

## Pasting properties of calcium-fortified rice

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### Abstract

Calcium-fortified rice is normal rice fortified with calcium and processed by consecutive steps, i.e. infusion or soaking of the rice grain in a calcium salt solution, draining and drying. Heating during infusion causes pregelatinization of rice starch resulting in a change in the pasting properties of Ca-fortified rice. Pasting properties determine the cooking quality of rice. The purpose of the research was to evaluate the changes of the pasting properties in three varieties of calcium-fortified rice. These are: low amylose (LA), medium - (MA), high - (HA) rice and they were represented by the varieties: Memberamo, Ciherang and IR-42. The calcium salt used as a fortificant was Ca-lactate. Calcium fortification process was conducted at temperatures of 80°C and 90°C with infusion times of 10 minutes and 25 minutes. The pasting properties were determined by Brabender Amilograph (Visco amilograph) with the parameters being peak viscosity, breakdown viscosity, and gelatinization temperature. The research showed that calcium fortification of rice resulted in a calcium-fortified rice that had a higher gelatinization temperature than that of normal rice, low pasta viscosity and a flat curve of starch granules breakdown. These data explained that calcium-fortified rice took a long time to cook and resulted in a cooked-rice with a hard texture due to its decreased water binding capacity. Based on the rice amylose content, the higher the rice amylose the higher the gelatinization temperature, and the lower the paste viscosity. From these data it was found that there was a decrease in the cooking quality of calcium - fortified rice.

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## Introduction

Pasting properties and gelatinization are physicochemical properties of starch or cereal important to the food processing industry and applications. These properties are quality parameters in rice because the amylose/amylopectin content of rice starch is trusted to establish the eating and cooking quality of cooked-rice (Jin-Song, 2008). Rice grain consists of a hard outer layer (pericarp) and a main component, endosperm, which is composed of starch granules (Champagne, 2004). The starch granules contain amylose and amylopectin molecules. According to the level of amylose content, there are three rice varieties i.e. low amylose, medium amylose and high amylose rice (Arraullo *et al.*, 1976). The low amylose rice contains less than 20% amylose, the medium has about 20 - 25% amylose and the high amylose rice contains more than 25% amylose. The texture of cooked - high amylose rice is harder than low amylose rice and the gelatinization temperature of high amylose rice (low amylopectin) is higher than low amylose rice (Lii *et al.*, 1996), therefore more

cooking time is required for high amylose rice.

Calcium-fortified rice is normal rice fortified with calcium (Ca<sup>2+</sup>) using calcium salt such as Ca-lactate or Ca-gluconate. Calcium fortification of rice aims to provide an affordable and readily available calcium-food source for communities. Nowadays, the calcium intake of children and adolescents in Asia is relatively low in comparison to their Western counterparts. This could be partly attributable to non-milk based diets, poor dietary habits in some individuals, inadequate information and knowledge of calcium rich foods and their bioavailability (Lee dan Jiang, 2008). In Indonesia, calcium intake has reached 237 mg (median of 176 - 316) per woman per day, whereas the South East Asia RDA (Recommended Daily Allowances) of calcium is 700 - 1000 mg per day (Kruger *et al.*, 2010). Consequently, a calcium-food source is necessary to obtain sufficient calcium requirements.

Rice consumption per capita in Indonesia, where rice is a staple food, reaches 139.15 kg/year-adult (Anonym, 2010). Therefore, the calcium fortification of rice to become a calcium-source food alternative

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is very appropriate. The advantages of this alternative are that the calcium fortification process of rice is very simple and rice consumption habits would not be changed. The processing of calcium-fortified rice is achieved through stages of soaking in calcium salt solution at temperatures between 80 - 90°C or infusion processing, draining, drying at temperatures of 50-60°C until a moisture content of 10 - 12% is reached and packing (Wariyah *et al.*, 2008). Physically, the appearance of the calcium-fortified rice is more translucent, with fissures and a harder texture, but it is nevertheless still favored by Indonesians. The physical changes of calcium-fortified rice showed that part of the rice starch was pregelatinized because of soaking at high temperature. Miah *et al.* (2002), explained that the soaking of rice grain in a parboiling process at a high temperature (80°C) with lengthy soaking increased rice translucence. The appearance of natural starch is white, whereas gelatinized starch is translucent. Moreover, soaking at high temperature could increase the breaking resistance of dried rice. The high level of starch gelatinization causes high retrogradation with a resulting hard texture of the dried fortified-rice.

