

Effects of Different UV Irradiations on Properties of Cassava Starch and Biscuit Expansion

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ABSTRACT

Commercial cassava starch was modified by using 1% (w/w) lactic acid solution for 15 min and the drained starch was irradiated with different UV wavelengths of either UVBA (280-420 nm), UVB (310-330 nm) or UVC (254 nm) for 7 to 15 h. The acidified starch, irradiated with UVB or UVC for 7 and 9 h, achieved the desired baking expansion. No significant change in the specific volumes was shown for the starch irradiated with UVB for 9 h, UVC for 7 and 9 h. The starch which has been irradiated with UVB for 9 h gave the highest specific volume of $12.23 \pm 0.12 \text{ cm}^3/\text{g}$, while UVC irradiated samples of 7 and 9 h gave 12.10 ± 0.75 and $11.33 \pm 0.62 \text{ cm}^3/\text{g}$, respectively. The specific volumes of the samples were significantly correlated to the losses of dough weights during baking ($r^2 = 0.94$). As for the rapid visco analysis, the peak viscosity of the samples irradiated with UVB for 7 and 9 h were 196.55 ± 2.41 and $195.67 \pm 0.83 \text{ RVU}$, while those of the UVC irradiated samples were 176.55 ± 1.83 and $169.54 \pm 3.24 \text{ RVU}$, respectively. These values were higher than the values obtained from the other treatments but lower than the commercial starch. In addition a linear relationship between the peak viscosity and the specific volume of the samples, was observed ($r^2 = 0.81$), pointing that the starch irradiated with UVB or UVC for 7 to 9 h was capable of absorbing and holding water during gelatinization and responded for the baking expansion. A significant increase in the pasting temperatures indicated formation of network structure which occurred in the amorphous regions, due to no change in the typical A-pattern of the X-ray diffractions of the samples obtained. A reduction in amylose contents of the irradiated starches was also observed. From the scanning electron micrographs, fracture appearance and slight exocorrosion on the surface of the starch granules were similar in the different treatments. The texture profile analysis showed the deformation curves of the biscuits made by the UVB irradiated starch similar to those of the wheat rolls. The satisfactory sensory qualities in the biscuits were obtained.

Key words: cassava starch, baking expansion, UV irradiations, pasting properties

INTRODUCTION

Cassava (*Manihot esculenta* Crantz) starch is economically important for food industry in Thailand (Sriroth *et al.*, 2000), but direct utilization

as a major ingredient for bakery products, particularly as bread or biscuit making, is still limited because cassava starch has no expansion ability during baking. Only wheat flour formed a viscoelastic dough, caused by glutenin and gliadin

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proteins, capable of retaining gas during fermentation and at the early stages of baking. After starch gelatinization and protein coagulation the dough converts into an elastic bread (He and Hosney, 1991).

Uniquely, the sun-dried and fermented cassava starch, known as *Polvilho azedo* or sour cassava starch, could provide the property of high baking expansion (Cardenas and Buckle, 1980). This traditional product, originated in Brazil, is commonly used to make typical bread-like products, biscuits and snacks, having an alveolar loose crumb structure and a crispy crust, which are special kinds of gluten-free food (Camargo *et al.*, 1988). It was found that sun light, particularly at certain UV wavelengths, is essential for the baking properties. The oxidative modification of cassava starch with lactic acid together with sun drying, proved to obtain baking behavior of an increase in specific volumes of tested biscuits, but this did not occur with oven-drying method (Plata-Oviedo and Camargo, 1998). This observation could be due to the combined reactions of lactic acid and the solar UV radiation. Recently, it was found that the lactic acidified cassava starch, exposed to UV irradiation from a broad band of mercury vapor lamp at 250-600 nm, markedly responded to an expansion ability (Bertolini *et al.*, 2000). Moreover, the findings presented that sour cassava starch and the UV irradiated, acidified cassava starches, had very low final viscosity measured using rapid visco analyzer. However, change in the values for peak viscosity or consistency at peak temperature during the starch gelatinization was still not clear (Bertolini *et al.*, 2000; Camargo *et al.*, 1988).

