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Effects of sugar and coconut milk addition on freeze-thaw stability of starches: comparison of slow and fast frozen methods

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Abstract

This research aimed to evaluate the effect of water, sucrose and coconut milk on starches processed by fast and slow frozen methods and subjected to repeat freezing and thawing. The rice, tapioca and blend starch gels contain water, 45°Bx of sucrose and coconut milk were treated to 5 freeze-thaw cycles. The result showed that the fast freezing inhibited syneresis better than slow freezing. The repeated freezing and thawing found the liquid was separated from starch gel. The percentage of syneresis was lower in sucrose (7.04 – 22.73%) and coconut milk (12.9 – 36.00%) addition to starch gel samples than non-addition (26.18 – 53.50%). Starch gels which were subjected to 5 cycles freeze-thaw stability found to have small porous and some fissure structure in sucrose and coconut milk added. These results suggest that retrogradation induced by freeze-thaw treatment was retarded by sucrose, coconut milk and added tapioca starch to rice starch.

Keywords: frozen starch, freeze thaw, starch gel, sugar, coconut milk

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1. Introduction

ASEAN countries, including Thailand, prefer their meals made from native starch as main course and dessert. Most native starches such as rice and tapioca starch are used as material for dessert cooking by mixing them with sugar and/or coconut milk [1]. These desserts and foods have short shelf-life. In order to extend their shelf-life, these are some approaches chemical treatment, thermal processing or cooling and frozen processing. The freezing approach to preserve food by reducing temperature to below freezing point, leading to lower a_w value of food and to delay microbial growth in food. This is the most favorite method for ready-to-eat food production, as it extends the shelf-life and consumers could prepare, cook and eat conveniently [2]. However, the freezing method can induce changes in physical and chemical properties of foods. Starchy food is known to be affected by retrogradation when frozen or stored under low temperature. The rate of freezing such as slow freezing induces the association of starch chain resulting in harder texture and more syneresis value to starch gel [3, 4]. Those phenomena can be prevented by using rapid freezing to retard nuclei formation during the nucleation and propagation stages of starch chain association [5].

Numerous studies reported about the freeze-thaw stability could effect to modify starch and some hydrocolloids on starch gel properties. Some studies reported that ingredients might improve or retard the change in starch quality, for instance, inulin, xanthan gum or starch blending [6 – 14]. However, few studies were investigated about the effect of native starch and some major ingredients such as sugar and coconut milk. Sugar has been shown to retard or accelerate the retrogradation and gelatinization temperature of the gel. [15 – 19] reported that sugar reduced the crystallinity of starch molecules on the retrogradation but increased the gelatinization temperature.[16, 20]. found that adding sugar lead to varying results or increase the re-crystallization of amylose complex. Coconut milk is often added in the food to increase flavor and taste. During food processing, the formation of lipid and amylose complex, especially short chain and medium chains fatty acid that contain in coconut milk, could reduce retrogradation and make starch gel rigid [21, 22]. The ready to eat chilled and frozen Thai desserts, that contained starch with high moisture, sugar and coconut milk, are popular among consumers. This process could extend shelf life and make it more commercially available. In order to understand

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and maintain the dessert or food product quality in general, user of starch gel should understand physical changes during the freezing and thawing process. Repeated freezing and thawing increase phase separation and ice crystal growth, inducing syneresis and porous structure which in turn causes unacceptable sensorial qualities after thawing [4, 2, 23, 15]. This study investigated changes in syneresis and morphology of starch when subjected to freeze-thaw stability of sucrose and coconut milk added to common rice starch, tapioca starch and blend of this starch gels. The correlation of results could serve as knowledge base for extending shelf life of ASEAN or Thai ready to eat desserts which produced at commercial scale.

2. Materials and Methods

2.1 Material

Rice starch (33.8% amylose content) and tapioca starch (31.4% amylose content) were purchased from Choheng Rice Vermicelli Co., Ltd. (Nakhon Pathom, Thailand) and Thai Tham Factory (Chonburi, Thailand), respectively. Food grade sucrose (Mitr Phol Sugar Co.Ltd., Supanburi, Thailand) was used at 45 °Brix of sucrose solution preparation. Coconut milk (Thai Agri Food Co., Ltd. (Nakhon Pathom, Thailand) was purchased from local supermarket.

