Carbohydrate Polymers 90 (2012) 1032–1037

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of waxy rice flour and cassava starch on freeze–thaw stability of rice starch gels

Sanguansri Charoenrein*, Nutsuda Preechathammawong

Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

ARTICLE INFO

Article history:
Received 3 March 2012
Received in revised form 13 June 2012
Accepted 13 June 2012
Available online 21 June 2012

Keywords:
Waxy rice flour
Cassava starch
Freezing
Texture
Rice starch
Retrogradation
Microstructure
Syneresis

ABSTRACT

Repeatedly frozen and thawed rice starch gel affects quality. This study investigated how incorporating waxy rice flour (WF) and cassava starch (CS) in rice starch gel affects factors used to measure quality. When rice starch gels containing 0–2% WF and CS were subjected to 5 freeze–thaw cycles, both WF and CS reduced the syneresis in first few cycles. However CS was more effective in reducing syneresis than WF. The different composite arrangement of rice starch with WF or CS caused different mechanisms associated with the rice starch gel retardation of retrogradation, reduced the spongy structure and lowered syneresis. Both swollen granules of rice starch and CS caused an increase in the hardness of the unfrozen and freeze–thawed starch gel while highly swollen WF granules caused softer gels. These results suggested that WF and CS were effective in preserving quality in frozen rice starch based products.
© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Frozen ready-to eat food products are convenient to use since they require less time to prepare than raw food. With proper frozen storage, these products can be kept for up to one year; therefore, a variety of new frozen foods are continually being launched onto world markets (Luh, 1999). However, upon freezing, water in the food is transformed into ice and as the ice separates out, the concentration of the unfrozen phase in contact with the ice increases. Both the ice formation and the increasing concentration of the unfrozen component result in physical stress on the food matrix (Reid, Kerr, & Hsu, 1994; Reid, 1999). When this frozen food is thawed for consumption, the moisture readily separates from the matrix and causes a change in the texture, drip loss, and often deterioration in the overall quality (Rahman, 1999).

Starch-based frozen food products undergo textural changes related to amylose and amylopectin retrogradation and show syneresis after thawing. These changes have been attributed to starch retrogradation (Ferrero, Martino, & Zaritzky, 1994; Jacobson & BeMiller, 1998; Varavinit, Anuntavuttikul, & Shobsngob, 2000) and may make such products unacceptable to consumers (Ferrero, Martino, & Zaritzky, 1993).

Controlling the freeze–thaw stability of starch pastes and gels by the addition of hydrocolloids has been widely investigated (BeMiller, 2011). Through the use of small quantities of hydrocolloids, it is possible to modify gels and starch-based products to improve their texture (Shi & BeMiller, 2002), produce a higher viscosity, and less syneresis (Mali et al., 2003). Furthermore, hydrocolloids reduce starch retrogradation and improve the gel stability in frozen starch gel systems (Ferrero et al., 1994; Lee, Baek, Cha, Park, & Lim, 2002). Ferrero et al. (1994) reported that adding xanthan gum to corn starch pastes minimizes amylose retrogradation, syneresis, and rheological changes after freezing. In addition, guar gum and locust bean gum were found to reduce syneresis in freeze–thawed corn starch and waxy Amaranthus paniculatus starch (Sudhakar, Singhal, & Kulkarni, 1996). In both of these studies, the authors based their conclusions on the pasting properties and rheological data and they attributed the reduction to a slowing of retrogradation brought about by an interaction between the hydrocolloid and the amylose. In another study, Ferrero and Zarizky (2000), using oscillatory rheological measurements and visual observation, reported that the hydrocolloid might interact with the amylose released outside the starch granule, inhibiting the development of a spongy matrix. It has been shown that konjac glucomannan reduces syneresis, spongy structure formation and moderately increases the hardness of freeze–thawed rice starch gels (Charoenrein, Tatirat, Rengsutthi, & Thongngam, 2011). The authors concluded that this effect was due to the high viscosity of the hydrocolloid and the even distribution of the rice starch granules in the hydrocolloid matrix.

There have been a few studies on using waxy starch/flour to improve the quality of frozen starch based food products, with

* Corresponding author. Tel.: +66 2 562 5025; fax: +66 2 562 5021.
E-mail address: fagisscr@ku.ac.th (S. Charoenrein).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.06.038

examples being bread made from frozen dough (Yi, Johnson, & Kerr, 2009), frozen Chinese steamed bread (Qin, Cheng, & Ma, 2007) and frozen fried dumplings (Hayakawa, Tanaka, Nakamura, Endo, & Hoshino, 2004). However, the explanation for the mechanism of addition of waxy flour/starch on product quality is not clear because these studies were carried out in real food systems. The current study attempted to investigate the possibility of using waxy rice flour (WF) and cassava starch (CS) to improve the freeze–thaw stability of rice starch gel as well as explain the causes of the effects. Both WF and CS are cheaper than most hydrocolloids and can be widely produced commercially in Thailand.

