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Paste and gel properties of low-substituted acetylated canna starches

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Abstract

Starches isolated from rhizomes of two cultivars of edible canna (namely; Thai-green and Thai-purple) were modified by acetylation in order to reduce retrogradation and increase gel stability. Acetylation was carried out by treating starches with 5, 7 and 9% (w/w) of acetic anhydride at room temperature and pH between 8.0-8.5. The extent of acetylation increased proportionally with the concentration of acetic anhydride used. The percentages of acetyl group determined by titration method were 1.41, 2.05 and 2.55 for Thai-purple starch and 1.43, 2.02 and 2.53 for Thai-green starch. Observation under scanning electron microscope revealed that all of the modified starch granules were still in intact form and there was no difference between native and modified starches. The viscoamylographs of 6% starch determined by Rapid Visco Analyzer at 160 rpm showed that acetylation decreased the pasting temperatures (3–5 °C) and slightly decreased the hot paste viscosity. The setback values of acetylated starches were approximately 15-46% lower than those of native starches. Effect of pH and agitation on the pasting properties of native and acetylated canna starch was not significantly different. There were some variations in pasting attributes between starch pastes from Thai-purple and Thai-green canna which were due to their chemical compositions and molecular structures. Hardness (firmness) of canna starches gel was analyzed by a texture analyzer using a 20 mm diameter-cylindrical plunger. With 6% starch solids in water at pH 6.8, all acetylated canna starches gave much softer gel than those of corresponding native starches. For example, the firmness values of Thai-green canna starches containing 1.43, 2.02, 2.53% acetyl group and the native were 168, 193, 508 and 1915 g, respectively. The data of setback viscosities from RVA profiles, hardness of gels by texture analysis, and syneresis from freeze-thaw study, all indicated that acetylation could increase gel stability and substantially reduce retrogradation of canna starches. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Canna starch; Acetylation; Paste; Gel; Modification; Esterification

1. Introduction

Starches are traditionally used in food as thickening agent or stabilizer in order to provide some properties such as texture, appearance and mouthfulness. Native starch may not be suitable for some food products. To improve properties for specific application, chemical modifications of starches are often made. Chemically modified starches have markedly altered physicochemical properties compared with their native starches (Rutenberg & Solarek, 1984). Acetylation of starches is an important substitution

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method that has been applied to starches that impart the thickening need in food application. Introduction of acetyl group has improved properties over its native form and has been used for its stability and resistance to retrogradation. Hoover & Sosulski (1985) found that acetylation increased the stability of legume starch under low temperature storage. Acetylation of Korean rice starch increased viscosity, solubility, swelling power, hardness, cohesiveness and adhesiveness of starch gel and decreased initial gelatinization temperature (Jeong, Bae, & Oh, 1993).

Acetylated starches with a relatively low degree of substitution (DS) are widely used in food industries for many years because of their typical physicochemical characteristics such as low gelatinization temperature, high solubility, and good cooking and storage stability (Liu, Ramsden, & Corke, 1999; Wang & Wang, 2002). The physicochemical properties of acetylated starches depend

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on their chemical structures, DS and acetyl group distributions (Chen, Schols, & Voragen, 2004). Viscosity of starch pastes can be increased or decreased by acetylation, depending on the starch source and the esterification method. Increase in paste viscosities of *Canavalia ensiformis*, *Phaseolus vulgaris*, mucuna bean and rice starches have been reported by Adebowale and Lawal (2003); Betancur, Chel, and Canizares (1997); Gonzalez and Perez (2002); Hoover & Sosulski (1985), respectively. On the contrary, lower paste viscosity was also found in cassava starch as reported by Agboola, Akingbala, and Oguntimein (1991); Moorthy (1985).

There have been some reports on the physicochemical properties of edible canna starch (Perez, Breene, & Bahnassey 1998; Santacruz, Koch, Svensson, Ruales, & Eliasson 2002; Soni, Sharma, Srivastava, & Gharia 1990; Thitipraphunkul, Uttapap, Piyachomkwan, & Takeda, 2003a). They indicated the interesting properties of edible canna especially pasting properties. Soni et al. (1990) reported that Brabender viscosity of C. edulis starch is around three times higher than that of maize starch and has shown no thinning. The study of Perez et al. (1998) showed that canna starch produced a clear paste and had much higher viscosity than cassava starch at the same concentration. High viscosity of the canna starch is the interesting property for being used as a thickening agent, but its high tendency to retrograde makes it unsuitable (Thitipraphunkul et al., 2003a). In this study, the canna starches were therefore modified by acetylation in order to decrease the retrogradation and increase gel stability.

