

Molecular properties of cassava starch modified with different UV irradiations to enhance baking expansion

N. Vatanasuchart^a, O. Naivikul^b, S. Charoenrein^b, K. Sriroth^{b,*}

^a*Institute of Food Research and Product Development, Kasetsart University, 50 Paholyothin Road, Jatujak, Bangkok 10900, Thailand*

^b*Faculty of Agro-Industry, Kasetsart University, 50 Paholyothin Road, Jatujak, Bangkok 10900, Thailand*

Received 3 November 2004; revised 10 February 2005; accepted 14 February 2005

Available online 25 March 2005

Abstract

Commercial cassava starch was modified with 1% (w/w) lactic acid solution and irradiated with ultraviolet radiation: UVBA (280–420 nm), UVB (310–330 nm) and UVC (254 nm) for 7–15 h. Thermal properties and molecular size distributions of the cassava starch molecules were investigated to explain structural changes responsible for baking expansion ability. The acidified starches irradiated with UVB or UVC for 7 and 9 h achieved the desired baking expansion ability and showed a significant increase in the peak temperatures determined with the differential scanning calorimeter (DSC). The results indicated formation of stable network structures suitable for the expansion. However, the transition enthalpy of these starches did not significantly decrease from that of the commercial starch. Using high performance size exclusion chromatography (HPSEC), it was found that the amylose content of the commercial starch ($DP_n 2173 \pm 163$) was decreased to $DP_n 1551 \pm 62$ and 1427 ± 54 by UVB, and to $DP_n 1216 \pm 28$ and 1096 ± 30 by UVC irradiated for 7 and 9 h, respectively. Profiles of the molecular distributions showed that it was mainly amylose molecules that was degraded by UVB whereas both amylose and amylopectin molecules were degraded by UVC in the amorphous regions.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Cassava starch; Baking expansion; UV irradiation; Thermal properties; Molecular size distributions

1. Introduction

Solar ultraviolet (UV) radiation can be classified into UVA (315–400 nm), UVB (280–315 nm) and UVC (100–280 nm), the short wavelengths of less than 290 nm undergoing significant absorption by the atmosphere at the ozone layer (Nee, 1996; World Health Organization, 1994). Most research works on starch modification by UV irradiation have employed an artificial UVC source (Bertolini, Mestres, Colonna, Lerner, & Della Valle, 1998; Fiedorowicz, Tomasik, Sangguan, & Seung, 1999).

Several researchers have stated that sunlight, particularly certain UV wavelengths, as well as lactic acid fermentation are essential for the baking expansion ability of cassava starch (Bertolini, Mestres, Lourdin, Della Valle, & Colonna, 2001; Cardenas & de Buckle, 1980; Dufour, Larssonneur,

Alarcon, Braset, & Chuzel, 1996). In a study on the oxidative modification of cassava starch with lactic acid together with sun drying, baking behavior with an increase in specific volumes of tested biscuits was obtained, but this did not occur when the starch was oven dried (Mestres & Rouau, 1997; Plata-Oviedo & Camargo, 1998). Moreover, it was found that the lactic acidified cassava starch exposed to UV irradiation from a broad band mercury vapor lamp of 250–600 nm produced marked expansion ability (Bertolini, Mestres, & Colonna, 2000).

Recently, the effects of different frequencies and durations of UV irradiation on pasting properties of cassava starch in relation to biscuit expansion were observed by Vatanasuchart, Naivikul, Charoenrein, and Sriroth (2003). The peak viscosities of the starches irradiated with UVB for 7 and 9 h were 196.55 ± 2.41 and 195.67 ± 0.83 RVU, those of starches irradiated with UVC were 176.55 ± 1.83 and 169.54 ± 3.24 RVU, and those of starches dried with hot air were 121.07 ± 0.97 and 116.92 ± 1.89 RVU, respectively. This study found that the UVB irradiated starches possessing the desired expansion ability showed less change in the peak viscosity from that of commercial starch

* Corresponding author. Fax: +66 29 40 56 34.

E-mail address: ifrnvpv@ku.ac.th (K. Sriroth).

(235.84 ± 1.65 RVU). Lactic acidification together with sufficient UV energy resulted in partial depolymerization of the cassava starch molecules. Thus, when the starch paste was heated, the modified starch molecules more readily took up water molecules, resulting in a higher peak viscosity of the UVB irradiated samples than those treated with the UVC irradiation or hot air drying which provided too much starch depolymerization. Fiedorowicz et al. (1999) found that after UV irradiation of corn starches, there was evidence of the formation of crosslinkages between starch molecules at sufficient energy uptake.

This present study was undertaken to examine effects of irradiation of lactic acidified cassava starch with different UV wavelengths on changes in molecular properties responsible for baking expansion behavior. Thermal characteristics and profiles of apparent amylose and amylopectin size distributions of the modified starch samples were determined and compared.

2. Experimental

2.1. Materials

A total of 100 kg from the same batch of commercial cassava starch donated by Taiwa Public Co. Ltd. (Thailand) was used in this study. DL-Lactic acid, 85% syrup (Sigma No. L-1250) and amylose standard (Sigma No. A-0512), were purchased from Sigma Chemical Co. (Japan). Other chemical agents were of analytical grade from Merck (Germany).