WF, produced from waxy or glutinous rice, contains little or no amylose. WF produces a paste with a higher viscosity and lower retrogradation rate than non-waxy rice flour paste. Gels from WF are softer than those from non-waxy rice flour (Luh, 1999).

CS is a root starch with specific properties such as a low paste temperature and a low gelling point and a lower amylose content and retrogradation tendency compared with cereal starches (Moore, Canto, Soldi, & Amante, 2005).

The objective of this study was to determine the effect of the addition of WF and CS in frozen rice gels by investigating their syneresis, textural changes, and the correlation between these two properties. In addition, the microstructure of unfrozen and freeze–thawed gels was studied in order to gain a greater understanding of the interaction between both polysaccharides and rice starch. This research will make a contribution toward improvements in the quality of frozen rice-based products.

2. Materials and methods

2.1. Materials

Rice starch was supplied by the Thai Flour Industry Co., Ltd. (Bangkok, Thailand). CS (food grade) was purchased from the Siam Modified Starch Co., Ltd, Pathum Tthani, Thailand and WF (food grade) was purchased from the Choheng Rice Vermicelli Co., Ltd. Nakorn Pathom, Thailand. The amylose content of rice starch, WF and CS were 37.50 ± 0.38, 4.11 ± 0.08 and 17.13 ± 0.60 g/100 g dried solid, respectively by the method of Hoover and Ratnayake (2001). The moisture content of rice starch, WF and CS were 12.56 ± 0.01, 11.69 ± 0.01 and 12.69 ± 0.01 g/100 g, respectively by official method of AACC (2000).

2.2. Sample preparation

A rice starch suspension (8.0%, w/w rice starch on a dry basis) was prepared by stirring rice starch and water continuously at 250 rpm for 60 min. The suspension was partially gelatinized by placing it in a water bath at 80 °C for 25 min with continuous stirring at 200 rpm. Each sample of 10 mL was then loaded into a syringe (25 mL with a 20 mm diameter) and steamed for 9 min. Finally, the samples were placed in an incubator at 25 °C for 120 min.

Suspensions containing 1% and 2% WF or CS were prepared by adding WF or CS into the rice starch suspensions (8.0%, w/w rice starch on a dry basis) giving the total dry matter of suspensions were 9 and 10%, respectively. Suspensions were then gelatinized using the same process as was used for the control rice starch suspension. Each experiment was repeated twice.

2.3. Freezing and thawing

Starch gel samples were frozen in a cryogenic cabinet freezer (Minibatch 100 L; Bangkok Industrial Gas Co., Bangkok, Thailand) which allowed the flow rate of liquid nitrogen to be adjusted creating a cold atmosphere of −20 °C. Freezing lowered the sample temperature from around 20 °C to −20 °C in 90 min. Then, the samples were stored in a chest freezer (Sanyo refrigerator, model SF-C1497) at −18 °C for 22 h and thawed at ambient temperature (25 ± 2 °C) for 2 h. This freeze–thaw cycle was repeated for up to five cycles. The freezing experiments were carried out in two separate trials. After thawing, gel samples were removed from the syringes prior to performing the following tests.

2.4. Syneresis measurement

Syneresis measurements followed the method of Charoenrein, Tatirat, and Muadklay (2008). The thawed starch gel samples were removed from their syringes and put in a cylindrical plastic tube with a perforated bottom covered with filter paper (Whatman No. 41). These tubes were then placed in centrifuge tubes and centrifuged (centrifuge CN-1050, MRC Ltd., Holon, Israel) at $100 \times g$ for 15 min. The cylindrical plastic tube with cover was removed from the centrifuge tube, and the liquid which had separated from the starch gel was weighed. The percentage of syneresis was then calculated as the ratio of the weight of liquid separated from the gel to the total weight of the gel before centrifugation, and multiplied by 100. The data were reported as the average of five measurements.

2.5. Determination of the microstructure of frozen starch gel with scanning electron microscopy

The freeze–thawed rice starch gels with and without WF or CS were cut and gradually dehydrated in 50%, 70%, 90% and absolute ethanol at room temperature for 24 h at each concentration and finally dehydrated using a critical point dryer. The cut surface samples were mounted on a stub, coated with gold and observed using a JSM-5600LV microscope (JSM-5600LV; JEOL, England). The accelerating voltage and the magnification are shown on the micrographs in Fig. 1.

2.6. Determination of the microstructure of unfrozen starch gel with a confocal laser scanning microscope

The unfrozen rice starch gels with and without WF or CS were cut into sections of 1–3 mm thickness using a razor blade. The sections were stained by immersion into FITC-dextran (Fluorescein isothiocyanate dextran 0.01% (w/v) in distilled water) for 2 min followed by rinsing three times in distilled water. Each sample was mounted in a slide well and covered with a cover glass. Images were recorded using a confocal laser scanning microscope (CLSM; Axio Imager MI, Carl Zeiss Pty Ltd., Germany). A HeNe laser with an excitation wavelength of 488 nm was used. CLSM digital images were acquired using the LSM 5 PASCAL program.