2. Materials and methods

2.1. Raw materials

Two cultivars of edible canna (Thai-purple and Thai-green) were grown on experimental plots under identical environmental condition at the Corn and Sorghum Research Center, Kasetsart University, Thailand. Ten-month rhizomes were harvested for starch extraction. Starch was isolated from the rhizomes according to a procedure described by Thitipraphunkul et al., 2003a. All the chemicals used in the experiments were analytical grade.

2.2. Preparation of starch acetate

One hundred and seventy grams of canna starch was dispersed in 225 ml of distilled water at room temperature in 1000 ml beaker. Acetic anhydride (5, 7 and 9% (w/w)) was added drop-wise into the starch suspension while pH was being kept between 8–8.5 by the addition of 3% NaOH. When the addition of acetic anhydride was complete, pH of the slurry was adjusted to 6.5 with 0.5 N sulphuric acid and it was filtered through a Buchner funnel. The filter cake was resuspended in 500 ml water and filtered. The

suspending and filtering steps were repeated twice and the resulting filter cake was dried for 20 h at 50 °C in a hot air oven (modified from method described by Wurzberg, 1964).

2.3. Measurement of degree of substitution by titration method

Five grams of starch acetate and 50 ml of distilled water were dispersed in an Erlenmeyer flask with a stopper (Ogawa et al., 1999). Phenolphthalein was added to the suspension as an indicator, and then 0.1 M NaOH solution was added to give the red color. After the addition of 25 ml of 0.45 M NaOH solution, the mixture was stirred at room temperature for 30 min. The flask was corked to prevent evaporation of the produced acetate during the saponification reaction. Finally, the excess alkali in the sample mixture was titrated with 0.2 M HCl solution. A blank test (without the starch) was also carried out using the same procedure. Percentage of acetyl group was calculated as the following equations:

%acetyl

$$= \frac{(\text{value for blank} - \text{value for sample}) \text{ml} \times \text{normality of HCl} \times 0.043 \times 100}{(\text{sample weight}) \text{g}}$$

Reaction efficiency (%) =
$$\frac{DS}{\text{moles of acetyl/mole of anhydro} - D - \text{glucose unit}}$$

2.4. Scanning electron microscopy

Scanning electron micrographs were taken by a JEOL, JSM-5800 Scanning Electron Microscope (Jeol Ltd, Tokyo, Japan) at an accelerating voltage of 15 kV. Starch samples were spread on an aluminium stub using double-sided adhesive tape and the starch was coated with gold.

2.5. Pasting properties

Pasting properties of starch slurry at a concentration of 6% (w/w) were determined by a Rapid Visco Analyzer (RVA). The starch slurry was heated from 40 to 92.5 °C at the rate of 3 °C/min, maintained at 92.5 °C for 15 min, and then cooled to 40 °C at the same rate. Paddle speed was varied at 160, 240, 320 and 480 rpm.

For investigation of the effect of acidity on pasting characteristics, the starch sample was dispersed in citrate-phosphate buffer (pH 2.6, 3.0, and 4.0) and tested as the procedure mentioned above.

2.6. Texture analysis

After RVA testing, the canister containing starch paste was covered with paraffin film and kept at 4 °C for 18 h. Gel texture was determined using a TA-XT2 Texture Analyzer. Gel (with a dimension of 23 mm in height and 38 mm in diameter) in the canister was compressed at the speed of

Table 1
Effect of acetic anhydride concentration on the acetyl content and reaction efficiency of acetylated canna starches

Starches	Acetic anhydride (% w/w of starch)	Acetyl group (%)	DS	Reaction efficiency (%)
Thai-purple	5	1.41	0.05	62.97
	7	2.05	0.08	71.94
	9	2.55	0.10	69.67
Thai-green	5	1.43	0.05	62.97
	7	2.02	0.08	71.94
	9	2.53	0.10	69.97

2.0 mm/s to the distance of 20 mm with a cylindrical probe having 20 mm diameter. The peak height at 20 mm compression was termed firmness, and the negative area of the curve during retraction of the probe was termed stickiness (modified from Liu, Ramsden, and Corke (1997)).

3. Results and discussion

3.1. Degree of substitution

Table 1 shows the acetyl groups contents (%), DS and reaction efficiencies obtained when canna starches were subjected to acetylation at different concentration of acetic anhydride. Obviously, within the range studied the acetyl content increased linearly with increasing the acetic anhydride concentration with regression coefficient (r^2) values of 0.995 and 0.998 for Thai-purple and Thai-green canna starches, respectively. Corresponding with the concentration of acetic anhydride used for modification (5, 7 and 9% w/w), the percentages of acetyl group were 1.41, 2.05 and 2.55 for Thai-purple starch and 1.43, 2.02 and 2.53 for Thai-green starch. These values were very close to those previously expected (1.5, 2.0 and 2.5%). Reaction

efficiencies for both canna starches were similar. Approximately 70% reaction efficiency was achieved in the treatment with 7 or 9% acetic anhydride, while with 5% acetic anhydride the efficiency was lower. As suggested by Wurzburg (1964), reaction efficiencies in the order of 70% could be obtained. Betancur et al. (1997) reported variation in reaction efficiencies (40–72%) of acetylated *Canavalia ensiformis* starch within 13 treatments with varying acetic anhydride concentration, pH, and time of reaction.