The solar UV can be classified into UVA (315-400 nm), UVB (280-315 nm) and UVC (100-280 nm), while the short wavelengths of less than 290 nm would undergo significant absorption by the atmosphere at the ozone layer (WHO, 1994). Most research works on starch modification with UV irradiation employed an artificial UVC source

(Bertolini *et al.*, 2000; Fiedorowicz *et al.*, 1999). Thus, this study was aimed to determine the effects of different UV wavelengths (especially UVB) irradiated to the lactic acidified cassava starch on expansion behavior of baked biscuits. Changes in pasting properties, X-ray diffractions and starch granule micrographs of the modified cassava starches were also examined. Textural properties and sensory tests of the formulated cassava biscuits were evaluated.

MATERIALS AND METHODS

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

Preparation of the UV irradiated, acidified cassava starches

The cassava starch (200 g, db) was dissolved in 600 ml of 1% (w/w, db) lactic acid solution and hydrolyzed for 15 min at 25°C. The acidified samples were drained through Buchner funnel using vacuum pump and moisture content was obtained at approximately 42%. The acidified sample (150 g) was crushed into fine particles and evenly spreaded with 2 mm thickness on 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 (1) four lamps of UVBA at 280-420 nm (Philips, TL 20W/12), irradiating the energy of 64% from UVB and 36% from UVA; (2) four lamps of UVB at 310-330 nm (Philips, TL 100W/01), irradiating the energy of 90% from UVB and 10% from UVA and (3) five lamps of UVC at 254 nm (Sylvania, 30W). The samples

were irradiated for the 7, 9, 11 and 15 h and hot air drying treatment at 40°C for the same period of time was used as a comparison.

Chemical compositions

Proximate composition, contents of hydrocyanic acid and sulfur dioxide of the commercial cassava starch were determined (AOAC, 1995; O' Brien, 1991).

Baking properties

Baking expansion ability, a specific volume of biscuits, was determined using standard formulation adapted from the recipe of Pao de Queiji (Maria's Cookbook, 2002). Biscuits were made from 45 g (db) of cassava starch, 45 g whole milk, 10 g soybean oil, 0.5 g salt, 5 g egg and water. The cassava starch was pregelatinized in boiling mixture of milk, oil and salt. It was mixed into a dough and let stand for 5 min, followed by an addition of egg and water. The amount of water used for the commercial starch, hot air-acidified starch, UVBA, UVB and UVC irradiated, acidified starches was 18, 18, 25, 30 and 30 g, respectively. The variations were due to its ability in water absorption to obtain the same consistency. Total preparation time was 10 min. A portion of 14 g dough was dropped on baking paper and baked at 210°C for 20 min. After cooling, weights and volumes (by seed displacement) of six biscuits were measured and calculated to get an average dough weight loss (g) and specific volume (cm³/g).

Pasting properties

Paste viscosity of the cassava starch was measured using rapid visco analyzer (RVA) (Sirroth and Piyachomkwan, 2000). The 10% starch slurry was prepared from 2.5 g (db) sample in 25 g distilled water, as calculated to obtain 14% moisture content of the starch sample. The RVA programming system was set to start at 50°C,

heated to 95°C, maintained for 2.5 min, then, cooled to 50°C, holding for 2 min. The total running time for each sample was 13 min.

Determination of amylose content

Colorimetric method was used for determining the changes in amylose contents of starch samples after treatments (AACC, 2000).

Characterisation of starch samples

Wide-angle X-ray diffraction patterns of the starches were examined using a JEOL, JDX 3530, Japan. The degree of relative crystallinity was calculated from the ratio of diffraction peak area and total diffraction area (Cheetham and Tao, 1998). The microscopic observation of starch granules was performed using scanning electron microscopy (SEM) with a JEOL, JSM 6301F, Japan, with the magnification of 7500X (Atichokudomchai *et al.*, 2000).