2.7. Pasting profile

The pasting properties of the rice starch suspension (8%, w/w) with 0–2% WF or CS were determined using a Rapid Visco-Analyzer (model RVA-4C, Newport Scientific Pty Ltd., Warriewood, Australia). The slurry was held at 50 °C for 1 min, heated to 95 °C at a constant rate of 12 °C/min and then held at 95 °C for 2.5 min. It was subsequently cooled to 50 °C at the same rate and then held at 50 °C for 2 min. The data were reported as the average of triplicate measurements.

2.8. Texture measurement

The unfrozen and freeze–thawed rice starch gels with and without WF or CS after the first cycle (25 ± 2 °C) were transferred from the syringe into a rectangular mold (approximately 150 mm wide by 40 mm long and 30 mm deep), which had a gap for sample cutting and the middle of the gel was cut into a sample 20 mm in length.

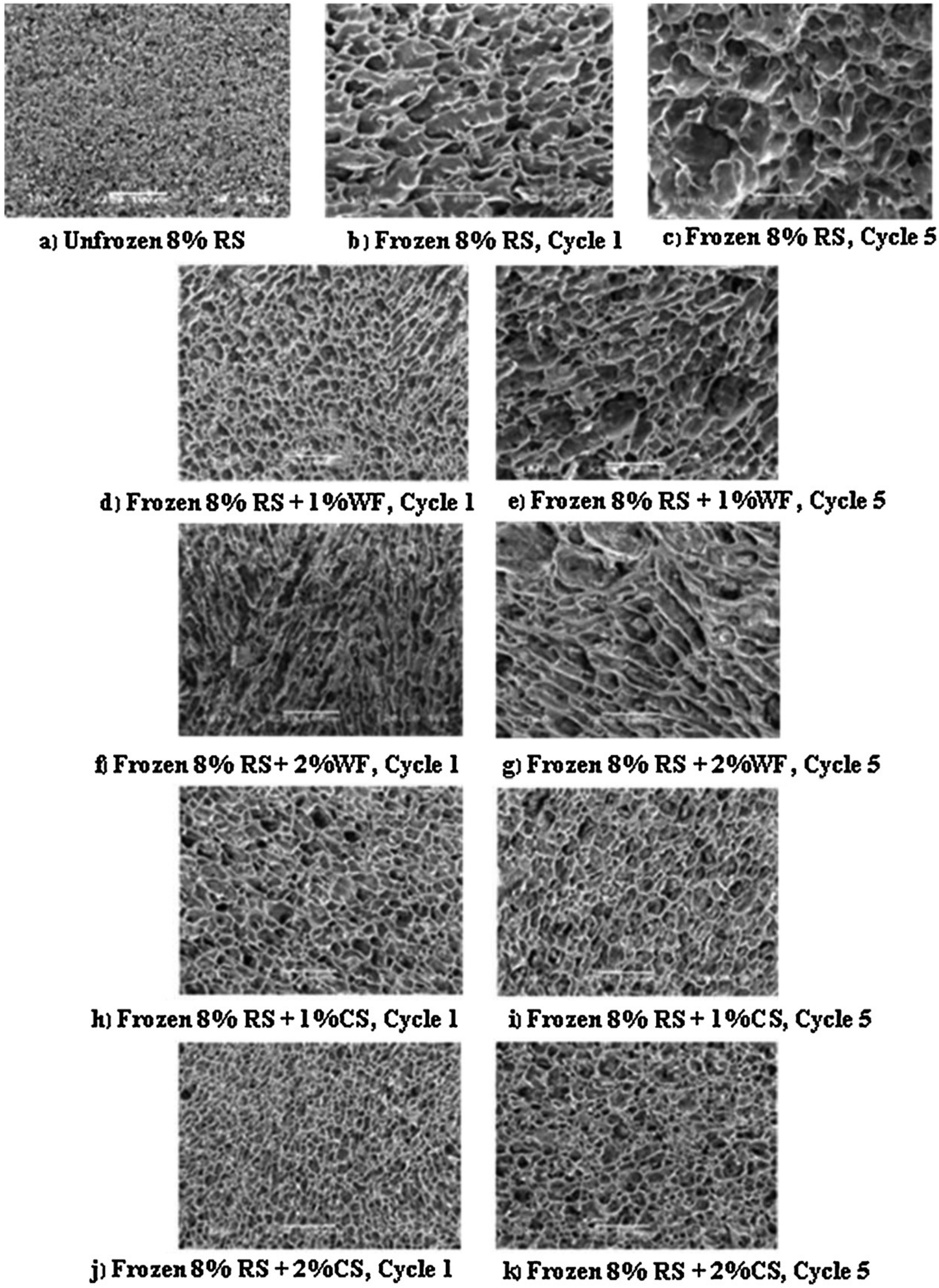

Fig. 1. Scanning electron microscope images of rice starch gels (8%, w/w total solid) containing 1 and 2% waxy rice flour or cassava starch unfrozen and after one and five freeze–thaw cycle (250×, bar = 100 μm).