2.2. Modification of the cassava starches by lactic acid hydrolysis and different UV irradiations

The cassava starch (200 g, dried starch basis) was dispersed in 600 g of 1% (w/w) lactic acid solution, and a hydrolysis period of 15 min at 25 °C was allowed, using the method adapted from Plata-Oviedo et al. (1998). The acidified starches were drained with a Buchner funnel using a vacuum pump and the 150 g samples with a final moisture content of approximately 42% were transferred to a stainless steel tray. Then, the samples were placed in three different UV cabinets, which were lined with highly polished aluminum and supplied with air circulator. There were (i) four UVBA lamps (Philips, TL 20W/12) emitting radiation of 280–420 nm, which was 64% UVB and 36% UVA; (ii) four UVB lamps (Philips, TL 100W/01) emitting energy from 310–330 nm, which was 90% UVB and 10% UVA and (iii) five UVC lamps emitting energy at 254 nm (Sylvania, 30W), as well as different exposure periods of 7, 9, 11 and 15 h used for modification (Nee, 1996). The UV irradiated acidified starches were compared to the acidified starches dried in a conventional hot air oven at 40 °C for the same periods and to the commercial cassava starch used without any treatment. The dried starch sample was sieved through

a 100 mesh sifter to obtain fine and homogenous powder. The final moisture content of the treated starches for 7, 9, 11 and 15 h were 15.14 ± 0.50 , 14.51 ± 0.28 , 13.52 ± 0.46 and $12.79 \pm 0.16\%$, respectively; that of the commercial starch was $11.71 \pm 0.13\%$.

2.3. Baking test

The test for the baking expansion ability was performed by baking cassava rolls prepared using a procedure adapted from a recipe for *pao de queiji* (Maria's Cookbook, 2002). Cassava rolls were made with 45 g (dried starch basis) of the cassava starch, 45 g whole milk, 10 g soybean oil, 0.5 g salt, 5 g egg and water. A 14 g portion of dough was weighed on baking paper and baked at 210 °C for 20 min. After baking, the volumes of six cassava rolls were determined by the sesame seed displacement method and their weights were measured. Calculation for specific volume (cm^3/g) was done by dividing the obtained volume of the baked roll by its weight (Plata-Oviedo et al., 1998).

2.4. Thermal properties

Thermal properties of UV irradiated acidified cassava starch, hot-air dried acidified starch and the commercial starch were examined by using a differential scanning calorimeter (DSC) (Perkin-Elmer Pyris I, USA), equipped with a cooling system according to the method adapted from Siroth et al. (1999). A starch sample (3.4 mg, dried starch basis) was weighed in the aluminum DSC pan and deionized water was added to obtain a 30% starch suspension. The cover was carefully put on and sealed hermetically using sealing tools. Weights of the sealed pans before and after determination were recorded to check for water leakage due to improper sealing. The pans were kept overnight before determination. The sample pan was placed carefully in the DSC and was heated at 10 °C/min from a temperature of 30–95 °C. An empty pan was used as reference and the instrument was calibrated using indium standard. Endothermal curves exhibiting onset, peak and end temperatures (°C) and transition enthalpy (J/g of the sample weight) of the starch sample were recorded.

2.5. Molecular size distribution of the UV irradiated acidified cassava starches

Molecular size distribution of amylose and amylopectin were characterized with high performance size exclusion chromatography (HPSEC) according to the method of Govindasamy, Oates, and Wang (1992). The system consisted of a pump (LC-10AT, Shimadzu, Japan), auto-injector (SIL-10A, Shimadzu, Japan) and three SEC columns (Ultrasphere Linear, Ultrasphere 120 and Ultrasphere 120, serially placed in a column oven (CTO-10AS, Shimadzu, Japan) maintained at 40 °C. A differential

refractive index detector (Model RID-10A) was connected to the columns.

The mobile phase was deionized water, which was filtered through a 0.45 μm cellulose nitrate filter and degassed by ultrasonic bath (2210 Branson, USA) before use; flow rate of the deionized water was 0.8 ml/min. A starch sample (0.04 g, dried starch basis) was weighed in a test tube and 10 ml of distilled water was added to obtain 0.4% (w/v) starch suspension. It was then placed in a shaking boiling water bath for 20 min for gelatinization and then gelatinizing was continued to complete in ultrasonic processor (VC 501–30W, Sonic & Material, Inc., CT, USA) for 18 s. The sample was filtered through an 8 μm cellulose nitrate filter, prior to HPSEC injection of the 20 μl portion; each sample was determined in duplicate. Retention times from HPSEC chromatograms were recorded and time variations were depended on the number average molecular weight (M_n) of standard dextran and of the test samples. The apparent amylose molecule fractions of the starches obtained with different treatments were compared.

Standard dextran (Fluka Chemie Ag CH-9471 Buchs, Switzerland) solutions were prepared with a range of M_n from 3260–500,500 $\mu\text{g/ml}$ and injected onto the columns. The degree of polymerization (DPn) of linear amylose molecules in the starch sample (obtained by the equation $\text{DPn} = M_n/162$) was calculated from the peak area under the amylose fraction of the HPSEC chromatogram, and the molecular size distributions of amylose and amylopectin molecule fractions were determined (Sriroth & Piyachomkwan, 2003).