Evaluation of cassava biscuits made from the UV irradiated, acidified starch

Cassava biscuits were made from 50 g of starch, 45 g whole milk, 10 g soybean oil, 0.5 g salt, 23 g grated cheese, 15 g egg, 2.5 g sugar and 30 g water (Maria's Cookbook, 2002). Wheat rolls were made from 100 g of wheat flour, 1.5 g yeast, 8 g shortening, 65 g water, 6 g sugar and 1 g salt. The 10 g doughs were baked at 210°C for 18 min. The texture profile analysis (TPA) was determined by TA.XT2i/25 texture analyzer, using a P50 cylinder stainless probe, set at 2 mm/sec cross-head speed for the 50% strain of compression. The hardness (g), cohesiveness, gumminess (g), springness (sec) and chewiness (gsec) for six cassava biscuits and wheat rolls were also determined. Moreover, the intensity of sensory attributes, such as, crust, air cells, crumb structure and flavor, using 1 to 5 rating scale, and their preferences and overall acceptability, using 1 to 9 hedonic scale, of the samples were evaluated.

Statistical Analysis

The properties for commercial cassava starch and modified cassava starches were measured in duplicate and reported as mean and standard deviation. The different UV wavelengths and exposure periods were statistically analyzed using ANOVA and DMRT at the 95% level of confidence.

RESULTS AND DISCUSSION

Baking properties

Commercial cassava starch contained a pure content of starch at 99.82% with very low hydrocyanic acid of 0.14 ppm, but sulfur dioxide was not detected. As for baking properties, the acidified cassava starch irradiated with UVB or UVC for 7 and 9 h achieved the high baking expansion. No significant difference in the specific volume was shown for the starch samples neither irradiated with UVB for 9 h nor with UVC for 7 and 9 h. However, samples of UVB irradiated for 9 h gave the highest specific volume of $12.23 \pm 0.12 \text{ cm}^3/\text{g}$ while those of UVC irradiated for 7 and

9 h gave 12.10 ± 0.75 and $11.33 \pm 0.62 \text{ cm}^3/\text{g}$, respectively (Figure 1 and 2). As a study of Demiate *et al.* (2000), the samples of UVB or UVC irradiated for 7 and 9 h, showed the desired baking expansion characteristics of the biscuits. But UVBA irradiated or hot air dried samples for 7 to 11 h, had significantly much lower specific volumes than the samples, irradiated with UVB or UVC. Also a poor expansion was observed for the hot-air treated samples and the commercial starch. Within each treatment, the obtained specific volumes seemed

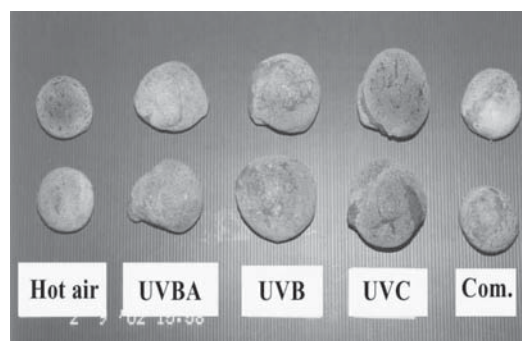
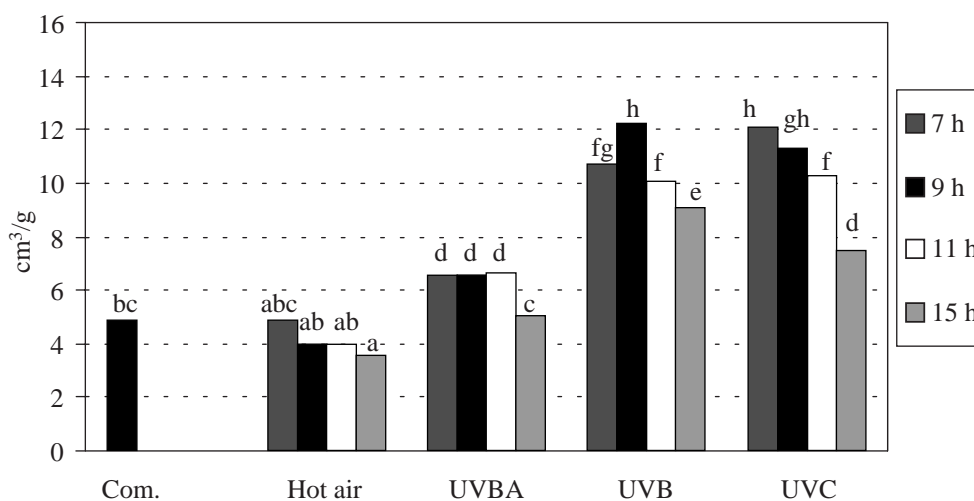