The texture was determined at ambient temperature (25 ± 2 °C) using the texture profile analysis method (five replicates per treatment) with a Texture Analyzer (TA-XT plus, Stable Micro System, Surrey, UK). Samples were compressed with a 100 mm diameter probe at a test speed of 0.5 mm/s. The deformation level was 40% of the original sample height and the gels were compressed twice. Hardness was expressed as the maximum force exerted during the first compression cycle.

Table 1
Syneresis values of rice starch gel (8.0%, w/w total solid) containing waxy rice flour (WF) or cassava starch (CS) 0–2% in each cycle.

Sample	Syneresis (%)				
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Rice starch	$38.1^{aA} \pm 0.7$	$52.7^{aB} \pm 0.6$	$55.8^{aC} \pm 2.1$	$56.7^{abC} \pm 1.1$	$57.5^{aC} \pm 1.6$
Rice starch + 1% WF	$27.0^{bA} \pm 4.0$	$52.6^{aB} \pm 0.9$	$54.5^{aBC} \pm 4.5$	$56.5^{abC} \pm 0.7$	$57.5^{aC} \pm 0.4$
Rice starch + 2% WF	$14.1^{dA} \pm 2.6$	$47.6^{cB} \pm 0.8$	$55.4^{aC} \pm 1.3$	$56.0^{bC} \pm 1.8$	$56.8^{aC} \pm 0.6$
Rice starch + 1% CS	$28.5^{bA} \pm 3.2$	$46.6^{bB} \pm 1.3$	$48.4^{bBC} \pm 1.9$	$49.7^{bC} \pm 0.7$	$49.3^{bC} \pm 1.5$
Rice starch + 2% CS	$21.9^{cA} \pm 1.9$	$39.3^{dB} \pm 0.9$	$43.1^{cC} \pm 2.0$	$45.5^{cC} \pm 1.7$	$45.4^{cC} \pm 2.2$

Mean values in each column with different lower case letter superscripts (a–d) are significantly different ($p \leq 0.05$).
Mean values in each row with different upper case letter superscripts (A–C) are significantly different ($p \leq 0.05$).

2.9. Statistical analysis

A completely randomized design was used. The difference between means was determined using Duncan's new multiple range test with the level of significance set at $p \leq 0.05$. All statistical analyses were performed using SPSS 12.0 for Windows.

3. Results and discussion

3.1. Percent syneresis

The percentage syneresis (% syneresis) for freeze–thawed starch was used to evaluate the ability of starch to withstand the undesirable physical changes which occur during freezing and thawing. Syneresis in a freeze–thawed gel is caused by an increase in molecular associations between starch chains—in particular the retrogradation of amylose (Morris, 1990) which results in the expulsion of water from the gel structure (Saartratra, Puttanlekb, Rungsardthong, & Uttapap, 2005). Thus, the amount of water released due to syneresis is a useful indicator of the tendency of starch to retrograde (Karim, Norziah, & Seow, 2000). However, in starch gel containing ingredients such as hydrocolloids or sugars, which can bind to water molecules, syneresis is reduced (Arunyanart & Charoenrein, 2008; Baker & Rayas-Duarte, 1998; Yoshimura, Takaya, & Nishinari, 1998).

The effect of WF and CS on the % syneresis in rice starch gels is presented in Table 1. Freeze–thawed rice starch gels without WF or CS had a high syneresis value (38.1%) after the first cycle and had a significantly higher value after two freeze–thaw cycles. After that, the values changes slightly through cycles 3–5. High syneresis in this sample resulted from a high amylose content (37.50%) in the rice starch. A previous study (Charoenrein et al., 2008) showed that gels made from medium-amylose rice flour (17.6%) had a significantly lower % syneresis after the first freeze–thaw cycle than did gels made from high-amylose rice flour (32.5%). This result implies that amylose plays an important role in the retrogradation associated with freezing and thawing.

However, freeze–thawed rice starch gel with WF displayed a markedly lower % syneresis. Starch gel containing 1% WF which had shown 27.0% syneresis after the first freeze–thaw cycle, showed an obvious increase in its syneresis value to 52.6% after two freeze–thaw cycles. After that, the syneresis values changed only slightly through cycles 3–5. Starch gel containing 2% WF, which had 14.1% syneresis after the first cycle, showed an increase in syneresis value to 47.6%, after two freeze–thaw cycles. At this concentration too, after the second and through to the fifth freeze–thaw cycle, the % syneresis slightly increased but was slightly lower than had occurred with 1% WF. The addition of CS showed a similar trend with WF addition; however, their syneresis values were slightly lower.

