Changes in Lipid Colour of Grain and Pasting Properties of Brown Rice cv. Khao Dok Mali 105 during Storage

Jirasak Kongkiattikajorn[1/] Lamul Wiset[1/] and Songsin Potchanachai[1/]

ABSTRACT

This research was to find out the changes of the total lipid, free fatty acid contents, the colour of brown rice, gel consistency and pasting properties during storage of the rice for 0-7 months at 25°C and 37°C. The experinent was designed as a factorial in CRD with two storage conditions, eight times of storages and conducted at the Laboratory of the School of Bioresources and Technology, King Monkut's University of Technology, Thonburi during 2000-2003. Storage produced changes in the total free fatty acid, the colour of the brown rice, gel consistency and RVA pasting properties as a varietal, times and temperatures dependent phenomenon. The significant difference between the colour of the brown rice, total free fatty acid contents and the pasting behaviour of brown rice flour was shown in the rice stored at 25 and 37°C. Aging had no apparent effect on the levels of total lipid contents during storage. Free fatty acid contents decreased from 5.31 to 3.70 % and 5.31 to 2.09 % of total lipids for rice stored at 25 and 37°C. respectively. There was the negative correlation between total fatty acid contents and colour of brown rice at 37°C. The relationship between pasting properties and total free fatty acid contents of rice storage at 25 and 37°C. also represented the linear regression. This study indicated the changes of free fatty acid contents, physical and physicochemical properties on rice during aging were functionality of the storage temperatures and times.

Key words : lipid, colour brown rice grain, grain and pasting properties

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[1/] School of Bioresources and Technology, King Monkut's University of Technology Thonburi, Bangkok 10140

Introduction

In general, the physicochemical properties of freshly harvested rice can change quite dramatically during the first 3-4 months of storage (Chrastil, 1990). The most notable changes that occur during this natural aging process involve rheological properties that, in turn have a significant effect on the cooking and eating qualities of rice (Perez and Juliano, 1981). Rice flour derived from inadequately aged grains, has also been observed by local manufacturers to give unsatisfactory performance in the preparation of several indigenous food products. Inconsistent quality is brought about by variations in the aging process is also a problem. Thus, freshly rice flour has usually to be stored or aged under proper temperature, time and relative humidity to achieve high consistent quality before usage. However, studies of aging have, generally been focused on whole-grain rice rather than the flour.

It is accepable that starch pasting properties are the major factors contributing to noodle quality. High peak viscosity is considered to be negatively associated with noodle quality, as it reduces the firmness of noodles (Miskelly and Moss, 1985). Moreover, the final viscosity from the (rapid viscoanalysis) was significantly related to the firmness, elasticity, and surface smoothness of noodle (Ross *et al.*, 1997). Final viscosity has a positive effect on the firmness and elasticity of the noodle quality.

During the holding period of the viscosity test, the material slurries are subjected to high temperature and mechanical shear stress which further disrupt starch granules in the grains, resulting in amylose leaching out and alignment. The ability of starches to with stand heating at high temperature and shear stress is an important factor in many processes. The peak viscosity often correlates with quality of end-product and also provides an indication of the viscous load likely to be encountered by a mixing cooker. During cooling, re-association between starch molecules, especially amylose, will result in the formation of a gel structure and, therefore, viscosity will increase to a final viscosity. This phase is commonly described as the setback region and is related to retrogradation and reordering of starch molecules. The low setback values indicate low rate of starch retrogradation and syneresis.

Most physicochemical properties of rice change during storage. As rice aged, cooked rice texture became fluffier and harder (Villareal *et al.*, 1997). Perdon *et al.* (1997) suggested that rice aging is a complex process that is seen in the paddy, brown rice, milled rice, rice starch and cooked rice. One of the most sensitive indices of the aging process in rice was the change in pasting properties which was usually measured by thermoviscometry (Perdon *et al.* 1997). The data have been inconsistent because the viscosity of rice paste increases dramatically after short- to intermediate-term storage (months) of milled rice (Shibuya, *et al.*, 1974) and decreases during longer-term storage (years) (Sowbhagya and Bhattacharyat, 2001). Attempts have been made to explain the changes in functionality associated with aging have focused on the properties of rice components, such as starch, protein, and lipids, and the interactions between them during storage (Chrastil and Zarins, 1992). As with functionality, changes in starch, lipid and protein components were most apparent at an elevated storage temperature although gross changes in starch, amylose, and protein contents of the rice grain (Villareal *et al.*,1976) during storage were minimal. However, it is now apparent that the minor components at the granule surface (lipids and proteins) have a disproportionate influence on granule properties and that aging-induced changes in these components may account for the changes in physicochemical properties seen after storage.