Figure 1 Biscuits made from the acidified cassava starches, irradiated for 7 h.



Note: Means followed by the same letter are not significantly different at the 5% level of probability.

Figure 2 Specific volumes of the baked biscuits, made from the acidified cassava starches, treated with different UV irradiations.

to decrease with a longer irradiation time to 15 h. The specific volumes of the UVC irradiated samples reduced from 12.10 ± 0.75 for 7 h to $7.47 \pm 0.97 \text{ cm}^3/\text{g}$ for 15 h. This means that expansion property of the cassava starch would be accounted for a slight oxidative depolymerization, otherwise, the ability during baking was no longer possible (Camargo *et al.*, 1988). Thus, the 1% lactic acidification, incorporating a sufficient energy from the UVB or UVC irradiation for 7 and 9 h, could induce the high baking expansion of the cassava starch in this study.

Losses of dough weight were measured after baking the biscuits made from the cassava starch, so to investigate baking expansion mechanism by mean of water evaporation. The sample irradiated with UVB for 9h, possessing the highest specific volume, showed the highest loss of dough weight of $5.74 \pm 0.01 \text{ g}$. A significant linear relationship between specific volumes and dough weight losses ($R^2 = 0.94$) was obtained (Figure 3), indicating that an increase in specific volumes was induced by increased loss of water during baking. As for the starch gelatinization by heating, water absorbed in the starch molecules was vaporized causing a high pressure which acted as driving force for the expansion (Bertolini *et al.*, 2001).

Pasting properties

Paste viscosity of the 1% lactic acidified cassava starch which has been exposed to different UV irradiations for the periods of 7, 9, 11 and 15 h was observed. For the 7 and 9 h, the samples irradiated with UVB presented the peak viscosity of 196.55 ± 2.41 and $195.67 \pm 0.83 \text{ RVU}$, while those irradiated with UVC were 176.55 ± 1.83 and $169.54 \pm 3.24 \text{ RVU}$, respectively. Within each UV treatment these peak viscosities were significantly higher than the values observed for 11 and 15 h, but significantly lower than commercial cassava starch of $235.84 \pm 1.65 \text{ RVU}$ (Figure 4 and 5). When different energy effects were observed for a change in peak viscosity, the samples irradiated with UVB and UVC showed significantly higher peak viscosity than the other treatments for the period of 9 h (Figure 6) similar to the result found for the period of 7 h. Moreover, a significant linear relationship between peak viscosities and specific volumes of the starches was observed ($R^2=0.81$) (Figure 7). The results implied that the modified cassava starches could produce a network structure formed by hydrogen bonds. Thus during gelatinization the starch paste could easily take up water molecules into the network, resulting in the high peak viscosity of the samples found in this study. Furthermore, final viscosity observed for

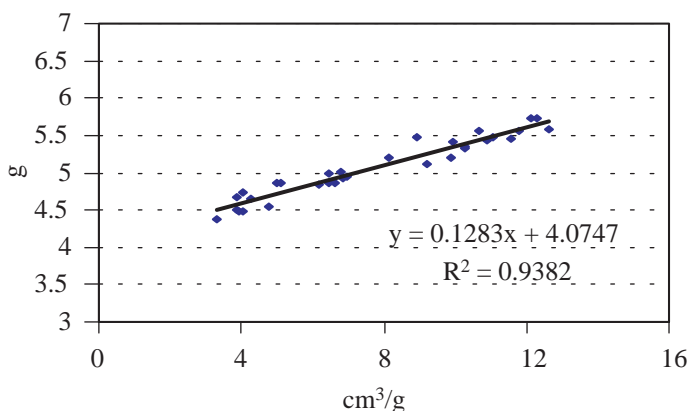


Figure 3 Linear correlation between specific volumes and dough weight losses (significant difference at 1% level of probability).