2.6. Statistical analysis

Factorial in completely randomized design (CRD) was used as an experimental design. The effects of the different UV irradiations and different exposure periods on the baking expansion and the thermal and molecular properties of the modified cassava starch were determined and compared to those of the hot-air dried and the commercial starch. The SPSS for Windows program, version 9.0, was employed for analyzing the results obtained from two replications. Means and standard deviations for each treatment were calculated and the analysis of variance (ANOVA) and Duncan's multiple range test (DMRT) were used for comparing differences of the mean values at the 0.05 confidence level.

3. Results and discussion

3.1. Baking test

The results showed that the acidified cassava starches irradiated with UVB for 7, 9, 11 and 15 h had effective baking expansion; their specific volumes were 10.67 ± 0.56 , 12.23 ± 0.12 , 10.08 ± 0.31 and $9.06 \pm 0.20 \text{ cm}^3/\text{g}$,

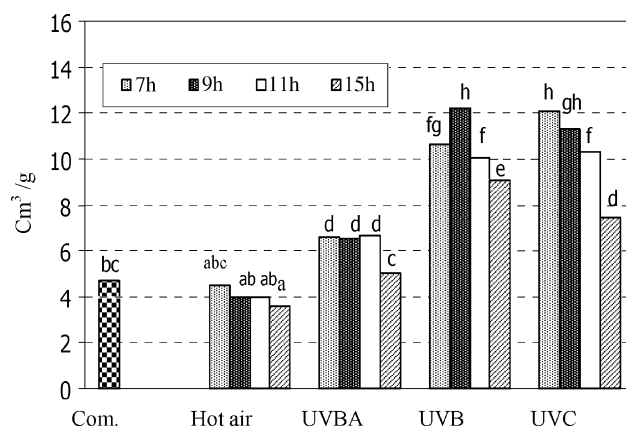


Fig. 1. Specific volumes of cassava rolls made with the UV irradiated, acidified cassava starches (bars not sharing a common letter are significantly different at $P < 0.05$).

respectively (Fig. 1). These values were significantly higher than those of the cassava starches treated with UVBA or hot air drying and the commercial starch. No significant difference in the specific volume was found for the starches irradiated with UVB for 9 h and UVC for 7 and 9 h. The starch irradiated with UVB for 9 h had the highest specific volume of $12.23 \pm 0.12 \text{ cm}^3/\text{g}$; samples irradiated with UVC for 7 and 9 h had 12.10 ± 0.75 and $11.33 \pm 0.62 \text{ cm}^3/\text{g}$, respectively. This finding indicates that the 1% lactic acidified cassava starch exposed to UVB irradiation of narrow band wavelengths (310 to 330 nm) achieved high baking expansion property with exposure periods of 7–11 h. The specific volumes obtained from UVB irradiation were comparable to those obtained from UVC irradiation in terms of the baking expansion characteristics of the cassava rolls (Fig. 2). Thus, modification by irradiation with UVB or UVC for periods of 7, 9 and 11 h gave a desired baking expansion of the cassava starch.

Likewise, Demiate, Dupuy, Huvenne, Cereda, and Wosiacki (2000) found that cassava starch immersed in 1% lactic acid solution for 4 h and sun dried for 8 h had a high specific volume of $11.5 \text{ cm}^3/\text{g}$. Whereas the acidified cassava starch which was irradiated with broad band

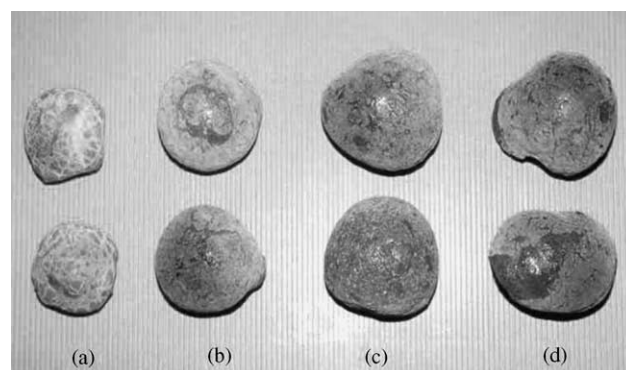


Fig. 2. Cassava rolls made with the acidified cassava starches dried with hot air (a), irradiated with UVBA (b), UVB (c) and UVC (d) for 9 h.

mercury vapor lamp, emitting at 250–600 nm, showed the very high specific volume of 13.2 cm³/g. The baking expansion might involve the reassociation of size-reduced starch molecules of amylose and/or amylopectin in amorphous regions (Bertolini et al., 2000).

Moreover, the rheological behaviors of cassava starch dough could relate to the baking expansion enhanced by the UV irradiation and lactic acid treatment. Fan, Mitchell, and Blanshard (1999) presented a model for dough expansion during oven rise and stages of the bubble growth in viscous fluid. Their results showed that as the viscosity increased, the associated internal bubble pressure increased dramatically and this gave rise to larger tensile stresses on the cell surface which resulted in cell rupture at the end of oven rise. In addition, Bertolini et al. (2001) found that the expansion of sour cassava starch during baking can be attributed to the pressure increase by water evaporation, then the low melt viscosity due to starch depolymerization would reduce the resistance force to expansion. Bubble growth finally led to a cell structure with a matrix formed by the size-reduced cassava starch. In this present work, the depolymerized starch dough would have low viscosity of the bubble wall and low viscous resistance for the bubble growth, thus baking expansion was produced by forming amorphous matrix structure with hydrogen bonds. When degradation was too extensive the bubble walls lost their integrity earlier, they ruptured at lower strains causing no expansion of the starches treated with high intensity energy.