Although the effect of the addition of different starches or flours on the syneresis value in starch gel has not been reported, the effects of some hydrocolloids on the reduction of syneresis in starch paste/gel have been widely studied. For example, xanthan gum effectively reduced syneresis in freeze–thawed corn starch gel (Ferrero et al., 1994), and in high-amylose and waxy corn starch gel (Weber, Queiroz, & Chang, 2008) while xanthan, alginate and guar gum reduced syneresis in freeze–thawed sweet potato starch gel (Lee et al., 2002). Muadklay & Charoenrein (2008) found that xanthan gum also reduced syneresis in freeze–thawed cassava starch gel. Charoenrein et al. (2011) reported that konjac glucomannan reduced syneresis in freeze–thawed rice starch gel. It has been hypothesized that the effects of hydrocolloids in the reduction of syneresis are due to the retardation of amylose retrogradation (Ferrero et al., 1993, 1994) and an increase in the viscosity of the starch paste (Lee et al., 2002). Shi and BeMiller (2002) suggested more specifically that this effect was likely due to interactions between certain leached molecules, primarily between amylose and certain gums.

3.2. Microstructure of freeze–thawed rice starch gels

To elucidate the relationship between syneresis and the addition of WF and CS to rice starch gels, the microstructure of freeze–thawed gels was examined using SEM. Images of treated specimens are shown in Fig. 1. The microstructure of rice starch gel before freezing is shown in Fig. 1a. Clear differences were observed in the microstructure of rice starch gels after one and five freeze–thaw cycles for both gels with and without WF or CS. All freeze–thawed starch gels developed a spongy structure which can be attributed to ice crystal formation and amylose retrogradation. A thick fibrillar network of starch gel was formed in the spongy structure during the repeated freeze–thaw cycles; similar findings were reported by Ferrero et al. (1993) and Charoenrein et al. (2011). In rice starch gel with no WF or CS added, the microstructure after the first freeze–thaw cycle was characterized by large pores in the gel (Fig. 1b). After the fifth freeze–thaw cycle, the starch gels had a bigger pore size, the matrix surrounding the pores was stronger and the pores were very clearly defined (Fig. 1c). These structural findings correlated well with the changes in the syneresis values found after 1–5 freeze–thaw cycles of rice starch gel to which no WF or CS had been added. After one freeze–thaw cycle, the starch gels containing 1% WF appeared to have smaller and less well-defined pores embedded in a weak matrix (Fig. 1d). After five freeze–thaw cycles, the pore size in these gels had increased but the pores were still less well-defined than in starch gels without WF (Fig. 1c and e). Rice starch gels with 2% WF showed similar results to those of 1% WF (Fig. 1f and g). However, rice starch gels with 1 and 2% CS (Fig. 1h–k) showed slightly less spongy structures after one and five freeze–thaw cycles as compared with gels containing WF. The specimen images showed that CS was able to effectively stabilize the microstructure of rice starch gels after the first to fifth freeze–thaw cycle slightly more than WF. These microstructural results (of a less spongy structure formation in rice starch gels with CS) correlated well with the lower syneresis values found after 1–5 freeze–thaw cycles as compared to rice starch gels with WF.

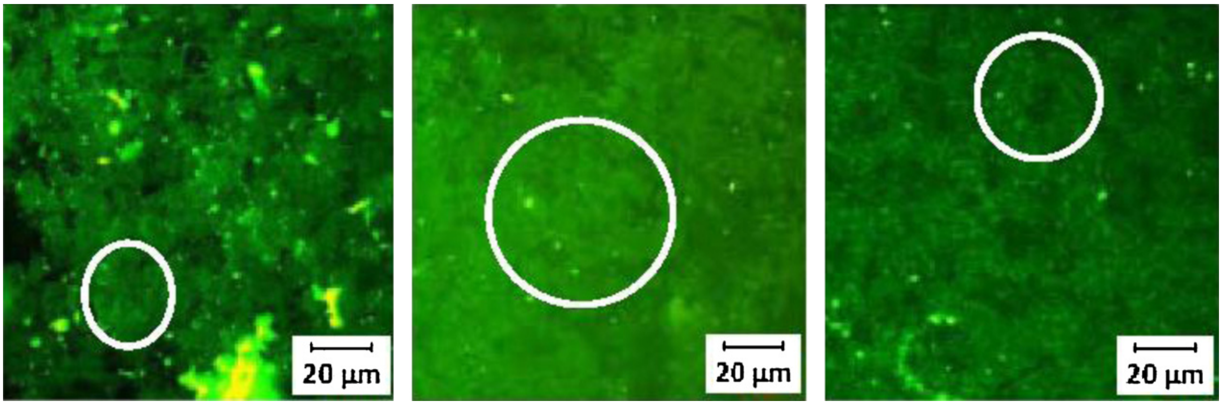

Fig. 2. Confocal laser scanning microscope images of unfrozen rice starch gels (8%, w/w total solid) in the absence (a) and presence (b) of 2% waxy rice flour; and (c) in the presence of 2% cassava starch (c). Circles indicate the association of swollen rice starch granules in (b), less association of swollen rice starch granules in the spread of swollen waxy rice starch granules in (b) and dense pack of less swollen rice and cassava starch granules in (c), bar = 20 μm.