2.2 Starch gel preparation

Starch gels were classified as rice starch gel (RS), tapioca starch gel (TS) and rice starch/tapioca starch blend gel (RS/TS) in ratio of 1:0.85. The starch suspensions (15%, w/w of starch on a dry basis) were prepared by mixing with water or 45 °Bx sucrose solution or coconut milk and stirred continuously at 250 rpm for 5 minutes. Then the suspension was stirred continually at 200 rpm at 80oC for 20 min.

2.3 Freezing and thawing

Forty grams of starch gel were loaded into cylindrical tubes and then frozen. The slow frozen method was done in a chest freezer (Sanyo, SF-C1497, Thailand). While air blast frozen (March cool, 2009 model, Thailand) at -25 °C for 3 hours was remarked as fast frozen. The storage temperature of gel was recorded as the core temperature of gel reached approximately -18 °C for 24 hours. Starch gels were stored continuously for 7 days. After that the gels underwent the thawing process at 30±3 °C in water bath for 2 hours. Six cylindrical tubes from each thawing condition were selected for syneresis and determination of microstructure. The remaining 6 cylindrical tubes were then put back into the freezer for repeated tests up to 5 freeze-thaw cycles.

2.4 Syneresis

The syneresis measurement method was modified from [4]. Forty grams of hot starch pastes were transferred into 150 ml centrifuge tubes and stored at 4 °C for 21 days. The storage tubes then warm up to 30±3 °C and centrifuged at 8000 rpm for 15 min. The percentage of syneresis was calculated as ratio of liquids separated (ml) to total weight of the gel before centrifugation as follow:

%syneresis = (liquid separated (ml))/(total weight of the gel (g))×100

2.5 Microstructure

The starch gel sample was freeze-dried using vacuum freeze dryer (Scanvac cool safe55, Denmark). Freeze dried sample was cut and mounted on aluminium stubs, coated with gold. The scanning of image was observed at 50x with the accelerated voltage of 15 kv.

2.6 Statistical analysis

All experiments were performed in triplicates using completely randomized design. Differences between the mean values were established using Duncan's new multiple range tests at a confidence level of 95%. All statistical analyses were performed using SPSS version 25.

3. Results and Discussion

3.1 Percentage of syneresis

When starchy product is frozen, the formation of ice crystals and starch aggregation region take place that leads to phase separation within food matrix [11]. These created undesirable qualities such as becoming harder, drier and unacceptable (rejected) by consumers. The syneresis percentage for starchy products in different systems was monitored for the ability of starch to impede the undesirable physical changes during freezing and thawing. The syneresis in a frozen gel is a useful indicator of starch retrogradation tendency. It is measured by an increase in molecular association or aggregation between starch chain-amylose (with short term retrogradation) and amylopectin with long term retrogradation [24,25].which results in the releasing of water from the gel structure. However, the addition of sugar, fat and some hydrocolloids could interact with water molecules and reduces the syneresis [7, 10, 2, 4].

The effect of rice starch, tapioca starch and blend gel on the % syneresis presented in Table 1 and 2. Freeze-thawed rice starch gel with water, sugar or coconut milk had significant higher syneresis value after the first and second cycle and slightly changed through cycle 3-5. The freeze-thaw rice starch gel with

Table 1. Syneresis value of rice (RS), tapioca (TS) and blend (RS/TS) starch gels (15%w/w) addition sugar and coconut milk in each cycle using slow frozen method.