Rice starch pregelatinization causes a change in water absorption behavior during cooking. According to Majzoobi *et al.* (2011), the natural structure and starch molecules of pregelatinized starch become damaged and the degree of starch crystallization decreases. In pregelatinized wheat starch, there is cold viscosity at a temperature of 25°C, whereas natural starch does not behave in that way. Gelatinization causes substantial changes in both the chemical and physical nature of granular starch due to the rearrangement of intra- and intermolecular hydrogen bonding between water and starch molecules, resulting in the collapse or disruption of molecular orders within the starch granules. This causes irreversible changes in the starch properties including loss of organized structure of the starch, granule swelling, loss of birefringence and crystallinity (Anastasiades *et al.*, 2002, in Majzoobi *et al.*, 2011). This condition affects the cooking and eating qualities of the rice.

In addition to the physicochemical change of heating, the addition of calcium to rice changes starch conformation. An increase in rice hardness was estimated to be due to calcium trapping and complex formation with glucose polymer of the starch (Lee *et al.*, 1995). According to Hettiarachchy *et al.* (1996), calcium fortification of rice causes cross-linkage among starch molecules caused by the Ca<sup>2+</sup> binding with ionic-dipole bonds. The straight - chain of amylose which has a helix structure, the interaction among molecules occurs through intramolecular or

intermolecular bonding with -OH group. Hancock and Tarbet (2000) explained that cross-linked formations could occur among OH-group of amylose molecules through phosphate compound bridges. Rice-calcium interaction caused physicochemical changes that were estimated to decrease rice-water binding capacity during cooking. The purpose of this research was to evaluate the change in the pasting properties of calcium-fortified rice, so it can be used to predict its cooking quality change.

## Materials and Methods

Rice grains of low -, medium- and high amylose or LA, MA and HA, represented by the varieties Memberamo, Ciherang and IR-42 were obtained from The Rice Research Institute, Sukamandi, Subang, West Java, Indonesia. Rice grains were milled and polished twice using a Da ichi blower rice polisher (type N50 from Da ichi Engineering Co, Ltd) and the polished rice was used for research. The LA, MA and HA were analysed for their moisture content using the gravimetric method (AOAC, 1990), starch content with Direct Acid Hydrolysis (AOAC, 1990), amylose content with Iod binding method (Juliano, 1971), rice density (Bhattacharya *et al.*, 1972 in Sidhu *et al.*, 1975), and measurement of gelatinization temperature and pasting properties with a Brabender Amilograph (Visco amilograph model RV, Wingather V2.5, Brookfield Engineering Laboratories, Inc.).

The processing of calcium-fortified rice referred to Wariyah *et al.* (2008), with calcium infusion at temperatures of 80°C and 90°C for periods of 10 and 25 minutes using a shaker waterbath (Kotterman D-3162). Calcium salt as a fortificant was Ca-lactate (Sigma). The drained fortified-rice was dried with a Fluidized Bed Drier (Armfield seri 1253-2). The pasting properties and gelatinization temperatures of calcium-fortified rice were determined by Brabender Amilograph and analysis of calcium content using an Atomic Absorption Spectrometer (AAS, GBC 932 AA).

## Results and Discussion

### *Rice characteristics*

The characteristics of LA, MA and HA are shown in Table 1. The starch content of the three rice varieties ranges between 84.09 - 88.00% (db) or 75.33 - 77.15 (wb). The MA (Ciherang) had the highest starch content at 88,00% (db). According to Cheng *et al.* (2005), the starch content of rice depends on the variety, and their research showed that the starch content of many varieties of rice was between 66.22-

Table 1. Rice characteristics

Parameter	Varieties		
	LA (Memberamo)	MA (Ciherang)	HA (IR-42)
Moisture (%db)	12.65	12.88	12.87
Starch (%db)	86.13±1.79	88.00±3.31	84.09±1.06
Amylose (%db)	18.30	25.96	29.63
Ca <sup>2+</sup> (mg/100g dry matter)	6.13±0.05	5.40±0.09	6.24±0.07
Density (g/ml)	1.41	1.41	1.41
Length (mm)	9-10	8.5-10	7-8