all the treated samples was similarly low which agrees with other studies (Plata-Oviedo and Camargo, 1998; Bertolini *et al.*, 2000). Very low setback viscosities were also observed after modifications. As compared to the setback viscosity of the commercial starch of 82.05 ± 1.95 RVU, the values of 28.78 ± 0.15 , 30.21 ± 0.41 and 29.71 ± 0.76 RVU were found for the samples irradiated with UVB and 20.48 ± 1.33 , 20.50 ± 0.47 and 19.00 ± 0.82 RVU for the samples irradiated with UVC for 7, 9 and 11 h, respectively.

In addition, the pasting temperature of the

samples irradiated with UVB or UVC for 7, 9 and 11 h was significantly 1°C higher than that for the commercial starch of $69.48 \pm 0.08^\circ\text{C}$, whereas the hot air and UVBA treated samples showed no change. This result implied a high stability of the network, leading to a high pasting temperature during the starch gelatinization (Fiedorowicz *et al.*, 1999).

Determination of amylose content

The result showed a significant decrease in the amylose contents for the samples irradiated

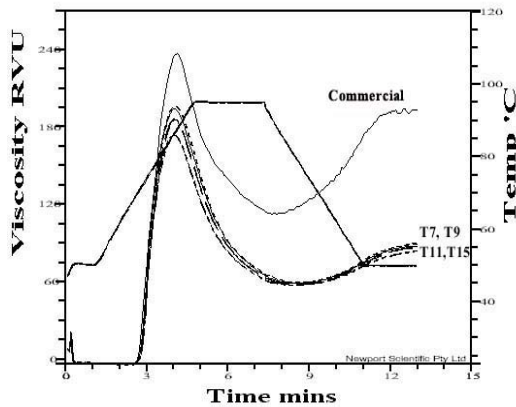


Figure 4 RVA graphs of the acidified cassava starch, irradiated by UVB for 7 (T7), 9 (T9), 11 (T11) and 15 (T15) h.

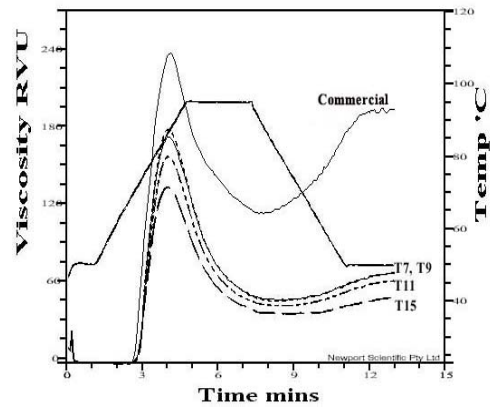


Figure 5 RVA graphs of the acidified cassava starch, irradiated by UVC for 7 (T7), 9 (T9), 11 (T11) and 15 (T15) h.

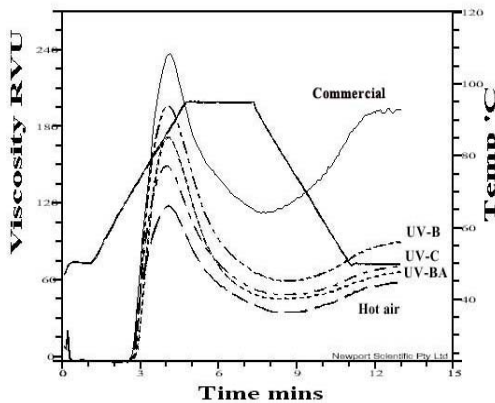


Figure 6 RVA graphs of the acidified cassava starch, irradiated for 9 h.