3.2. Morphology of starch acetate

Scanning electron micrographs of the native and modified starches are shown in Fig. 1. No difference in both shape and surface of starch granules were observed for all levels of substitution. The starch granules of all the modified starches were still in intact granular form, typically round/oval-shaped granules with smooth surface and were identical to the native starches with regard to external appearance.

3.3. Pasting properties of native and modified canna starches

Viscoamylographs of 6% native and acetylated Thaigreen and Thai-purple canna starches determined by Rapid Visco Analyzer at 160 rpm are shown in Fig. 2. The patterns of both native canna starches were characterized by quite stable viscosity with slight breakdown during the holding period at 95 °C. The viscosities of acetylated starches were found to be lower than those of the native starches. The profiles of acetylated Thai-green canna starches with acetyl group of 1.5, 2.0 and 2.5% were very similar to each other, while those of Thai-purple starches were different.

Some key parameters from pasting profiles (Table 2), e.g. pasting temperature, peak viscosity, breakdown and setback

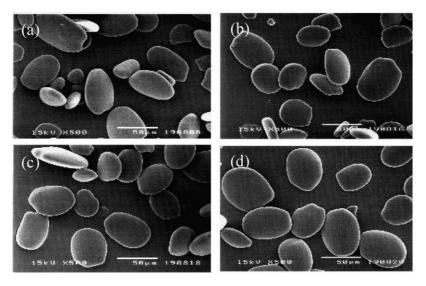


Fig. 1. Scanning electron micrographs (\times 500) of native Thai-green canna starch (a), modified Thai-green canna starch with 5% acetic anhydride (b), with 7% acetic anhydride (c) and with 9% acetic anhydride (d).

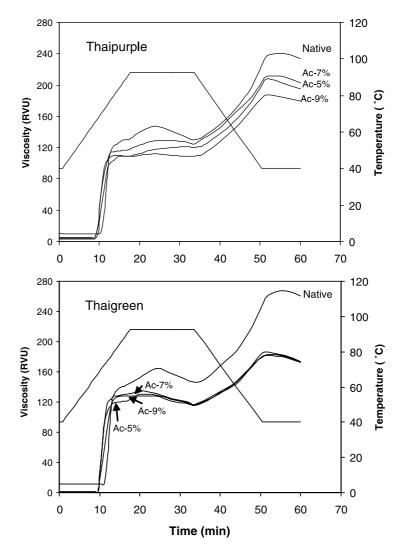


Fig. 2. Pasting profiles of native and acetylated canna starches (6% w/w) measured by rapid viscoanalysis.

were plotted against the percentage of acetyl group substitution as shown in Fig. 3. The results of pasting temperature showed that these values were lower in acetylated starch than in native starches and diminished as the acetyl groups content increased. The pasting temperatures of acetylated Thai-green and Thai-purple starches with 2.5% acetyl group were 65.0 and 64.8 °C, respectively, whereas those of native starches were 70.6 and 70.0 °C,

respectively. Lowering of the pasting temperature of acetylated starches was due to the insertion of acetyl groups into the starch molecules, especially into the amorphous region. The integrity of bonds between molecules was reduced since the acetyl groups added obstructed the formation of H-bonding (Rutenberg & Solarek, 1984). This resulted in the decreased integrity of the amorphous region. Swelling of the acetylated starches was therefore

Table 2 Pasting properties of native and acetylated canna starches (6% w/w).

Sample	%Acetyl	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temp. (RVU)
Thai-green (TG)	0.0	154.13 ± 0.65 d	10.04 ± 2.06 a	259.83 ± 2.24 b	115.75 ± 0.82 c	$70.58 \pm 0.04 \text{ d}$
TG-Ac 5%	1.5	126.38 ± 1.47 a	13.63 ± 0.18 ab	174.54 ± 2.06 a	61.79 ± 0.77 a	$66.80 \pm 0.28 \text{ c}$
TG-Ac 7%	2.0	134.17 ± 0.12 c	20.08 ± 1.06 c	175.88 ± 2.18 a	61.79 ± 0.77 a	$66.03 \pm 0.04 \text{ b}$
TG-Ac 9%	2.5	128.88 ± 0.53 b	$17.75 \pm 2.36 \text{ b}$	175.88 ± 0.65 a	$64.75 \pm 1.18 \text{ b}$	65.00 ± 0.00 a
Thai-purple (TP)	0.0	140.63 ± 2.06 c	7.17 ± 3.77 a	$237.13 \pm 0.65 d$	$103.67 \pm 1.06 \text{ d}$	$70.03 \pm 0.32 d$
TP-Ac 5%	1.5	110.79 ± 1.36 a	2.00 ± 0.12 a	$197.17 \pm 1.30 \text{ b}$	$88.38 \pm 0.06 \text{ c}$	$67.03 \pm 0.04 \text{ c}$
TP-Ac 7%	2.0	122.63 ± 0.06 b	3.21 ± 0.18 a	205.38 ± 0.65 c	$85.96 \pm 0.88 \text{ b}$	$65.90 \pm 0.14 \text{ b}$
TP-Ac 9%	2.5	110.92 ± 0.94 a	4.17 ± 2.12 a	178.79 ± 1.00 a	72.04 ± 0.18 a	64.78 ± 0.18 a