This study was to investigate changes in pasting propertied following rice storage and the content of lipid and free fatty acid as well as the factor that influenced these changes.

Materials and Methods

Rice samples

One hundred kilograms of the paddy rice Khao Dok Mali 105 was obtained from the Rice Research Centre, Pathum Thani province and used as experiment materials. The contaminant free paddy rice was clean and driy with air on the floor to 14-15% moisture content prior to pack into polypropylene bags of 70 micrometer thickness. Each bag contained 400 g of rice. The bags were placed at 25 and 37 °C in thermostatically controlled incubators. Triplicate samples were withdrawn for analysis after an initial period and at one month intervals thereafter until 7 months. Storage trials were designed as completely randomized with 2 storage conditions and 8 time storages as a factiorial in CRD. The factor A had two storage conditions at 25 °C in 40-50 % relative humidity and 37 °C in 30 % relative humidity and factor B hed 8 storage times for 0-7 months. Samples were analyzed for moisture content, physical, chemical and physicochemical properties of rice. The moisture content was estimated by oven drying 1 g of a sample at 115°C for 3 hours. Every month, the brown rice was ground into flour and sieved to 50 mesh powder and analyzed for lipid content and its physicochemical properties.

Physical analysis

Colour measurements of brown rice were performed in colorimeter Minolta Model DP-301. Colour values (L, a and b) were measured using a white standard tile which was used to calibrate the colorimeter (L = 100.01, a = - 0.01, b = - 0.02) before measurements. The measurements of colour obtained in units of approximate visual, uniformity throughout the colour solid were gived by the opponent colour scales. Therefore L measured lightness (luminosity) and variesd from white to black. The a and b value chromatically gave designations of colour as follows; a-value measured redness when positive, gray when zero, and greenness when negative, b-value measured yellowness when positive, gray when zero, and blueness when negative. Gel consistency was determined by Cagampangs method (Cagampang *et al.* 1973).

Chemical analysis

Total lipid and total free fatty acid contents of the brown rice were determined according to Dhaliwal *et al.* (1991).

Rapid viscoanalysis (RVA)

The pasting properties of brown rice flour was determined with a rapid viscoanalyser (Newport Scientific, Warriewood, NSW, Australia). The following conditions of sample mass and temperature profile were determined as optimum after examining sample masses in the range from 2.0 to 3.5 g. Brown rice flour (2.8 g, 12 % moisture) was slurried with distilled water (25 ml). The temperature profile involved an initial 10 s high-speed (960 rotations/min), stir that dispersed the sample prior to the beginning of the measuring phase at 160 rotations/min. Temperature was held at 50°C for 1 min and then raised to 95 °C in 3.75 min, held for 2.5 min, cooled to 50°C in 3.75 min, and held for 5 min. The RVA instrument provided the following parameters: peak viscosity (PV)-highest viscosity during "heating" final viscosity (FV)-the viscosity at the completion of the cycle; setback (SB)-FV minus PV. Values were reported in °C or rapid viscoanalyser units (RVU), each of which is approximately equal to 10 mPas. All determinations were replicated three times to estimate mean values and standard deviations. The data were analysed by a one-way analysis of variance by mean comparisons using least significant difference (LSD) at the 5 % probability level. Pearson correlation coefficients between all possible parameters were determined on both storage temperatures at 25 and 37 °C and times.

The experiment was conducted at the School of Bioresources and Technology, King Monkut's Unirersity of Technology during 2000-2003.

Results and Discussion

The b value at 37°C was higher than the storage at 25 °C due to storage time. There was increase in b value after storage at 25 and 37°C for 5 months and 2 months respectively (Table 1).