The microstructure of the unfrozen gel described in 3.3 below demonstrates how WF and CS help reduce syneresis and modify the microstructure of freeze–thawed starch gels.

3.3. Microstructure of unfrozen rice starch gel

Starch gels can be regarded as composites where the swollen granules (amylopectin) are embedded into a continuous matrix of aggregated amylose molecules (Ahmad & William, 1998). During the preparation of rice starch gels, rice starch granules suspended in excess amounts of water (starch 8%, w/w total solid) swelled upon heating. After agitation and subsequent steaming for 9 min, it is assumed that amylose molecules leach from the swollen rice starch granules creating granule ghosts. Granule ghosts are formed from starch granules when they are heated in water without or with little shear.

There have been several reported studies of formation of granule hosts during gelatinization (Fannon & BeMiller, 1992; Obanni & BeMiller, 1996). It is possible to visualize the influence of WF and CS on the starch gel microstructure using CLSM and a fluorescent dye. The starch was stained with FITC-dextran which was absorbed by the starch granules. Fig. 2a–c shows the optical sections of the rice starch gel and the rice starch gel with 2% WF and CS. Fig. 2a shows swollen starch granules or starch ghosts of different sizes unevenly distributed throughout most of the volume fraction with the swollen starch granules tending to group together. Fig. 2b shows swollen starch granules in a different arrangement. The highly swollen starch granules of WF are distributed and cover more swollen rice starch granules than those in Fig. 2a. This finding corresponded with the pasting properties of rice starch, WF and CS as shown in Table 2. The pasting temperature of WF (69.60 °C) was much lower than for rice starch (88.38 °C); therefore, WF granules were swollen to a higher degree and earlier than rice starch granules. It was hypothesized that the spread of highly swollen granules of WF might lower the degree of rice starch retrogradation and consequently reduced the extent of spongy structures of freeze–thawed gel. Fig. 2c shows swollen CS granules connected with swollen starch granules of rice starch. CS had a pasting temperature (71.15 °C) that was closer to that of rice starch than that of WF; therefore, both starch granules absorbed water and were swollen to a relatively similar extent and were connected together. This arrangement could also reduce the retrogradation and spongy structure of the sample. Since WF and CS also absorbed some water during gel preparation, this might be another reason for the lower syneresis values in the gel with WF or CS added. In addition, in the RVA measurement, higher values for peak viscosity, breakdown, final viscosity and setback were observed in rice paste with WF or CS (Table 2). The interaction between rice starch and WF or CS particles might be responsible for increase in these viscosity values and helps explain the influence of WF and CS on the microstructure of unfrozen starch paste.

3.4. Texture

The textural properties of the rice starch gels with and without WF or CS before and after freezing and thawing were studied and the results are shown in Table 3. It was found that before freezing, starch gel samples containing 1 and 2% WF were not as hard as were those without WF. The more WF that was added, the softer the gels were. However, starch gel with CS showed the opposite results. The textural results in the current study can be clearly elucidated by examining the microstructure of unfrozen gels using

Table 2
Viscosity (RVA) profiles of rice starch (RS), waxy rice flour (WF), cassava starch (CS) and rice starch with waxy rice flour or cassava starch suspension.

Sample	Pasting temperature (°C)	Viscosity (RVU)				
		Peak viscosity	Trough	Break down	Final viscosity	Setback
RS	88.38^{a}	117.96^{f}	112.87^{f}	5.09^{g}	136.42^{f}	23.55^{e}
WF	69.60^{g}	214.83^{d}	138.33^{e}	76.50^{c}	152.25^{e}	13.92^{f}
CS	71.15^{f}	209.25^{d}	116.08^{f}	93.17^{b}	154.79^{e}	38.71^{d}
RS + 1% WF	85.30^{b}	189.08^{e}	163.08^{d}	26.00^{f}	241.88^{d}	78.80^{c}
RS + 2% WF	84.08^{c}	265.17^{b}	219.13^{a}	46.04^{e}	319.54^{b}	100.41^{b}
RS + 1% CS	83.18^{d}	222.33^{c}	171.63^{c}	50.70^{d}	274.08^{c}	102.45^{b}
RS + 2% CS	81.58^{e}	317.21^{a}	212.33^{b}	104.88^{a}	327.13^{a}	114.80^{a}

Suspension concentration for RS, WF and CS, RS + 1%WF or CS and RS + 2%WF or CS were 8–10% dry basis, respectively.
Mean values in each column with different lower case letter superscripts (a–c) are significantly different ($p \leq 0.05$).

Table 3
Hardness of rice starch gel (8.0%, w/w total solid) containing waxy rice flour (WF) or cassava starch (CS) at 0–2% before and after subjecting to one freeze–thaw (FT) cycle.