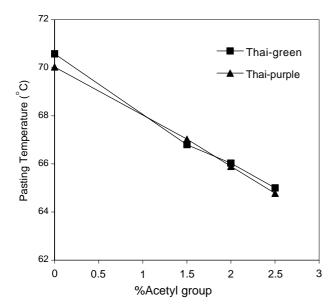


Fig. 3. Effect of percentage of acetyl group substitution on pasting temperature of canna starches.

easier than the native starches. There have been many reports on the lowering of pasting temperature of low substituted acetylated starches (Betancur et al., 1997; Gonzalez et al., 2002; Hoover & Sosulski, 1985; Liu et al., 1997). This characteristics is one of the many advantages achieved with acetylation. It allows the suggestion of employing these modified starches in processes where a thickening agent must gel at lower temperatures, or simply to reduce energy costs during the manufacture of products where these starches are used (Betancur et al., 1997).

For the peak viscosity of the modified Thai-green and Thai-purple starches, as shown in Fig. 4, they were found lower (129 and 111 RVU, respectively) than those of the corresponding native starches (154 and 141 RVU, respectively), but did not follow the order of acetyl contents. These

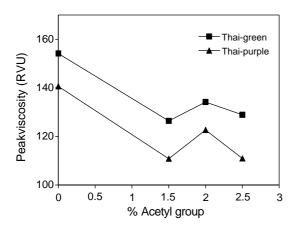


Fig. 4. Effect of percentage of acetyl group substitution on peak viscosity of canna starches.

results were contrary to some other investigators (Betancur et al., 1997; Jeong et al., 1993; Liu et al., 1999) that reported an increasing of viscosity when the acetyl groups were introduced into starch granules. They pointed out that the acetylation increased the viscosity by weakening of associative forces in the amorphous areas of the granules. The difference might be attributed to molecular structure or arrangement of starch molecules which varied with type of starches. Decreasing of the peak viscosities of acetylated canna starches was possibly due to their chemical compositions as well as the hydrophobic behavior of acetyl group. As reported by Thitipraphunkul et al. (2003a), canna starches contained high amounts of phosphate group and calcium. Both of them have been reported to have profound influence on pasting properties of potato starches (Inatsu et al., 1983). Phosphate group and calcium were supposed to form bonding; therefore canna starches could behave like a cross-linked starch. Since phosphate groups were distributed mostly in crystalline region, linked to C6 and C3 of anhydroglucose unit of canna amylopectin molecules (Thitipraphunkul, Uttapap, Piyachomkwan, & Takeda, 2003b), even the amorphous region was weaken by inserting acetyl groups inserted but the crystalline region was likely to be strong enough to withstand heat and shear force around granules. This could be the reason why the peak viscosity was not increased by acetylation. It was uncertain to specify the cause of peak viscosity lowering in acetylated canna starches, but it could be due to the hydrophobicity of acetyl group. Acetylation influenced the interactions between the starch chains by disrupting inter- and intra-molecular hydrogen bonds, thereby weakening the granular structure of starch leading to an increased acceptability of the starch granules to water or by altering the hydrophilicity of the starch and thus reduced bonding with water molecules. The interplay between these two factors would lead to increase or decrease peak viscosity, depending on type of starches.

The effect of acetylation on setback of canna starches is shown in Fig. 5. The setback values of acetylated starches were approximately 15-46% lower than those of native starches. This indicated that the retrogradation determined by associations between amylose chains was substantially reduced by acetylation. The acetyl groups restricted the tendency of the starch molecules to realign after cooling, thus facilitating lower setback values for the modified starches. The effect was more pronounced in Thai-green canna starch. The lower influence of acetylation on setback of Thai-purple canna starch was considered to be related to the amylose content. As reported by Chen et al. (2004), the DS of the amylose populations were 40-200, 25-54 and 27–82% higher than those of the amylopectin populations for acetylated potato, SuShu2 and Xushu18 (sweet potato) starch fractions, respectively. They also indicated that amylose, which was mainly located in the amorphous regions, was equally acetylated. Since Thai-green canna starch contains higher amount of amylose than Thai-purple canna starch (Thitipraphunkul et al., 2003a), it is possible

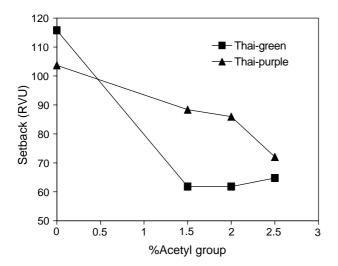


Fig. 5. Effect of percentage of acetyl group substitution on setback of canna starches.

that there are more acetylated amylose chains distributed in hot paste of the Thai-green canna starch. It has been known that setback depends mainly on the amylose. Therefore, more acetylated amylose chains, less setback would be obtained.