The storage of rice caused increasing in b value that came from brown pigments increased during storage. Brown pigments increasing provided an index for evaluating the intensity of browning reactions that was caused by Maillard reaction. The reaction was achieved by the determination of furosine (e-N-(furoylmethyl L-lysine), an amino acid formed during acid hydrolysis of the Amadori compound fructosyl-lysine, lactulosyl-lysine and maltulosyl-lysine produced by reaction of e-amino groups of lysine with glucose, lactose and maltose, respectively (Fernandez-Artigas *et al.*, 2001; Guerra-Hernandez *et al.*, 1999). Breakdown products such as carbonyl and amino compounds reac (Maillard reaction) and then coloured compounds form. Another possible cause of yellowing in stored rice should be melanoidins formulation due to the oxidation of phenols. The Maillard reaction is one of the most important modifications in cereals that contain proteins and reducing carbohydrates. This result indicated browning reaction occurred during storage due to induction by heating and long storage conditions. Many indices were based on Maillard reaction products that had been proposed to assess the effects of heat treatment and long storage on foods. The Maillard reaction was enhanced by the drying step (Guerra-Hernandez *et al.*, 1999) and continued during the storage.

Aging the paddy. brown rice of Khao Dawk Mali 105 contained 2.50% lipid in both 25 and 37 °C conditions had no apparent effect on the content. The storage temperature and time affected free fatty acid of lipid content of rice flour. When stored at 25°C, there was a significant change in total fatty acid content after 6 months storage. Rice storage at 37°C in free fatty acid fraction of lipid content decreased and occurred after storage and gradual decrease till 7 months. The decrease in free fatty acid fraction of lipid content after storage at 37°C was lower than that of at 25°C (Table 1).

Under condition studied, lipids did not undergo oxidation during storage, as reflected by a constant total lipid content due to the paddy rice being packed in polyethylene bag. However, it was presumably non-starch lipids (free fatty acids) that were primarily involved in hydrolysis and oxidation reactions.

Table 1. Colour, total free fatty acid content and gel consistency of brown rice during storage at 25 and 37°C for 0 -7 months.

Temperature (°C)	Storage duration (month)	b value	Free fatty acid content (% lipid content)	Gel consistency (mm)
25	0	21.82±0.12a	4.5±0.10a	80.02±1.27a
	1	22.03±0.02ag	4.34±0.12ab	79.35±1.01a
	2	22.16±0.14ab	3.74±0.09c	76.51±0.71b
	3	22.14±0.05ac	4.27±0.25ad	75.24±1.00b
	4	22.25±0.14adh	3.72±0.23c	73.32±0.71c
	5	22.54±0.70bcdf	4.19±0.09bd	73.17±0.95c
	6	22.75±0.32fg	3.58±0.11c	73.14±0.78c
	7	22.79±0.23fg	3.70±0.18c	73.21±0.38c
37	0	21.82±0.12a	4.50±0.10a	80.02±1.27ad
	1	22.40±0.32bcdg	4.11±0.22bd	79.12±0.87ad
	2	22.54±0.20bcfh	3.51±0.12ce	75.51±0.85b
	3	22.92±0.24fi	3.33±0.16e	72.23±0.78ce
	4	22.95±0.42fj	2.81±0.15f	73.45±1.05ce
	5	23.12±0.21fk	2.82±0.16f	71.26±0.95ef
	6	23.35±0.34ijk	2.64±0.27f	71.43±0.76ef
	7	23.32±0.41ijk	2.09±0.17g	70.26±0.82f

Means ± SD, in the same column followed by a conmon letter are not significant different at the 5% by DMRT.

± = standard deviation and +b = yellowness, -b = blueness.

When rice was stored at temperatures of 25 and 37 °C, there was decrease in gel consistency till 2 months and then gradually decrease in on further storage. The storage temperature and time affect on gel consistency of rice flour as (Table 1). When rice was stored at temperature of 25°C, there was a decrease in gel consistency till 4 months which did not change on further storage. Storage at 37 °C decreased in gel consistency was also occurred after storage and reached a minimum value till 7 months.

The results of gel consistency indicated that gel consistency of aged rice 0-1 month at 25 and 37 °C were somewhat comparable and after 1 month storage, the gel consistency of rice flour decreased however all aged rice at 0-7 months could be comparable to that of soft flour type.

The effect of storage temperatures and times on peak viscosity of rice flour. When rice was stored at the relatively low temperature of 25°C, there was a slow but it was gradually an increase in peak viscosity. Conversely, when rice was stored at the relatively high temperature of 37 °C, a decrease in peak viscosity had occurred after two months storage and reached a minimum value till 7 months (Table 2).

The storage temperature and time affected on pasting temperatures of rice flour (Table 2).

