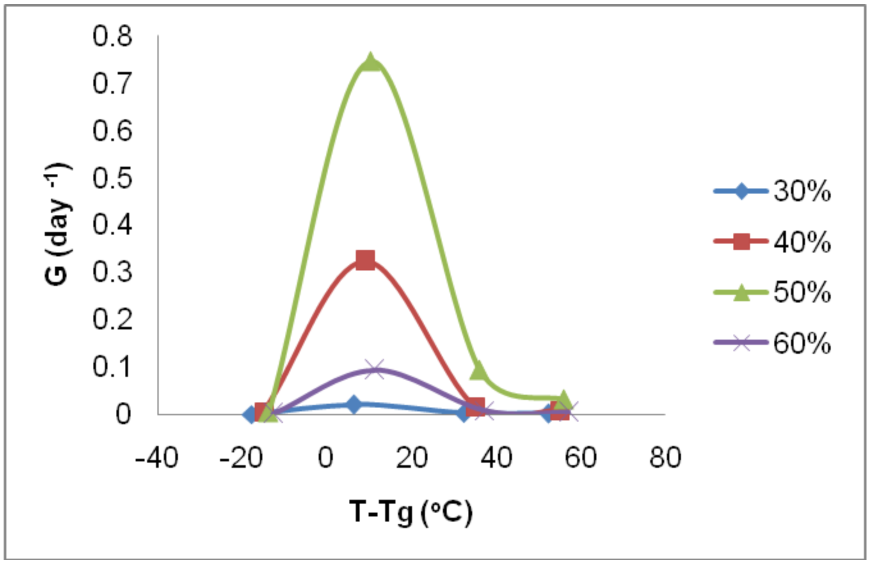


Figure 4 Retrogrdation rate, $G = k^{1/n}$, of RD6, a), and Supanburi 1, b), rice starch gel with 30-60% stored at -20, 4, 30 and 50°C.

From *n* and *k* values, retrogradation rate (*G*) of rice starch gels (30-60% water content) at various storage temperatures could be calculated and presented in Figure 4. The plots of retrogradation rate and water content were bell-shaped which was shown the maximum retrogradation rate of starch gels at 50% water content at all storage temperatures. In addition, the results showed that retrogradation rate of Supanburi 1 were higher than RD6 starch gels. Because starch retrogradation occurs at two kinetically distinct processes: (1) rapid gelation of amylose via formation of double helix followed by helix-helix aggregation and (2) slow recrystallization of the short chains of amylopectin [18, 27-29]. Thus, the higher in the retrogradation rate of Supanburi 1 are depended on amylose content of starch and the higher in ratio of long chains (DP 12-24) to short chains (DP 3-11).

CONCLUSIONS

The effect of storage temperature (-20, 4, 30 and 50°C) and water content on retrogradation of rice starches was investigated using DSC. It was found that rice starches stored at 50°C had higher T_p than that stored at -20, 4 and 30°C. The maximum retrogradation of RD6 and Supanburi 1 starch gels occurred at 4°C storage temperature at all levels of water content.

Kinetic of recrystallization process of RD6 and Supanburi 1 starch gels were shown that *n* values of RD6 gels were less than of RD6 and they would be < 1. Retrogradation rate was highest in starch gel containing 50% water content and stored at 4°C and retrogradation rate of Supanburi 1 starch gels were higher than RD6 starch gels.

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REFERENCES

[1] Wu JY, Eads TM. Carbohydr Polym 1993; 20: 51-60.
[2] Atwell WA, Hood LF, Lineback DR, Varriano-Marston E, Zobel HF. Cereal Food World 1988; 33: 306.
[3] Orford PD, Ring SG, Carroll V, Miles MJ, Morris VJ. J Sci Agric 1987; 39: 169-177.
[4] Roulet Ph, MacInnes WM, Gumy D, Wursch P. Starch 1990; 42: 99-101.
[5] Kalichevsky MT, Orford PD, Ring SG. Carbohydr Res 1990; 198: 49-55.
[6] Ward KE, Hoseney RC, Seib PA. Cereal Chem 1994; 71: 150-155.
[7] Russell PL. J Cereal Sci 1987; 6: 147-158.
[8] Gudmundsson G, Eliasson AC. Carbohydr Polym 1990; 13: 295-315.
[9] Zeleznak KJ, Hoseney RC. Cereal Chem 1986; 63: 407-411.
[10] Keetels CJAM, Oostergetel GT, van Vliet T. Carbohydr Polym 1996; 30: 61-64.
[11] Colwell KH, Axford DWE, Chamberlain N, Elton GSH. J Sci Food Agric 1969; 20: 550-555.
[12] Joupilla K, Kansikas J, Roos YH. Carbohydr Polym 1998; 36: 143-149.
[13] Garcia V, Colonna P, Lourdin D, Buleon A, Bizot H, Ollivon M. J Thermal Anal 1996; 47: 1213-1228.
[14] Lionetto F, Maffezzoh A, Ottenhof MA, Farhat IA, Mitchell JR. Starch 2005; 57: 16-24.
[15] Noosuk P, Hill SE, Farhat IA, Mitchell J R, Pradipasena P. Starch 2005; 57: 587-598.
[16] AOAC, Official methods of analysis, Association of Official Analytical Chemists. Maryland. 2000; Method 999.10.
[17] Turi EA. 1997. The basis of thermal analysis. Thermal Characterization of Polymeric Materials. Vol. 1, New York. 1997; 205-482.
[18] Gidley MJ. Carbohydr Res 1987; 161: 301-304.
[19] Stivala SS, Crecenzi V, Dea ICM. Recent advances in starch retrogradation. Industrial Polysaccharides: The Impact of Biotechnology and Advanced Methodologies, New York. 1987; 387-430.
[20] Marsh RDL. 1986. A study of the retrogradation of wheat starch systems using X-ray diffraction. PhD thesis. University of Nottingham: Nottingham, UK.
[21] Baik MY, Kim KJ, Cheon KC, Ha YC, Kim WS. J Agric Food Chem 1997; 45(11): 4242-4248.
[22] Longton J, Legrys GA. Starch 1981; 33: 410-414.
[23] Breslauer KJ, Kaletunc G. Plasticization effect of water on carbohydrates in relation to crystallization. Characterization of Cereals and Flours: Properties, Analysis and Applications. New York. 2003; 117-149.
[24] Lai VMF, Lu S, Lii CY. Cereal Chem 2000; 77: 272–278.
[25] Mita T. Carbohydr Polym 1992; 17: 269-276.
[26] Zhang W, Jackson DS. 1992. J Food Sci 1992; 57: 1428-1432.
[27] Miles MJ, Morris VJ, Orford PD, Ring SG. Carbohydr Res 1985; 135: 271-278.
[28] Ring SG, Colonna P, I'Anson KJ, Kalichevsky MT, Miles MJ, Morris VJ, Orford PD. Carbohydr Res 1987; 162: 227-293.
[29] Goodfellow B, Wilson RH. Biopolymers 1990; 30: 1183-1189.