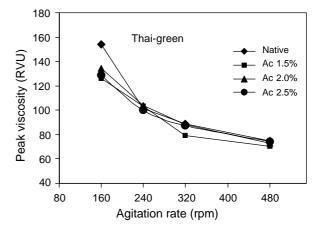
3.4. Effects of acidity and shear force on stability of native and acetylated canna starches

In food processing, starch are frequently subjected to acidic environment and shear forces developed by agitation or flowing through the pipelines. Thereby, the effects of acidity and shear force on stability of native and acetylated canna starches were investigated by preparing starch suspension having pH at 2.6, 3.0, 4.0 and 6.8 and examined by RVA with agitation rates of 160, 240, 320 and 480 rpm.

3.4.1. Shear stability

Fig. 6 shows peak viscosities of native and acetylated canna starches at various agitation rates. The peak viscosities of both native and modified canna starches decreased obviously when agitation rate was increased from 160 to 240 and 320 rpm, and decreased slightly at 480 rpm. Shear forces generated by high speed agitation acted on the swollen granules and disrupted them, resulting in decrease of paste viscosity. Except at the agitation rate of 160 rpm, the peak viscosities of acetylated Thai-green canna starch with all levels of DS were very close to those of native starch. Unlikely, the peak viscosities of Thai-purple acetylated canna starch were noticeably lower than those of native starch for all agitation rates. The result indicated that the acetylation had more pronounced effect on properties of Thai-purple canna starch than on those of Thai-green canna starch.

The more interesting parameter that could better describe the shear resistance of native and modified canna starches pastes was the value of breakdown which was shown in



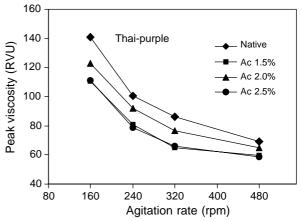


Fig. 6. Effect of agitation rate (rpm) on peak viscosities of native and acetylated canna starches

Fig. 7. Compared to acetylated starches, native starches were more sensitive to the change of agitation rate, especially at 160-320 rpm. This seemed to be related to less swelling ability of acetylated starches as mentioned in the previous section. Breakdown values of native Thaipurple starch were higher than those of modified starches at all agitation rates whereas those of native Thai-green starch were lower than modified starches at 160 and 240 rpm, but became comparable or a bit higher at 320 and 480 rpm. The different breakdown behavior between Thai-green and Thaipurple canna starches could be attributable to the distribution of acetylated groups within starch granules which was determined by the structure as well as chemical compositions of each cultivar. The distribution of acetyl groups in amylose and amylopectin fractions are under investigated and will be reported later. Another parameter; setback which provide the information on retrogradation ability of starch, is shown in Fig. 8. Setback values of both canna starches decreased with increasing of agitation rate. With higher agitation rate, high velocity of dispersed starch molecules, especially amylose molecules, made reassociation of the molecules difficult. Therefore, retrogradation as well as setback values were lower. Native canna starches

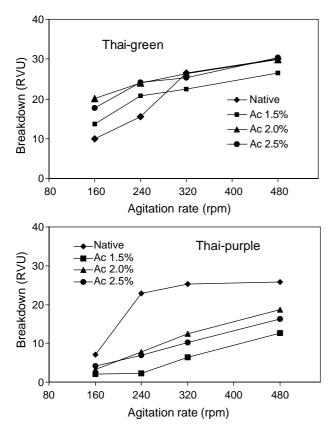


Fig. 7. Effect of agitation rate (rpm) on breakdown of native and acetylated canna starches

had higher setback values than acetylated starches at all agitation rates.