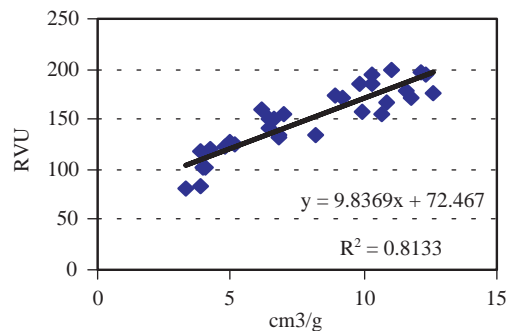


Figure 7 Linear correlation between peak viscosities and specific volumes.

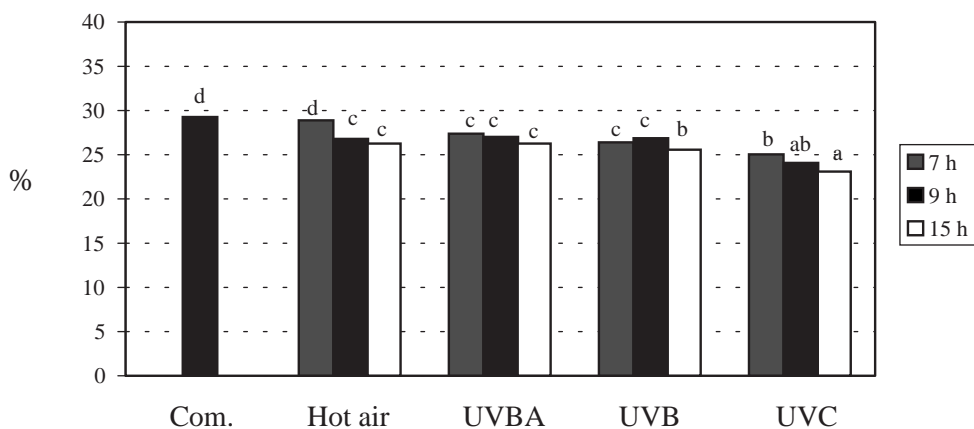
with UVBA (27.34 ± 0.68 , 26.99 ± 0.24 and $26.26 \pm 0.45\%$), UVB (26.40 ± 0.01 , 26.82 ± 0.16 and $25.53 \pm 0.77\%$) and UVC (25.08 ± 1.05 , 24.03 ± 0.21 and 23.00%) observed for 7, 9 and 15 h, respectively, as compared to the commercial starch of $29.27 \pm 0.23\%$. But more degradative effects were found for the UVC irradiated samples. From the evidence of good baking expansion of the samples irradiated with UVB or UVC for 7 and 9 h, it suggested that depolymerization of amylose molecules could involve in the network formation, resulting in the expansion. Previous studies on modifications of different starches showed that both amylose and amylopectin were simultaneously degraded by acid hydrolysis and/or the UV irradiation (Bertolini *et al.*, 2000; Fiedorowicz *et al.*, 2000).

Characterizations of the starches

X-ray diffractograms of the acidified starches treated with the hot air and irradiated with UVBA, UVB or UVC for a period of 9 and 15 h, appeared to have a similar typical A-type pattern (Figure 9a, 9b). When the degree of relative crystallinities were determined, the samples treated with the hot air, UVBA, UVB or UVC for 9 h had

31.5, 31.0, 32.0 and 30.5%, respectively, showing almost no change from the commercial starch of 32.5%. For the 15 h treatments, the peaks looked sharper at 17° and 18° , showing an increase in the relative crystallinities to 33.5, 34.5, 34.0 and 34.5%, respectively. This means that the irradiations for 9 h which produced a network structure responsible for the good expansion did not disturb the crystallinity of the cassava starches and did not change the proportion of the amorphous and crystalline regions. In other words, the reactions occurred in the amorphous regions of the starch granules.