3.2. Thermal properties

In this study, 1% lactic acidified cassava starches irradiated with UVBA, UVB or UVC were compared to

the hot-air dried and the commercial starch to investigate their thermal characteristics by using the DSC. The effects of UV irradiation on the transition enthalpy for the starches irradiated for 7, 9 and 15 h was 12.77 ± 0.18 , 12.87 ± 0.21 and 13.02 ± 0.10 J/g when irradiated with UVB, respectively, and 12.76 ± 0.10 , 12.88 ± 0.06 and 13.32 ± 0.25 J/g when irradiated with UVC, respectively (Table 1). When the starch irradiated with UVB or UVC for 7 and 9 h was compared to the commercial starch (13.10 ± 0.03 J/g), there was no significant difference in transition enthalpy among the samples. However, the findings indicated a slight decrease in the transition enthalpy for the acidified cassava starch irradiated with UVB or UVC for 7 and 9 h.

An explanation for this finding is that the degradative changes in the starch molecules which contributed to the baking expansion did not affect the typical values of the transition enthalpy of the cassava starch. On other words, the enthalpy for melting the amorphous and crystalline structures of the cassava starch was not different from that for the commercial starch. Similarly, Camargo, Colonna, Buleon, and Molard (1988) and Mestres et al. (1997) found no significant change in the enthalpy of the sun-dried, fermented cassava starches compared with the native starch. Also UV irradiation of corn starches which showed a highly oxidative molecular degradation in conjunction with cross-linking after irradiation for 15 h did not differ in transition enthalpy from the native corn starch (Fiedorowicz et al., 1999).

Moreover, the present study found that the acidified starches irradiated with UVC for the longest period of 15 h showed an increase in melting enthalpy to 13.32 ± 0.25 J/g, which was significantly higher than the melting enthalpies of the starches treated for 7 and 9 h, but which was not

Table 1
Thermal properties of the UV irradiated, acidified cassava starches

Sample treatments	Enthalpy (J/g)	Gelatinization temperature (°C)		
		Onset	Peak	End
Commercial starch	$13.10 \pm 0.03^{\text{de}}$	$64.34 \pm 0.08^{\text{abc}}$	$69.47 \pm 0.14^{\text{bc}}$	$80.70 \pm 0.91^{\text{a}}$
Hot air, h				
7	$11.52 \pm 0.34^{\text{a}}$	$63.76 \pm 0.47^{\text{a}}$	$68.82 \pm 0.42^{\text{a}}$	$79.77 \pm 0.46^{\text{a}}$
9	$12.71 \pm 0.01^{\text{bc}}$	$64.89 \pm 0.11^{\text{bcde}}$	$69.74 \pm 0.11^{\text{cde}}$	$79.18 \pm 0.09^{\text{a}}$
15	$12.90 \pm 0.07^{\text{bcd}}$	$65.20 \pm 0.12^{\text{def}}$	$70.21 \pm 0.22^{\text{ef}}$	$79.57 \pm 0.32^{\text{a}}$
UVBA, h				
7	$12.57 \pm 0.09^{\text{b}}$	$63.96 \pm 0.23^{\text{a}}$	$69.06 \pm 0.31^{\text{ab}}$	$78.92 \pm 0.16^{\text{a}}$
9	$12.82 \pm 0.02^{\text{bcd}}$	$65.10 \pm 0.70^{\text{cdef}}$	$69.99 \pm 0.32^{\text{de}}$	$79.38 \pm 0.07^{\text{a}}$
15	$12.67 \pm 0.14^{\text{bc}}$	$65.46 \pm 0.04^{\text{ef}}$	$70.20 \pm 0.07^{\text{ef}}$	$79.11 \pm 0.04^{\text{a}}$
UVB, h				
7	$12.77 \pm 0.18^{\text{bcd}}$	$64.16 \pm 0.14^{\text{ab}}$	$69.39 \pm 0.06^{\text{bc}}$	$80.28 \pm 1.69^{\text{a}}$
9	$12.87 \pm 0.21^{\text{bcd}}$	$65.03 \pm 0.10^{\text{cdef}}$	$70.18 \pm 0.02^{\text{ef}}$	$79.58 \pm 0.65^{\text{a}}$
15	$13.02 \pm 0.10^{\text{cde}}$	$65.55 \pm 0.32^{\text{ef}}$	$70.57 \pm 0.19^{\text{fg}}$	$79.65 \pm 0.10^{\text{a}}$
UVC, h				
7	$12.76 \pm 0.10^{\text{bcd}}$	$64.54 \pm 0.69^{\text{abcd}}$	$69.59 \pm 0.11^{\text{cd}}$	$78.95 \pm 0.09^{\text{a}}$
9	$12.88 \pm 0.06^{\text{bcd}}$	$65.54 \pm 0.09^{\text{ef}}$	$70.68 \pm 0.01^{\text{g}}$	$79.45 \pm 0.24^{\text{a}}$
15	$13.32 \pm 0.25^{\text{e}}$	$65.82 \pm 0.05^{\text{f}}$	$70.90 \pm 0.08^{\text{g}}$	$79.49 \pm 0.25^{\text{a}}$

Results are expressed as an average of two replications. Means in a column not sharing a common superscript are significantly different at $P < 0.05$ by ANOVA and DMRT.