3.4.1.1. Acid stability. This research investigated only the effect of acid environment on the stability of canna starches since most of food products have acidic pH in nature and the acetylated canna starches will be saponified when subjected to alkaline condition. As can be observed in the Fig. 9–11, pasting properties of canna starches were greatly affected by pH of the medium. Profiles of the change in peak viscosity, breakdown and setback of acetylated canna starches with pH were similar to those of native canna starches, even though the extents of pH influence on each starch were different. As shown in Fig. 9-11 when the pH was decreased, peak viscosity and setback decreased while breakdown increased. Similar trend was also found in yam and cassava starches (Mali et al., 2003). Acidic treatment affected the pasting properties of canna starches by partial hydrolysis of glycosidic linkages of starch molecules in the granules. Decreasing of peak viscosity and increasing of breakdown at low pH illustrated that the starch granules became fragile and broke down easily under heat acidic treatment. At extremely low pH values (2.6 and 3.0), all canna starches exhibited significantly less setback, i.e. less tendency of retrogradation. This might be ascribed to the short-chain starch molecules appeared due to the acid

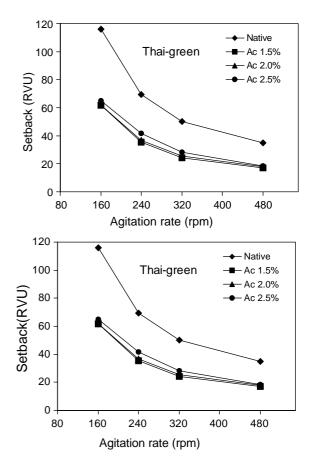


Fig. 8. Effect of agitation rate (rpm) on setback of native and acetylated canna starches

hydrolysis, which were too active to form a highly ordered crystalline structure (Wang & Wang, 2002). When comparing the pasting attributes between native and acetylated canna starches, it was found that peak viscosities of acetylated canna starches were relatively lower than those of corresponding native starches. Their breakdown values were similar while setbacks of acetylated starches, especially Thai-green canna starch, were significantly lower. These results could be explained as described in the previous section.

3.5. Gel properties

The texture of canna starch gels was analyzed by a texture analyzer using a 20 mm diameter-cylindrical plunger. Fig. 12 shows the illustration of compression force-time curves of native and modified canna starches. With 6% starch solids in water at pH 6.8, all acetylated canna starches gave the gels that were much less hard than those of corresponding native starches (Table 3). For example, the hardness values of 1.41, 2.05, 2.55% acetyl groups and native Thai-purple starches were 136, 114, 222 and 1963 g, respectively. No significant difference in gel hardness was observed due to degree of substitution. It has been known that the extent of the amylose gel network and

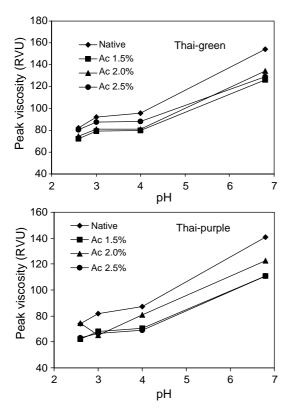


Fig. 9. Effect of pH on peak viscosities of native and acetylated canna starches

deformability of swollen granules are the main factors contributing to gel strength (Luyten, van Vliet, & Walstra, 1992). Much softer gel of acetylated canna starches indicated that acetyl groups introduced into the starch

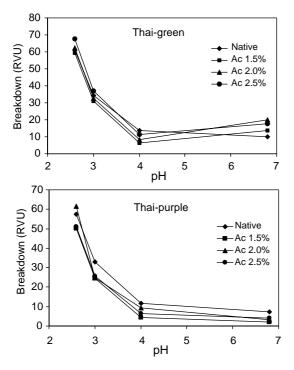


Fig. 10. Effect of pH on breakdown of native and acetylated canna starches

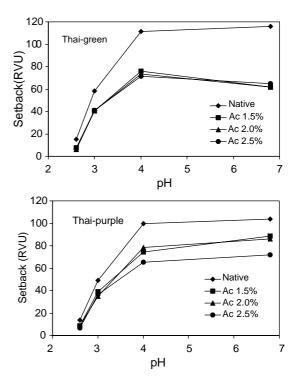


Fig. 11. Effect of pH on setback of native and acetylated canna starches

molecules impeded the formation of amylose gel network, as well as association of amylose and amylopectin molecules (re-association of starch molecules referred to 'retrogradation'). As shown in Fig. 12, peak of fracturability (signify the brittleness of gel) could be observed in both native Thai-green and Thai-purple canna starches but not in all acetylated canna starches. This suggested that the gels of native starch were hard and brittle while those of acetylated starch were soft and elastic. Adhesiveness (derived from integrated negative area of texture profile and used to express the attraction between the gel and an external surface) of native canna starch gels were also higher than those of acetylaed starch gels (Table 3). In case of acetylated canna starches, it was noticed that there was a long tail of negative curve. This tail was not found in gels of native canna starches. The results obtained from texture analysis revealed a great difference between textures of native and acetylated canna starches and confirmed that the retrogradation of canna starches could be extensively reduced by acetylation.