Sample	Hardness (N)	
	Before freezing	After 1 FT cycle
Rice starch	$1.65^{b} \pm 0.06$	$3.92^{c} \pm 0.17$
Rice starch + 1% WF	$1.48^{c} \pm 0.06$	$2.87^{d} \pm 0.06$
Rice starch + 2% WF	$1.25^{d} \pm 0.09$	$1.74^{e} \pm 0.11$
Rice starch + 1% CS	$2.05^{a} \pm 0.02$	$5.23^{b} \pm 0.23$
Rice starch + 2% CS	$2.04^{a} \pm 0.02$	$7.32^{a} \pm 0.29$

Mean values in each column with different lower case letter superscripts (a–c) are significantly different ($p \leq 0.05$).

CLSM. It can be seen from Fig. 2a and b that WF retarded the aggregation of swollen rice starch granules. In addition, the setback and final viscosity of WF were much lower than those of rice starch and CS (Table 2), indicating that the swollen rice starch granules were embedded in a soft matrix of waxy rice starch gel. The CLSM images of the rice starch gel with CS showed the connection of both swollen starch granules of rice starch and CS (Fig. 2c) which caused higher hardness in the gels. After the first freeze–thaw cycle, the hardness in all samples increased. Though the retrogradation of starch molecules in starch-rich regions is enhanced during freezing and thawing (Yuan & Thompson, 1998) leading to an increase in the hardness of a gel, an increase in the hardness of the rice starch gel was much more obvious after freezing and thawing than in those gels containing 0–2% WF (137, 94 and 38%, respectively). Moreover, there was obviously higher hardness of the freeze–thawed gels containing 0–2% CS (137, 155 and 259%, respectively). It should also be noted that the hardness of the freeze–thawed starch gels containing 2% WF was relatively similar to that of the unfrozen starch gels without WF or CS.

4. Conclusions

The addition of CS and WF was shown to be an effective agent for the reduction of the spongy structure formation in freeze–thawed rice starch gels. CS was slightly better than WF in terms of syneresis reduction especially after 2–5 freeze–thaw cycles. WF was able to retard the textural changes which resulted from a gel with a spongy structure. The microstructure of the unfrozen starch gel demonstrated that swollen starch granules form dense associations in rice starch gels containing no WF or CS, while in gels containing WF, the highly swollen WF starch granules spread and covered swollen rice starch granules. In gels containing CS, the connection of both swollen starch granules of rice starch and CS was evident. This research shows that either CS or WF can be a useful additive for preserving quality in frozen rice starch-based food products.

Acknowledgements

The authors gratefully acknowledge funding support from the Thailand Research Fund Grants under project RSA 5080014 and from the Kasetsart University Research and Development Institute (KURDI) under the SRU-FPF project.