The scanning electron micrographs of the starch granules of the acidified samples, irradiated with UVB or UVC revealed a round and oval shape, some with truncated concave edges similar to the commercial starch (Figure 10a, 10b). Most of the modified starch granules appeared a similar fracture surface as canals of exocorrosion sink into the granules but some of them had a slight pitting or erosion by acid attack. The starch granule micrographs of the samples irradiated with UVC for 15 h exhibited enlarged canals and looked dry and more shrinkage at the surface.



Note: Means followed by the same letter are not significantly different at the 5% level of probability.

Figure 8 Amylose contents of the UV irradiated, acidified cassava starches.

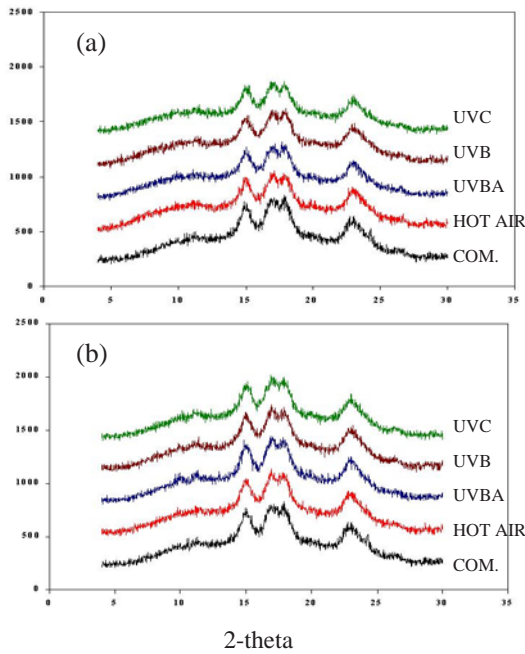


Figure 9 X-ray diffractograms of type A patterns for (a) 9 h and (b) 15 h.

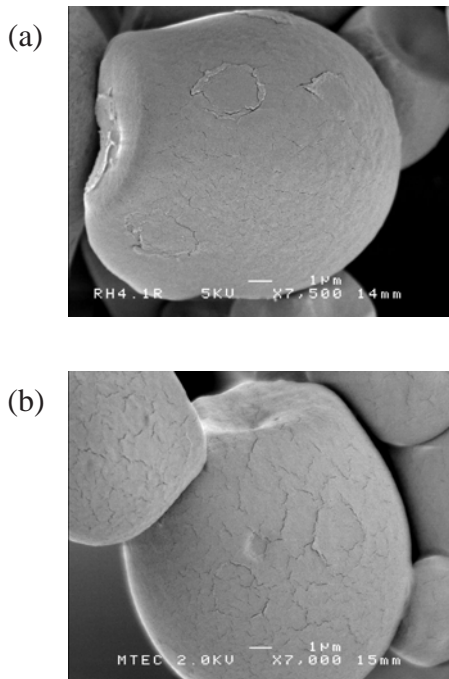


Figure 10 Cassava starch granules with (a) UVB, irradiated for 9 h and (b) UVC irradiated for 7 h.

Evaluation of the cassava biscuits made from the UV irradiated, acidified starch

The results from the TPA indicated that the cassava biscuits, made from the UVB irradiated acidified cassava starch, appeared to have force deformation curves typically similar to the wheat rolls (Figure 11). These curves provided the textural characteristics as observed by the two compressions. The values of hardness, springness and chewiness of the cassava biscuits were significantly lower than those of the wheat rolls, except for the cohesiveness, while there was no significant difference in gumminess among the samples (Figure 12). Cohesiveness and gumminess have been associated with the intermolecular forces within the food system, which would account for an integrity of the network structure (Numfor *et al.*,1995).