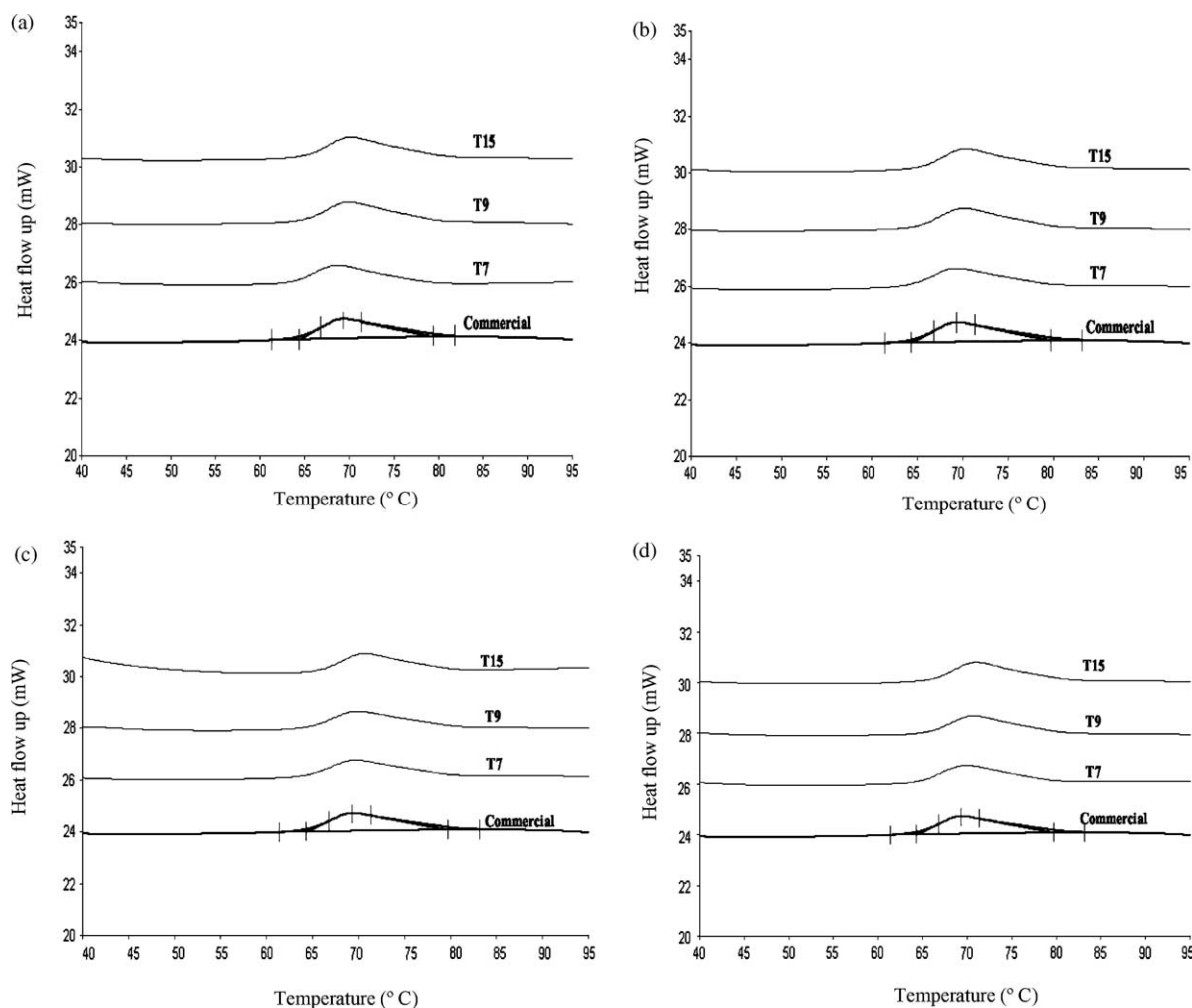


Fig. 3. DSC thermograms of the acidified cassava starches dried with hot air (a), irradiated with UVBA (b), UVB (c) and UVC (d) for periods of 7 (T7), 9 (T9) and 15 (T15) h.

different from that of the commercial starch. This implied a more perfect crystal structure induced by the high intensity energy of the short wavelengths of UVC radiation and the long exposure time (World Health Organization, 1994). Therefore, good baking expansion was not obtained with this treatment. Figs. 3a–d exhibit similar patterns of DSC thermograms for the modified starches as compared to the commercial starch. A slight shift of DSC thermograms was observed with the starches treated for the long exposure period of 15 h, particularly with UVC irradiation.

It seems that starch degradation induced by the UV and acid treatment for 15 h allowed the crystal to perfect more readily and such changes could occur during the hot air drying periods for 15 h at 40 °C. The findings relate to changes in the degree of relative crystallinities of the modified starches. The values obtained from treatment for 9 h were 31.5, 31.0, 32.0 and 30.5% for the samples dried with hot air, irradiated with UVBA, UVB and UVC, respectively, whereas the values obtained from the starches treated for 15 h were increased to 33.5, 34.5, 34.0 and 34.5%, respectively (Vatanasuchart, 2004).