sample		Syneresis (%)				
		Cycle1	**Cycle2**	**Cycle3**	**Cycle4**	**Cycle5**
water						
	RS	$38.31^{aB}\pm4.42$	$47.88^{aA}\pm3.76$	$51.88^{aA}\pm1.58$	$53.50^{aA}\pm2.67$	$52.51^{aA}\pm3.21$
	TS	0.0^{cC}	$26.18^{cB}\pm2.54$	$32.68^{cA}\pm3.23$	$30.02^{cA}\pm5.50$	$30.89^{cA}\pm5.91$
	RS/TS	$22.38^{bC}\pm3.05$	$31.04^{bB}\pm1.96$	$48.66^{bA}\pm0.82$	$47.38^{bA}\pm1.09$	$45.98^{bA}\pm5.81$
sugar						
	RS	$11.80^{aC}\pm1.08$	$15.68^{aC}\pm3.57$	$18.81^{aAB}\pm2.42$	$19.99^{aAB}\pm3.49$	$22.73^{aA}\pm1.26$
	TS	0.00^{bNS}	0.00^{bNS}	0.00^{cNS}	0.00^{cNS}	0.00^{cNS}
	RS/TS	0.00^{bB}	0.00^{bB}	$0.82^{bB}\pm0.72$	$7.04^{bA}\pm1.27$	$7.47^{bA}\pm4.10$
coconut						
	RS	$27.00^{aC}\pm2.69$	$29.93^{aBC}\pm2.21$	$31.36^{aABC}\pm1.68$	$34.64^{aAB}\pm3.98$	$36.00^{aA}\pm1.63$
	TS	0.00^{cC}	0.00^{cC}	$20.11^{bB}\pm1.35$	$24.77^{cAB}\pm2.09$	$27.67^{cA}\pm6.79$
	RS/TS	$12.9^{bC}\pm3.09$	$18.70^{bB}\pm1.97$	$28.96^{bA}\pm1.83$	$28.58^{bA}\pm1.81$	$31.20^{bA}\pm2.51$

a-c Mean values in each column in the each system with different superscripts are significantly different ($p\leq0.05$)
A-C Mean values in each row with different superscripts are significantly different ($p\leq0.05$)
NS mean values in each row are non-significantly different ($p>0.05$)

Table 2. Syneresis value of rice (RS), tapioca (TS) and blend (RS/TS) starch gels (15%w/w) addition sugar and coconut milk in each cycle using fast frozen method.

sample		Syneresis (%)				
		Cycle1	**Cycle2**	**Cycle3**	**Cycle4**	**Cycle5**
water						
	RS	$29.52^{aC}\pm4.42$	$40.16^{aB}\pm3.76$	$40.53^{aA}\pm1.58$	$40.62^{aA}\pm2.67$	$40.65^{aA}\pm3.21$
	TS	0^{cD}	$13.98^{cc}\pm2.54$	$26.98^{cB}\pm4.23$	$38.40^{cA}\pm4.50$	$41.21^{bA}\pm1.91$
	RS/TS	$13.85^{bC}\pm3.05$	$28.81^{bB}\pm1.96$	$29.69^{bA}\pm0.82$	$35.54^{bA}\pm1.09$	$36.88^{cA}\pm1.81$
sugar						
	RS	0^{aE}	0^{aD}	$11.11^{aB}\pm1.42$	$11.48^{aA}\pm1.49$	$11.72^{aA}\pm1.26$
	TS	0^{bNS}	0^{bNS}	0^{bNS}	0^{cNS}	0^{cNS}
	RS/TS	0^{bC}	0^{bC}	0^{bB}	0^{bA}	1.39^{bA}
coconut						
	RS	$10.85^{aC}\pm1.69$	$22.11^{aB}\pm1.21$	$23.66^{aAB}\pm1.68$	$24.02^{aAB}\pm1.98$	$25.43^{bA}\pm1.63$
	TS	0^{bC}	0^{cC}	0^{cC}	$7.25^{cB}\pm1.09$	$15.18^{bA}\pm2.79$
	RS/TS	0^{bD}	$14.04^{bC}\pm1.97$	$19.94^{bB}\pm1.83$	$24.26^{bA}\pm0.81$	$24.61^{aA}\pm1.51$

a-c Mean values in each column in the each system with different superscripts are significantly different ($p\leq0.05$)
A-C Mean values in each row with different superscripts are significantly different ($p\leq0.05$)
NS mean values in each row are non-significantly different ($p>0.05$)

Table 3. Percent of syneresis of rice starch at different freezing rate. The samples were subjected to one and five freeze-thaw cycle.