Table 1 illustrates the results of sensory tests for the cassava biscuits. The UVB irradiated starch gave the baked biscuits with a moderate brown color and firm crust. The crumb had moderately fine, tender and good elastic texture, but exhibited quite large air cells which were not

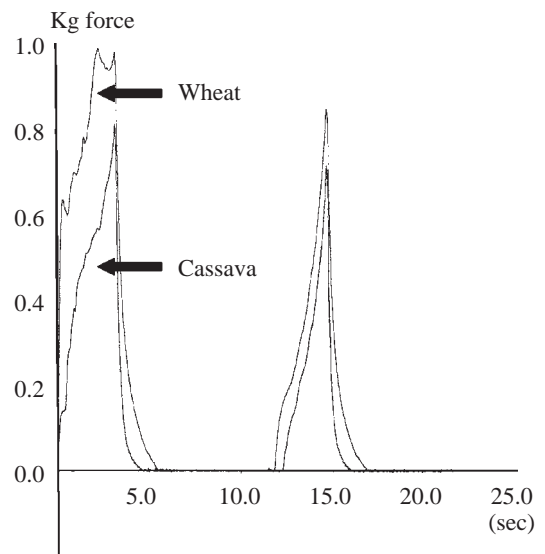


Figure 11 Force deformation curves of the cassava biscuits, as compared to the wheat rolls.

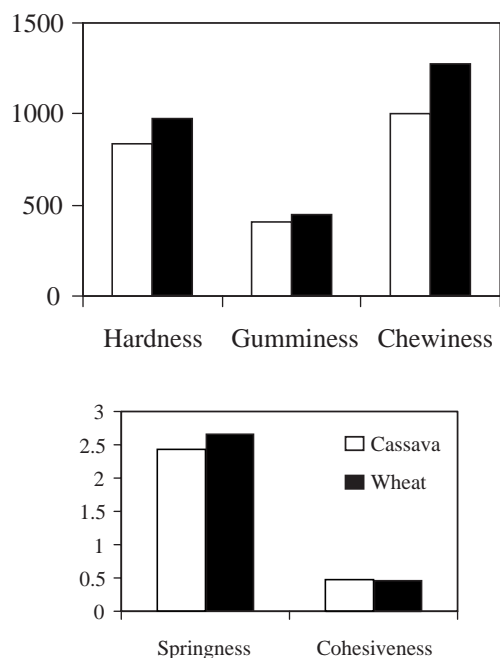


Figure 12 Textural characteristics of the cassava biscuits, as compared to the wheat rolls.

uniform in size. Likely, the biscuits had well balanced flavor. In addition, the preference scores obtained from most attributes were more than 6.0, indicating that the panelists rather liked the biscuits. It can be concluded that the satisfactory qualities in the biscuits were obtained, thus good acceptability by the panelists was achieved with a score of 6.4.

CONCLUSION

In this study, the combined effects of 1 % lactic acid solution and UVB or UVC irradiation for 7 and 9 h, could produce a good baking expansion of cassava starch. The reaction of sufficient UV energy caused the partial depolymerization of amylose molecules and formed a network structure with hydrogen bonding. Thus the structure was accessible to absorbing water and holding it during gelatinization which led to the high peak viscosities. Moreover, the increased pasting temperature could confirm the network formation. The X-ray diffractograms

Table 1 Sensory evaluation of the cassava biscuits, made from the UVB irradiated, acidified cassava starch.

Quality attributes		Descriptive test		Preference test, 1-9 hedonic scale
		1-5 rating scale of attributes	Perceived intensity	
Crust:	Color	2.7	Moderately brown	6.6
	Firmness	3.3	Moderately firm	6.1
Air cells:	Size	3.7	Quite large	5.7
	Uniformity	2.4	Rather poor	5.6
Crumb:	Fineness	2.6	Moderately fine	5.9
	Tenderness	3.5	Moderately tender	6.3
	Elasticity	3.2	Good elastic	6.2
Flavor:	Well-balanced	3.1	Moderate	6.5
	Sweetness	2.5	Slightly sweet	6.3
Overall acceptance				6.4

indicated that the reactions occurred in the amorphous regions due to no changes in the crystalline structure. Lastly, the textural characteristics of the cassava biscuits, made from the UVB irradiated, acidified starch, were similar to those of wheat rolls and the sensory qualities achieved satisfactory and acceptable to the panelists.

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