References

AACC. (2000). *Approved methods of the American association of cereal chemists* (10th ed.). St. Paul, MN: American Association of Cereal Chemists.
Ahmad, F. B., & William, P. A. (1998). Rheological properties of sago starch. *Journal of Agricultural and Food Chemistry*, *46*, 4060–4065.
Arunyanart, T., & Charoenrein, S. (2008). Effect of sucrose on the freeze–thaw stability of rice starch gels: Correlation with microstructure and freezable water. *Carbohydrate Polymers*, *74*, 514–518.
Baker, L. A., & Rayas-Duarte, P. (1998). Freeze–thaw stability of amaranth starch and the effects of salt and sugars. *Cereal Chemistry*, *75*, 301–307.
BeMiller, J. N. (2011). Pasting, paste and gel properties of starch–hydrocolloid combinations. *Carbohydrate Polymers*, *86*, 386–423.
Charoenrein, S., Tatirat, O., & Muadklay, J. (2008). Use of centrifugation–filtration for determination of syneresis in freeze–thaw starch gels. *Carbohydrate Polymers*, *73*, 143–147.
Charoenrein, S., Tatirat, O., Rengsutthi, K., & Thongngam, M. (2011). Effect of konjac glucomannan on syneresis, textural properties and the microstructure of frozen rice starch gels. *Carbohydrate Polymers*, *83*, 291–296.
Fannon, J. E., & BeMiller, J. N. (1992). Structure of corn starch paste and granule ramnants revealed by low-temperature scanning electron microscopy after cryopreparation. *Cereal Chemistry*, *69*, 456–460.
Ferrero, C., Martino, M. N., & Zaritzky, N. E. (1993). Effect of freezing rate and xanthan gum on the properties of corn starch and wheat flour pastes. *International Journal of Food Science and Technology*, *28*, 481–498.
Ferrero, C., Martino, M. N., & Zaritzky, N. E. (1994). Corn starch–xanthan gum interaction and its effect on the stability during storage of frozen gelatinized suspensions. *Starch/Stärke*, *46*, 300–308.
Ferrero, C., & Zarizky, N. E. (2000). Effect of freezing rate and frozen storage on starch sucrose–hydrocolloid system. *Journal of Science and Food Agricultural*, *80*, 2149–2158.
Hayakawa, K., Tanaka, K., Nakamura, T., Endo, S., & Hoshino, T. (2004). End use quality of waxy wheat flour in various grain-based foods. *Cereal Chemistry*, *81*, 666–672.
Hoover, R., & Ratnayake, W. S. (2001). Determination of total amylose content of starch. In R. E. Wrolstad, T. E. Acree, E. A. Decker, M. H. Penner, D. S. Reid, S. J. Schwartz, C. F. Shoemaker, D. M. Smith, & P. Sporns (Eds.), *Current protocols in food analytical chemistry*. New York: Wiley.
Jacobson, M. R., & BeMiller, J. N. (1998). Method for determining the rate and extent of accelerated starch retrogradation. *Cereal Chemistry*, *75*, 22–29.
Karim, A. A., Norziah, M. H., & Seow, C. C. (2000). Methods for the study of starch retrogradation. *Food Chemistry*, *71*, 9–36.
Lee, M. H., Baek, M. H., Cha, D. S., Park, H. J., & Lim, S. T. (2002). Freeze–thaw stability of sweet potato gel by polysaccharide gums. *Food Hydrocolloids*, *16*, 345–352.
Luh, B. S. (1999). Rice products. In C. Y. W. Ang, K. Liu, & Y. W. Huang (Eds.), *Asian foods: science and technology* (pp. 5–42). Lancaster, PA: Technomic Publishing.
Mali, H., Ferrero, C., Redigonda, V., Beleia, A. P., Grossmann, M. V. E., & Zaritzky, N. E. (2003). Influence of pH and hydrocolloids addition on yam (*Dioscorea alata*) starch pastes stability. *Food Science and Technology*, *36*, 475–481.
Moore, G. R. P., Canto, L. R., Soldi, V., & Amante, E. R. (2005). Cassava and corn starch in maltodextrin production. *Química Nova*, *28*, 596–600.
Morris, V. J. (1990). Starch gelation and retrogradation. *Trends in Food Science and Technology.*, *1*, 2–6.
Muadklay, J., & Charoenrein, S. (2008). Effects of hydrocolloids and freezing rates on freeze–thaw stability of tapioca starch gels. *Food Hydrocolloids*, *22*, 1268–1272.
Obanni, M., & BeMiller, J. N. (1996). Ghost microstructures of starch from different botanical sources. *Cereal Chemistry*, *73*, 333–337.
Qin, P., Cheng, S., & Ma, C. (2007). Effect of waxy wheat flour blends on the quality of Chinese steamed bread. *Agricultural Sciences in China*, *6*, 1275–1282.
Rahman, M. S. (1999). Food preservation by freezing. In M. S. Rahman (Ed.), *Handbook of food preservation* (pp. 259–284). New York: Marcel Dekker.
Reid, D. S., Kerr, W., & Hsu, J. (1994). The glass transition in the freezing process. *Journal of Food Engineering*, *22*, 483–494.
Reid, D. S. (1999). Dehydration and freezing stress. In Y. H. Roos, J. B. Leslie, & P. J. Lillford (Eds.), *Water management in the design and distribution of quality foods* (pp. 87–105). Lancaster, PA: Technomics Publication.
Saartratra, S., Puttanlekb, C., Rungsardthong, V., & Uttapap, D. (2005). Paste and gel properties of low – substituted acetylated canna starches. *Carbohydrate Polymers*, *61*, 211–221.
Shi, X., & BeMiller, J. N. (2002). Effects of food gum and viscosities of starch suspension during pasting. *Carbohydrate Polymers*, *50*, 7–18.
Sudhakar, V., Singhal, R. S., & Kulkarni, P. R. (1996). Starch–galactomannan interactions: Functionality and rheological aspects. *Food Chemistry*, *55*, 259–264.
Varavinit, S., Anuntavuttikul, S., & Shobsngob, S. (2000). Influence of freezing and thawing techniques on stability sago and tapioca starch pastes. *Starch/Stärke*, *52*, 214–217.
Weber, F. H., Queiroz, F. P. C., & Chang, Y. K. (2008). Freeze–thaw stability of normal, waxy and high amylose corn starch gels with added guar and xanthan gums. *Ciencia e Tecnologia de Alimentos*, *28*.
Yi, J., Johnson, J. W., & Kerr, W. L. (2009). Properties of bread made from frozen dough containing waxy wheat flour. *Journal of Cereal Science*, *50*, 361–369.
Yoshimura, M., Takaya, T., & Nishinari, K. (1998). Rheological studies on mixtures of corn starch and konjac-glucomannan. *Carbohydrate Polymers*, *35*, 71–79.
Yuan, R. C., & Thompson, D. B. (1998). Freeze–thaw stability of three waxy maize starch pastes measured by centrifugation and calorimetry. *Cereal Chemistry*, *75*, 571–573.