In investigating gelatinization temperatures of the cassava starches having a baking expansion ability, it was found that the acidified starches irradiated with UVB and UVC for 9 h had significantly higher onset and peak temperatures (65.03 ± 0.10 , 65.54 ± 0.09 and 70.18 ± 0.02 , 70.68 ± 0.01 °C) than those irradiated for 7 h (64.16 ± 0.14 , 64.54 ± 0.69 and 69.39 ± 0.06 , 69.59 ± 0.11 °C), respectively. Whereas peak temperatures of the starches irradiated for 9 h with UVB (70.18 ± 0.02 °C) or with UVC (70.68 ± 0.01 °C) were significantly higher than that of the commercial starch (69.47 ± 0.14 °C). The finding of a slight increase in onset and peak temperatures of the starches might be due to stability of crystalline structure induced by modification reactions. It is concluded that the onset and peak temperatures were not changed by 1% lactic acidification and UVBA, UVB or UVC irradiation for the short period of 7 h, while they were affected at the longer periods of 9 or 15 h; the temperatures tended to increase with an increase in the irradiation period. Likewise, Camargo et al. (1988) found that the peak temperature of fermented cassava starch was slightly higher than that of

non-fermented starch. A study on 6% hydrochloric acidified cassava starch by Atichokudomchai, Varavinit, and Chinnachoti (2002) showed that as hydrolysis time (from 12 to 96 h) increased, onset and peak temperatures of gelatinization increased due to the observed crystallites.

3.3. Molecular size distribution of the UV irradiated acidified cassava starches

Degradative changes in molecular size distributions were observed in the acidified cassava starches irradiated with UVBA, UVB or UVC for 9 and 15 h, as compared to the hot-air dried and the commercial cassava starch. Chromatograms of the modified samples obtained by HPSEC determination showed patterns of three distinctive peaks similar to that of the commercial starch (Fig. 4): fraction I, consisting of high molecular weight, mainly amylopectin molecules, fraction II, consisting of intermediate size molecules and fraction III, composed of low molecular weight or linear amylose molecules. When the acidified starches were irradiated with the UVBA, UVB or UVC for 9 h, fraction I had not shifted to a longer retention time, or a lower molecular weight (Fig. 4a). But starches irradiated

with high UV intensity energy, especially with UVC exhibited larger peak shoulder of fraction I than the other treatments and the intermediate size molecules of fraction II tended to increase in size. Fraction III of the acidified starches exposed to any of the UV radiation treatments, shifted to a longer retention time or lower molecular size; in particular, UVC caused a distinctive change in the molecular size distribution. Moreover, in the chromatograms of fraction III, the molecular size of the amylose molecules, appeared to be more affected by UV irradiation than that of amylopectin molecules. The findings indicated that both amylose and amylopectin molecules were degraded by UVC irradiation and the amylose molecules were degraded mainly by UVB irradiation; these molecular changes would be responsible for the baking expansion ability of the cassava starch. Wang and Wang (2001) found that molecules of both amylose and amylopectin were reduced simultaneously by acid hydrolysis of different starches similar to the present study, but their result indicated that the molecular size of the amylose portion increased due to the hydrolysis of amylopectin molecules.

When the acidified starches irradiated for the longest period of 15 h, the chromatograms of UVBA, UVB or UVC irradiated starch exhibited changes in the molecular sizes of fraction I; they were slightly shifted to a longer retention time, as compared to those of the commercial starch (Fig. 4b). Fraction III, representing the amylose molecules, of the starches irradiated with UVBA, UVB or UVC, apparently shifted to smaller average molecular sizes. Particularly, the UVC irradiated starches showed a substantial reduction in the molecular sizes of both amylose and amylopectin. Thus, the strong reactions caused by lengthy UVC irradiation resulted in too much depolymerization of the starch molecules to produce functional network structure for dough expansion during baking. Consequently, cassava starches subjected to UVC irradiation for 15 h exhibited ineffective baking expansion. Fiedorowicz et al. (1999) reported that both amylose and amylopectin molecules of UVC irradiated corn starches were depolymerized during irradiation periods of 5–15 h, but amylose molecules were more affected. This is similar to changes in the molecular size distributions observed in the present study.

In investigation of the degree of polymerization (DPn) of linear amylose molecules (Table 2), the acidified cassava starches irradiated for 7 and 9 h showed a significant reduction in the amylose molecules compared to the commercial starch ($DPn\ 2173 \pm 163$) to $DPn\ 1469 \pm 53$ and 1331 ± 27 for UVBA irradiated samples, to $DPn\ 1551 \pm 62$ and 1427 ± 54 for UVB irradiated samples and to $DPn\ 1216 \pm 28$ and 1096 ± 30 for UVC irradiated samples, respectively. In addition, the DPn values obtained from the starches irradiated with either UVBA, UVB or UVC for 7 h were not significantly different from those irradiated for 9 h. These findings agree with previous