	water		sugar		coconut milk	
	Cycle1	**Cycle5**	**Cycle1**	**Cycle5**	**Cycle1**	**Cycle5**
Fast freezing	$28.29^{b}\pm2.24$	$38.70^{b}\pm3.10$	0.0^{b}	$12.\ 62^{b}\pm1.09$	$11.15^{b}\pm1.76$	$26.64^{b}\pm2.13$
slow freezing	$37.91^{a}\pm3.65$	$50.23^{a}\pm5.22$	$10.10^{a}\pm1.08$	$20.38^{a}\pm1.38$	$26.67^{a}\pm3.21$	$37.10^{a}\pm2.46$

a-c Mean values in each column with different superscripts are significantly different($p\leq0.05$)

blending of tapioca starch displayed a lower syneresis value when compare with rice starch, meanwhile, the freeze thaw tapioca starch gel had zero syneresis value in the first cycle and begun releasing liquid from the gel at the second cycle of thawing. The percentage of syneresis could be explained with the amylose/amylopectin ratio in the starch. High syneresis value in rice starch resulted from high amylose content (33.75%) which could induce linear amylose molecules more re-associated and greater the retro gradation tendency [2]. while high amylopectin (low amylose content) resulted in low syneresis [4]. Previous studies showed that high amylose content starch (32.50% in [7] and 37.50% in [2]. had a significant higher syneresis than medium and low amylose content (17.6%). It was suggested that amylose play an important role in the retrogradation during the freezing and thawing. However the effect of the addition of different starch on the syneresis value of the freeze thaw cycle has not many been reported. Some reported blending rice starch gel with waxy starch and cassava starch on the reduction of syneresis significantly [2]. The effect of some hydrocolloids on the reduction of syneresis in starch have been widely reported by rea-

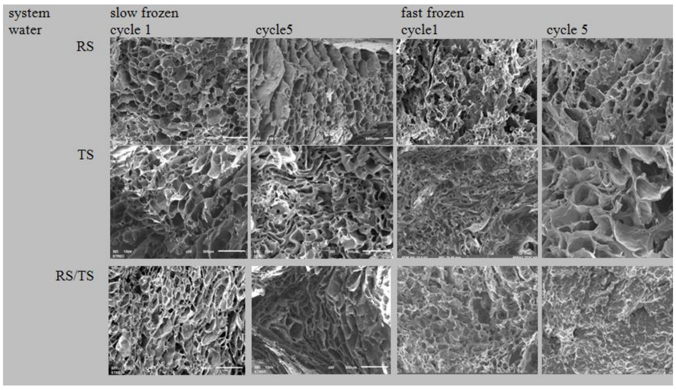

Figure 1: Microstructure images of rice (RS), tapioca (TS) and blend (RS/TS) starch gels (15%w/w) addition water after freeze and thaw for 1 and 5 cycles (50x, Bar = 500 μm) with slow and fast frozen methods.

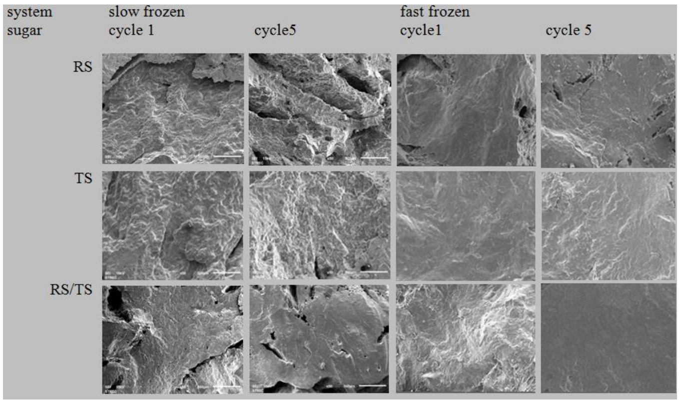

Figure 2: Microstructure images of rice (RS), tapioca (TS) and blend (RS/TS) starch gels (15%w/w) addition sugar after freeze and thaw for 1 and 5 cycles (50x, Bar = 500 μm) with slow and fast frozen methods.