By visual observation of canna starch gels, it was found that the native canna starches gave hard gels which were broken when testing probe was applied upon the gels. The broken holes still existed after the probe was pulled out. On the contrary, gels from all acetylated canna starches at entire levels of DS had soft and elastic appearance. The gels were not broken during pressing a probe into the gels. When removing the probe from gels, no holes were left and some gels stuck to the probe's surface were observed.

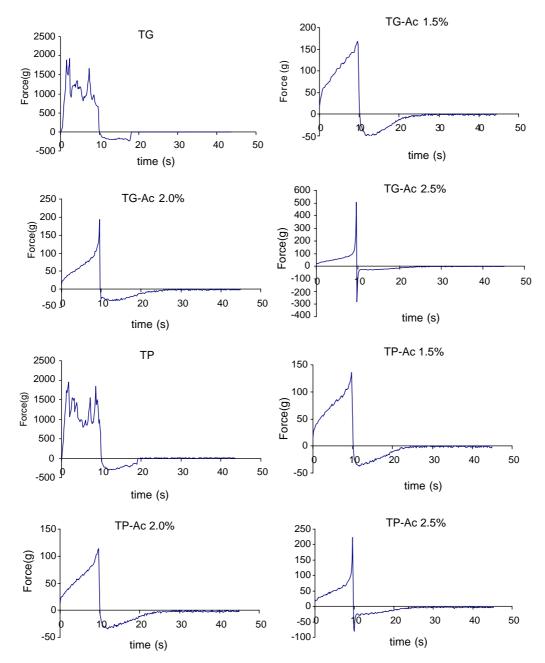


Fig. 12. Compression force-time curves of native and modified Thai-green and Thai-purple canna starches.

3.6. Freeze-thaw stability

Under freeze-thawed condition, gels from starches of both cultivars exhibited similar characteristics. The native

canna starch gels had a spongy-like texture and exuded a lot of water. On the other hand, the gels from acetylated canna starches were soft and elastic and discharged less water. Effect of freeze/thawing on the stability of starch

Table 3
Hardness and adhesiveness of starch gels from native and acetylated canna starches

Canna Starch	Hardness (g)		Adhesiveness (g.s)		Fracturability/Brittleness (g)	
	Thai-green	Thai-purple	Thai-green	Thai-purple	Thai-green	Thai-purple
Native	1915	1963	1438	1973	1888	1963
1.5% Acetyl	169	136	382	296	_	_
2.0% Acetyl	193	114	297	311	_	_
2.5% Acetyl	508	222	359	327	-	-

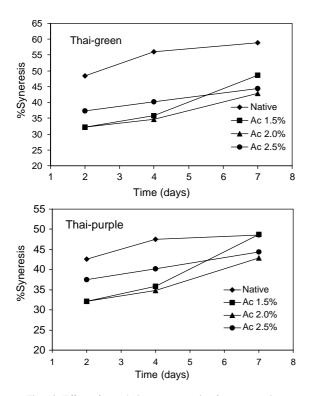


Fig. 13. Effect of acetylation on syneresis of canna starches

pastes is shown in Fig. 13. Acetylated Thai-green and Thai-purple canna starches at all levels of DS had lower degree of syneresis than their native starches. Both cultivars displayed a very similar pattern of changing in the degree of syneresis with storage time. However, this change seemed not to follow the order of DS, for example, acetylated canna starches with 2% acetyl group showed the lowest degree of syneresis. The result of improved freezethaw stability of acetylated starches at low DS agrees well with other earlier studies (Agboola et al., 1991; Betancur et al., 1997; Hoover & Sosulski, 1985). Syneresis in freeze/ thawed gels is due to the increase of molecular association between starch chains at reduced temperature excluding water from the gel structure. Drastically diminished syneresis after modification could result from impediment of interchain bonding between the starch molecules by the incorporated acetyl groups. The results obtained, therefore, supported that starch retrogradation could be reduced by acetylation.

4. Conclusion

The study on properties of acetylated canna starches has shown that acetylation with low DS (in a range of 1.5–2.5% acetyl group) induces gelatinization temperature reduction (3–5 °C). Retrogradation of canna starch pastes and gels is significantly decreased as evidenced by setback viscosities data from RVA profiles, hardness of gels by texture analysis, and syneresis data from freeze-

thaw studies. In addition, better clarity and softer texture of acetylated starch pastes and gels were noticed by visual observation. Effect of pH and agitation on pasting properties of native and acetylated canna starch is not significantly different. There are some variations in the pasting attributes between starch pastes from Thai-purple and Thai-green canna which can be related to their chemical compositions and molecular structures. Owing to these properties and the fact that the maximum FDA permissible level of acetyl in foods has been set at 2.5%, canna starch acetate derived from this experiment might be used as thickening and stabilizing agents in food products such as sauces, ice creams, fruit jellies, and baked products. However, it should be noted that one drawback of these acetylated starches is that their peak viscosities are reduced by 13-20%, when compared to the native canna starches.