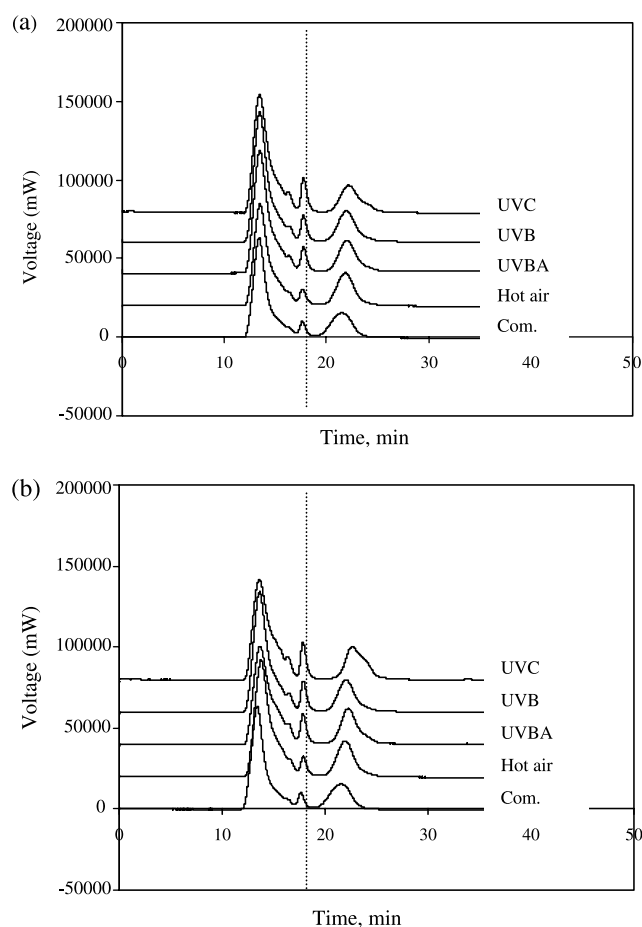


Fig. 4. Molecular size distributions of the acidified cassava starches irradiated for 9 (a) and 15 (b) h.

Table 2
Changes in the linear molecules of the UV irradiated, acidified cassava starches

Sample treatments	Degree of polymerization (DPn)	Retention times (min)
Commercial starch	2173 ± 163 ^g	21.57
Hot air, h		
7	1568 ± 147 ^{ef}	21.93
9	1593 ± 92 ^e	21.84
15	1382 ± 14 ^{def}	21.97
UVBA, h		
7	1469 ± 53 ^{ef}	22.00
9	1331 ± 27 ^{cde}	22.00
15	1015 ± 80 ^{ab}	22.24
UVB, h		
7	1551 ± 62 ^{ef}	21.94
9	1427 ± 54 ^{def}	21.94
15	1222 ± 137 ^{bcd}	22.08
UVC, h		
7	1216 ± 28 ^{bcd}	22.15
9	1096 ± 30 ^{bc}	22.17
15	812 ± 218 ^a	22.45

Results are expressed as an average of two replications. Means in a column not sharing a common superscript are significantly different at $P < 0.05$ by ANOVA and DMRT.

determinations of amylose contents by using the colorimetric method by Vatanasuchart et al. (2003).

When the retention times obtained from the chromatograms of fraction III were considered, the results clearly showed that UVC irradiation had the most influence on the linear amylose molecules of cassava starch and produced a greater effect when the irradiation was extended to the longest period of 15 h. These findings indicated that linear amylose molecules were shortened after prolonged irradiation.

Studies on X-ray diffraction for starches treated with acid and/or UV irradiation indicated that the amorphous background regions had a greater susceptibility to attack than the amorphous lamellae did (Atichokudomchai, Chinachoti, & Varavinit, 2001; Franco, Cabral, & Tavares, 2002; Jacob & Declour, 1998; Jenkins & Donald, 1997; Vatanasuchart, 2004). Therefore, amylose molecules embedded in the amorphous background regions were more likely to be degraded by reactions of both acid hydrolysis and UVB irradiation. Whereas, destructive reactions on amylose and amylopectin molecules by UVC radiation took place in the amorphous background and lamellae regions, respectively.

4. Conclusion

This present study found that the cassava starches modified with 1% lactic acid hydrolysis for 15 min and exposure to UVB or UVC radiation for 7, 9, 11 h had effective baking expansion properties. Since starch molecules in the amorphous regions were depolymerized partially by lactic acid hydrolysis and UV irradiation to the size-reduced starch molecules which were responsible

for baking expansion. As to the thermal properties, the modified cassava starches exhibited patterns of DSC thermograms similar to that of the commercial starch. The structural changes contributing to the baking expansion did not affect transition enthalpy for the cassava starch. However a slight increase in onset and peak temperatures of the starches irradiated with UVB or UVC for 9–15 h indicated stability of crystalline structure induced by modification reactions.

The HPSEC indicated that mainly amylose molecules were degraded by UVB irradiation and that both amylose and amylopectin molecules were degraded by UVC irradiation, and the changes observed for irradiation periods of 7 and 9 h were responsible for the baking expansion of the cassava starch. The degree of polymerization (DPn) clearly showed a reduction in amylose molecules in the UV irradiated acidified starches.

Thus, a reduction in amylose and amylopectin molecules of the acidified cassava starches irradiated with UVB or UVC for 7 and 9 h caused partial depolymerization which provided small linear fragments and facilitated formation of an amorphous matrix structure of starch dough during baking. Consequently, a good baking expansion of the cassava starch was achieved. In contrast, overly prolonged exposure of 15 h to the very high radiant energy of UVC radiation did not provide an effective starch structure for baking expansion. Whereas the findings showed UVBA irradiation generating too low radiant energy to produce baking expansion.

Acknowledgements

I would like to express my sincere appreciation to the Institute of Food Research and Product Development and the Department of Food Science and Technology, Faculty of Agro-Industry, Kasetsart University; and, especially, to the Cassava and Starch Technology Research Unit for their valuable supports and the National Center for Genetic Engineering and Biotechnology for the research funding.