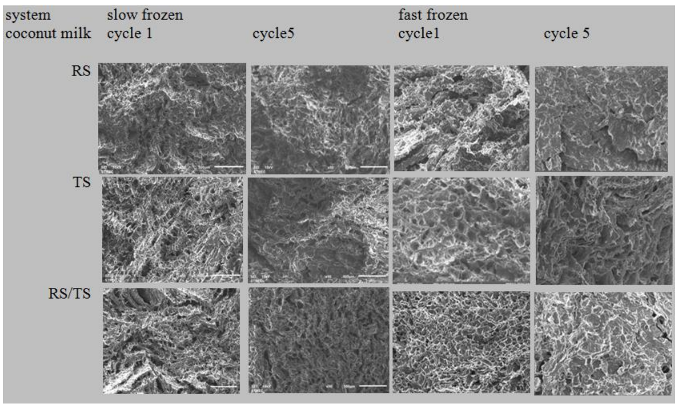

Figure 3: Microstructure images of rice (RS), tapioca (TS) and blend (RS/TS) starch gels (15%w/w) addition coconut milk after freeze and thaw for 1 and 5 cycles (50x, Bar = 500 μm) with slow and fast frozen methods.

son of the increasing of the viscosity of the starch paste and retardation of amylose re-association [26, 27, 23, 13, 14]. The freeze-thaw starch gel with addition of sugar and coconut milk showed less liquid separated from the starch polymer when compared with just adding water. Especially tapioca had zero syneresis value which was the same results with [4]. and blended starch gels exhibited liquid separation after the third cycle repetition. The adding of sugar led to the lowest liquid separation while adding coconut milk led to more liquid separation, respectively. It could be explained that sugar molecules can interact with starch molecular structure by intermolecular hydrogen bond and hydrated water molecules with the starch granule [19]. leading to lower amount of frozen water. High solid concentration in the gel facilitated the starch chains to be associated when kept at low temperature for a long time. Previous studies showed that freeze-thaw rice starch gel with sucrose added at the levels of 10 to 20% showed significantly lower syneresis percentage from the gel [15]. The adding of coconut milk in the starch gel had less liquid separation than addition of water. It might be due to the formation of lipid and amylose complex especially short chain and medium chain fatty acid in coconut milk that led to the reduction of retrogradation, syneresis and make starch gel more rigid [21, 22].

The effect of the frozen resulted that the fast frozen method in Table 3 had significant lowest liquid separation from the gel than in the slow frozen method. Several studies had been reported that fast freezing showed the results of lower syneresis or lower retrogradation on the frozen starch gel than slow freezing method [5, 7, 26]. The fast freezing method could be useful to prevent the ice nuclei formation and propagation state in the starch than occurred in slow methods. In this study, it was also found the same trend that the fast frozen method of the starch gel had significant lower liquid separated from the gel than in slow frozen method.

3.2 Microstructure

The SEM images of freeze thaw starch gels are shown in Figure 1-3. Ice crystals were observed as holes or pores in the gel matrix except with sugar adding. The slow frozen gel with chest freezer at -20 °C produced more porous and less homogeneous structure than fast frozen gel with air blast. It is clear that structure attributes are impacted by ice crystal formation and amylose retrogradation in starch during frozen after many repeated freeze-thaw cycles [10, 26]. The microstructure in the first freeze thaw cycle exhibits large pores in the gel and the morphology of the structure were the same in the previous research [23]. After the fifth freeze-thaw cycle, the surrounding starch gel become thicker matrix and less homogeneous like small pore surrounded with thick and some crack matrices. The probable cause is water from thawing process was trapped in the thick area of gel.

The freeze-thaw starch gel with addition sugar and coconut milk had less percentage of syneresis. The adding of coconut milk had the small porous structure meanwhile the adding sugar had rigid texture and microstructure gave no porous. This structure finding the correlated with the lower in the syneresis value also, and cause from the high solid concentration in the region facilitated the starch chains to associate forming thick filament and more condensed. It was in accordance with the research of [15]. who reported the SEM structure of rice starch were less porous and more condense when mixing starch gel from 10 up to 20% sucrose.

4. Conclusion

The addition of sucrose coconut milk and tapioca starch in the blending gel (RS/TS ratio 1:0.85) was found to be an effective agent for reduction of liquid separated from gel when undergoing repeated freeze-thaw cycles. Sucrose, coconut milk and tapioca starch are effective agents to enhance the freeze-thaw stability especially for ASEAN food and Thai dessert for fast frozen method than slow frozen method.

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