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References

Adebowale, K. O., & Lawal, O. S. (2003). Functional properties and retrogradation behavior of native and chemically modified starch of mucuna bean (*Mucuna pruriens*). Journal of the Science Food and Agriculture, 83, 1541–1546.

Agboola, S. O., Akingbala, J. O., & Oguntimein, G. B. (1991). Physicochemical and functional properties of low DS cassava starch acetates and citrates. Starch/Starke, 43, 62–66.

Betancur, A. D., Chel, G. L., & Canizares, H. E. (1997). Acetylation and characterization of *Canavalia ensiformis* starch. *Journal of Agriculture* and Food Chemistry, 45, 378–382.

Chen, Z., Schols, H. A., & Voragen, A. G. J. (2004). Differently sized granules from acetylated potato and sweet potato starches differ in the acetyl substitution pattern of their amylose populations. *Carbohydrate Polymer*, 56, 219–226.

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. Starch/Starke, 54, 148–154.

Hoover, R., & Sosulski, F. (1985). A comparative study of the effect of acetylation on starches of *Phaseolus vulgaris* biotypes. *Starch/Starke*, 37, 397–404.

Inatsu, O., Maeda, I., Jimi, N., Takahashi, K., Taniguchi, H., Kawabata, M., et al. (1983). Edible canna starch. I Some properties of edible canna starch produced in Taiwan. *Journal of Japan Society Starch Science*, 30, 38–47.

Jeong, J. H., Bae, J. S., & Oh, M. J. (1993). Physico-chemical properties of acetylated rice starches. Korean Journal of Food Science and Technology, 25, 123–129.

Liu, H., Ramsden, L., & Corke, H. (1997). Physical properties and enzymatic digestibility of acetylated ae, wx, and normal maize starch. Carbohydrate Polymers, 34, 283–289.

Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties of cross-linked and acetylated normal and waxy rice starch. Starch/Starke, 51, 249–252.

Luyten, H., van Vliet, T., & Walstra, P. (1992). Comparison of various methods to evaluate fracture phenomena in food materials. *Journal of Texture Studies*, 23(3), 245–266.

- Mali, S., 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. *Lebensm-Wiss U-Technology*, 36, 475–481.
- Moorthy, S. N. (1985). Acetylation of cassava starch using perchloric acid catalysis. *Starch/Starke*, *37*, 307–308.
- Ogawa, K., Hirai, I., Shimasaki, C., Yoshimura, T., Ono, S., Rengakuji, S., et al. (1999). Simple determination method of degree of substitution for starch acetate. *Bulletin of the Chemistry Society of Japan*, 72, 2785–2790.
- Perez, E., Breene, W. M., & Bahnassey, Y. A. (1998). Variations in the gelatinization profiles of cassava and arrowroot native starches as measured with different thermal and mechanical methods. *Starch/-Staerke*, 50, 70–72.
- Rutenberg, M. W., & Solarek, D. (1984). In R. L. Whistler, J. N. BeMiller, & E. F. Paschall, Starch derivatives: production and uses. Starch: chemistry and technology (pp. 312–388). London: Academic Press, 312–388.
- Santacruz, S., Koch, K., Svensson, E., Ruales, J., & Eliasson, A.-C. (2002). Three underutilised sources of starch from the Adean region in ecuador part I, physico-chemical characterisation. *Carbohydrate Polymer*, 49, 63–70.

- Soni, P. L., Sharma, H., Srivastava, H. C., & Gharia, M. M. (1990).
 Physicochemical properties of *Canna edulis* starch-comparison with maize starch. *Starch/Staerke*, 42, 460–464.
- Thitipraphunkul, K., Uttapap, D., Piyachomkwan, K., & Takeda, Y. (2003a). A comparative study of edible canna (*Canna edulis*) starch from cultivars. part I. Chemical composition and physicochemical properties. *Carbohydrate Polymers*, 53, 317–324.
- Thitipraphunkul, K., Uttapap, D., Piyachomkwan, K., & Takeda, Y. (2003b). A comparative study of edible canna (*Canna edulis*) starch from cultivars. part II. Molecular structure of amylose and amylopectin. *Carbohydrate Polymers*, 54, 489–498.
- Wang, H., Sun, D., Zeng, Q., & Lu, Y. (2000). Effect of pH, corn starch and phosphates on the pasting properties of rice flour. *Journal of Food Engineering*, 46, 133–138.
- Wang, Y., & Wang, L. (2002). Characterization of acetylated waxy maize starches prepared under catalysis by different alkali and alkaline-earth hydroxides. Starch/Starke, 54, 25–30.
- Wurzburg, O. B. (1964). In R. L. Whistler, Acetylation. Methods in Carbohydrate Chemistry Volume IV Starch (pp. 286–288). Orlando, FL: Academic Press, 286–288.