References

- Atichokudomchai, N., Chinachoti, P., & Varavinit, S. (2001). A study on some physicochemical properties of high crystalline tapioca starch. *Starch/ Stärke*, 53, 577–581.
- Atichokudomchai, N., Varavinit, S., & Chinachoti, P. (2002). Gelatinization transitions of acid-modified tapioca starches by differential scanning calorimeter (DSC). *Starch/ Stärke*, 54, 296–302.
- Bertolini, A. C., Mestres, C., & Colonna, P. (2000). Rheological properties of acidified and UV irradiated starches. *Starch/ Stärke*, 52, 340–344.
- Bertolini, A. C., Mestres, C., Colonna, P., & Lerner, D. (1998). Comprehensive studies of molecular changes occurring in sour cassava starch. In P. Colonna, & S. Guilbert (Eds.), *Biopolymer science, food and non food applications* (pp. 27–91). France: Montpellier, 27–91.

- Bertolini, A. C., Mestres, C., Lourdin, D., Della Valle, G., & Colonna, P. (2001). Relationship between thermomechanical properties and baking expansion of sour cassava starch (*polvilho azedo*). *Journal of the Science of Food and Agriculture*, 81, 429–435.
- Camargo, C., Colonna, P., Buleon, A., & Molard, D. R. (1988). Functional properties of sour cassava (*Manihot utilissima*) starch: *Polvilho azedo*. *Journal of the Science of Food and Agriculture*, 45, 273–289.
- Cardenas, O. S., & de Buckle, T. S. (1980). Sour cassava starch production: A preliminary study. *Journal of Food Science*, 45, 1509–1528.
- Demiate, I. M., Dupuy, N., Huvenne, J. P., Cereda, M. P., & Wosiacki, G. (2000). Relationship between baking behavior of modified cassava starches and starch chemical structure determined by FTIR spectroscopy. *Carbohydrate Polymers*, 42, 149–158.
- Dufour, D., Larssonneur, S., Alarcon, F., Braset, C., & Chuzel, G. (1996). Improving the bread-making potential of cassava sour starch. In D. Dufour, G. O'Brien, & R. Best (Eds.), *Cassava flour and starch: Progress in research and development*, 133–142. Available source: <http://www.ciat.cgiar.org>, November 10, 2003..
- Fan, J. Y., Mitchell, J. R., & Blanshard, J. M. V. (1999). A model for the oven rise of dough during baking. *Journal of Food Engineering*, 41, 69–77.
- Fiedorowicz, M., Tomasik, P., Sangguan, Y., & Seung, T. L. (1999). Molecular distribution and pasting properties of UV-irradiated corn starches. *Starch/Stärke*, 51, 126–131.
- Franco, C. M. L., Cabral, R. A. F., & Tavares, D. Q. (2002). Structural and physicochemical characteristics of lintnerized native and sour cassava starches. *Starch/Stärke*, 54, 469–475.
- Govindasamy, S., Oates, C. G., & Wang, H. A. (1992). Characterization of changes of sago starch components during hydrolysis by thermostable alpha-amylase. *Carbohydrate Polymers*, 18, 89–100.
- Jacobs, H., & Delcour, J. A. (1998). Hydrothermal modifications of granular starch, with retention of the granular structure: A review. *Journal of Agriculture and Food Chemistry*, 46, 2895–2905.
- Jenkins, P. J., & Donald, A. M. (1997). The effect of acid hydrolysis on native starch granule structure. *Starch/Stärke*, 49, 262–276.
- Maria's Cookbook (2002). Pao de Queiji. Available source: <http://www.maria-brazil.org>, March 1, 2002.
- Mestres, E., & Rouau, X. (1997). Influence of natural fermentation and drying conditions on the physicochemical characteristics of cassava starch. *Journal of the Science of Food and Agriculture*, 74, 147–155.
- Nee, T. S. (1996). *Basic principles in photomedicine*. In Manual for Workshop in Photodermatology (pp. 1–4). The 12th Regional Conference of Dermatology, May 11. Pattaya, Thailand.
- Plata-Oviedo, M., & Camargo, C. (1998). Effect of acid treatments and drying processes on physico-chemical and functional properties of cassava starch. *Journal of the Science of Food and Agriculture*, 77, 103–108.
- Sriroth, K., & Piyachomkwan, K. (2003). *Starch Technology*, Vol. 3. Bangkok: Kasetsart University Press.
- Sriroth, K., Santisopari, V., Petchalanuwat, C., Kurotjanawong, K., Piyachomkwan, K., & Oates, C. G. (1999). Cassava starch granule structure-function properties: Influence of time and conditions at harvest on flour cultivars of cassava starch. *Carbohydrate Polymers*, 38, 161–170.
- Vatanasuchart, N. (2004). *Modification of cassava starch with lactic acid hydrolysis and UV irradiation to enhance baking expansion*. PhD Thesis. Kasetsart University, Bangkok, Thailand.
- Vatanasuchart, N., Naivikul, O., Charoenrein, S., & Sriroth, K. (2003). Effects of different UV irradiations on properties of cassava starch and biscuit expansion. *Kasetsart Journal (Natural Science)*, 37, 334–344.
- Wang, L., & Wang, Y. T. (2001). Structures and physico-chemical properties of acid-thinned corn, potato and rice starches. *Starch/Stärke*, 53, 570–576.
- World Health Organization (1994). *Ultraviolet radiation: Environmental health criteria 160*. Geneva, Switzerland.