All pasting properties, peak viscosity setback and pasting temperature showed significant differences among the stored rice (Table 2) Pasting temperature of different rice storage flruos ranged from 73.5 - 84.9 °C for storage at 25°C, and 84.9 - 87.0 °C for storage at 37 °C. The pasting temperature of stored rice decreased after 1 month storage at 25 °C while the pasting temperature of stored rice at 37 °C slightly increased after 7 month storage. Tester and Morrison (1990a) suggested that amylopectin was largely responsible for granule swelling. Brown rice flour stored at 25 °C might take up water more quickly than fresh rice flour and induce higher swelling in a lower pasting temperature, while brown rice flour stored at 37 °C had similar pasting temperature to the fresh rice flour. There was a significant effect on RVA pasting properties of fresh brown rice flour and these differences were maintained during the aging process. The aging rice at 25 °C had an increase peak viscosity during storage. Peak viscosity of the aging rice at 37°C was decreased during storage. The strong re-association of amylose molecules of gelatinized rice caused the low peak viscosity and high final viscosity of viscographs of stored rice at 37°C. This is not surprising at the complexity of the

Table 2. Pasting properties of brown rice during storage at 25 and 37°C for 0 -7 month.

Temperature (°C)	Storage duration (month)	Pasting temperature (°C)	Peak viscosity (RVU)	Setback (RVU)	Final viscosity (RVU)
25	0	84.92+62ai	165.02+4.58a	80.12+1.73a	147.21+5.81a
	1	80.51+1.53b	182.73+4.65bd	87.53+2.18g	175.24+4.62b
	2	74.94+1.37cg	188.42+5.05b	75.42+1.57h	165.42+4.06b
	3	75.21+1.49cd	185.45+4.12bd	99.72+2.92b	196.53+5.93c
	4	73.52+1.57cg	207.82+6.29c	104.51+2.23cd	208.55+8.05d
	5	74.55+1.70ce	178.74+4.11bd	103.72+1.85cd	204.42+3.93cd
	6	72.51+1.15cf	206.25+6.73c	105.74+2.27d	217.91+6.37de
	7	73.53+19defg	208.54+5.77c	112.51+2.61i	223.43+3.25e
37	0	84.92+1.62ai	165.02+4.58a	80.12+1.73a	147.21+5.81a
	1	84.52+1.54ai	168.21+7.94a	100.45+1.64bc	195.62+6.85c
	2	84.04+1.28ai	151.02+5.29e	92.36+2.00j	197.81+4.89c
	3	83.21+1.60a	151.62+4.83e	121.32+3.32e	239.42+8.64g
	4	85.14+1.29ahk	139.24+6.33f	122.35+2.10e	241.63+9.18fg
	5	86.12+1.61hik	132.93+6.36fg	128.47+2.46f	251.85+7.02f
	6	85.42+1.74ai	128.94+5.54g	131.25+1.42f	250.52+7.86f
	7	87.05+1.82ijk	125.71+3.55g	129.91+2.37f	254.21+4.76f

Means + SD. in the same column followed by conmon letter are not significant differenct at the 5% level by DMRT.

\+ = standard deviation and +b = yellowness, -b = blueness.

changes seen in the current data where rice storage produced changes in pasting behaviour of the resulting flour as time and temperature dependent phenomenon. For instance, following storage of the rice grain at 4°C peak viscosity of the corresponding rice flour decreased at 4 months relative to fresh rice flour and then increased above the initial value during further storage. However it can be concluded that storage at this temperature effectively retarded the aging process. Aging was accelerated at the higher storage temperature as an observation from previous studies (Rajendra and Zakiuddin, 1991).

Decrease of peak viscosity values of rice stored at 37°C might be due to oxidation that led to a reduction in both the total and free fatty acid content (Aibara *et al.*, 1986). Thus, changes in the extent of amylose lipid complexation might be associated with the storage of rice. The effect of high temperature might be accelerate the oxidation of fatty acid more than low temperature. The total free fatty acid contents and peak viscosity of rice storage at 25°C were higher than that of at 37 °C. Peak viscosity changes have been attributed to the characteristics of the starch granules. Thus, the decrease in peak viscosity showed that the starch granules of stored rice were more resistant to swelling than those of fresh rice. The present data had indicated that the peak viscosity of rice flour stored at 25°C was initially increased upon aging of rice grain. Thus, pasting/ gelatinization might be influenced by the presence, orientation and nature of surface lipids and proteins. The latter were rich in basic amino acids and have intrinsically been hydrophilic. For example, changes at the granule could contribute to a decrease in hydrophilicity that would affect granule hydration and swelling. In either case, the changes induced by aging result from the increased hardness of the starch granules limiting granule hydration and swelling.

The difference in viscosity with different storage temperature might be attributed to the interaction among starch, protein and free fatty acid (FFA). Difference in pasting properties occurred only when all three components were present under certain condition. A distinct three-component forming complex contained starch composition, protein and lipid coponent (Zhang *et al.*, 2003). Complexation between starch amylose and lipids has been well documented in the literature (Brisson *et al.*, 1991; Zobel *et al.*, 1967). However, the mechanism of the starch-protein-lipid component interaction was unclear. Final viscosity and setback varied from 147.2 - 251.1 and 80.1 - 131.2 RVU respectively.

Final viscosity increases upon cooling which may be due to the aggregation of the amylose molecules (Miles *et al.*, 1985). Setback value is the recovery of the viscosity during cooling of the heated starch suspension. The higher setback value of the starch is associated with a greater tendency of the starch to retrograde (Wang and White, 1994), The amylose-lipid interaction likely restricted swelling of starch, thus delaying the pasting temperature. High setback of the stored rice flours may be due to the amount and the molecular weight of the amylose leached from the granules and the remnants of the gelatinized starch (Loh, 1992). Pasting properties of starch have been reported to be affected by amylose and lipids contents and by branch chain-length distribution of amylopectin. Amylopectin contributes to swelling of starch granules and pasting, while amylose and lipids inhibit the swelling (Tester and Morrison, 1990b). Also, the amylopectin chain-length and amylose molecular size produce synergistic effects on the viscosity of starch pastes (Jane and Chen 1992). These results indicate that the degree of change in the pasting properties depends on the combination effects of temperature, time and component on the starch granules during storage period.

Negative correlation between total free fatty acid and b value of brown rice stored at both 25 and 37°C. positive correlation as represented (Table 3).

The scatter diagram me of peak viscosity and total free fatty acid contents of rice storage at 25°C represents the correlation of the increase in total free fatty acid and increase in peak viscosity in the same direction while the rice storage at 37 °C represents the linear regression of total free fatty acid contents and peak viscosity in opposite direction. shows diagram of pasting temperature and total free fatty acid contents of rice storage at 25°C represents the correlation of the increase in total free fatty acid and increase in peak viscosity in the same direction. However the rice storage at 37°C did not show the correlation between pasting temperature and total free fatty acid.

The present study indicates that the

Table 3. Correlation coefficients (r) of functional properties for brown rice flour storage both at 25 and 37°C

Functional properties	b value	Free fatty acid	Pasting temp.	Peak viscosity	Setback	Final viscosity
Gel consistency	-0.895**	0.788**	-0.016	0.308	-0.881**	-0.928**
b value		-0.914**	0.271	-0.546*	0.931**	0.957**
Free fatty acid			-0.388	0.637**	-0.831**	-0.867**

* = significant

** = highly significant

gel consistency was negatively correlated with the b value, setback and final viscosity while b value was negatively correlated with the free fatty acid and peak viscosity, and was positively correlated with the setback and final viscosity (Table 3) Free fatty acid was positively correlated with the peak viscosity and was negatively correlated with the set-back and final viscosity. In brown rice flour the negative correlation of free fatty acid with the setback and final viscosity suggests the amylose-lipid complex inhibits the retrogadation of starch (Table 3).

This study suggests that free fatty acid might be involved in pasting properties by form complex with the component of rice during storage. These data forms was partly to investigate the changes in rice composition and functionality associated with storage that seeks to clarify the roles of lipid in regulating the aging process.

Conclusions

Pasting properties of aged rice was markedly dependent on the storage temperatures and times. The opposite effects on the stored rice at 25 and 37 °C might be due to the forming complex of starch-protein-lipid of starch granules, resulting from the different compositions of amylase and amylopectin. Under limited moisture content the rice was undergoing physical modification resulting in the different behaviour of pasting temperature and peak viscosity and increase of final viscosity. Pasting properties of brown rice flour, measured by using RVA, indicated that the integrity of aged rice at 25 °C granules become less while the aged rice at 37 °C granule was more rigid after storage. The modifications of starch granules or the degrees of re-association of starch molecules of brown rice flour was reflected by the changes of their forming complex properties of the flour before and after storage.

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