69.32% (wb). Lii *et al.* (1996) explained that rice types with high starch had a tight and rigid granular structure a low ability to swell and therefore a high gelatinization temperature. The amylose contents of Memberamo, Ciherang and IR-42 were 18.30; 25.96 and 29.63% (db) (Table 1), so the rice fell into the three categories of LA, MA and HA rice, respectively. Calcium content of LA is about  $6.13 \pm 0.05$  mg, MA  $5.40 \pm 0.09$  mg and HA  $6.24 \pm 0.07$  mg/100 g of rice. According to Anonym (1981), a calcium content of rice about 5.00 mg/100 g rice, this is very low level. The densities of the three samples were 1.41 g/ml, and the length of the grain more than 7.0 mm which is included in the extra long grain category.

#### Pasting properties of calcium-fortified rice

The pasting properties of the rice types were expressed by the peak viscosity, gelatinization temperature, breakdown temperature and peak viscosity of the paste. Table 2 showed the pasting properties of normal LA, MA, HA and Ca-fortified LA, MA and HA infused at temperatures of 80°C and 90°C for 10 and 25 minutes. The profile of viscosity during the gelatinization process is shown in Figure 1a-c for LA, MA and HA, respectively and for the Ca-fortified rice types. The gelatinization temperature of calcium-fortified rice tended to be higher than that of normal rice. The gelatinization temperatures of normal LA, MA, HA rice were 63.0°C; 72.5°C and 63.4°C, respectively, while the gelatinization temperatures of Ca-fortified rice were about 66.10 - 69.90°C (LA); 71.70 - 78.70°C (MA) and 70.90 - 72.20°C (HA). According to Fennema (1985), the presence of other compounds that can bind water more tightly would inhibit gelatinization. Calcium is a divalent ion that can bind water with ionic-dipole interaction. Therefore, the gelatinization temperatures of calcium-fortified rice types were higher than those of normal rice. The addition of Ca<sup>2+</sup> would increase water binding capacity, otherwise the water absorption of rice was decreased. Bryant and Hamaker (1997) showed that the addition of calcium salt of Ca(OH)<sub>2</sub> 1% to the corn flour and its starch increased the gelatinization temperature from 68°C to 78°C. This change was due to an increase in the interaction between Ca<sup>2+</sup> and starch molecules. Observation with a polarized light microscope showed that the addition of Ca(OH)<sub>2</sub> could increase

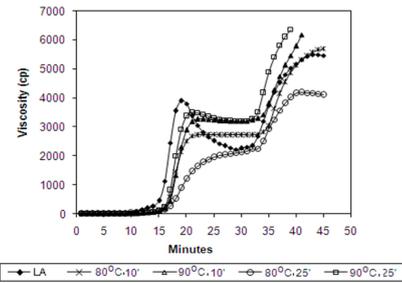


Figure 1a. Pasting properties of normal and Ca-fortified low amylose rice (LA)

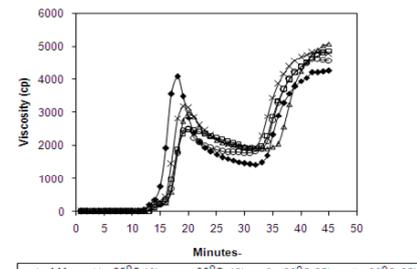


Figure 1b. Pasting properties of normal and Ca-fortified medium amylose rice (MA)

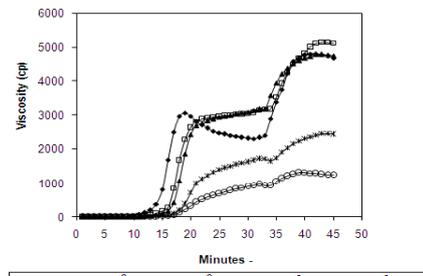


Figure 1c. Pasting properties of normal and Ca-fortified high amylose rice (HA)

granule structure integrity. The corn flour and starch solubility decreased because of crosslinking between the Ca<sup>2+</sup> and starch molecules. According to Keenan *et al.* (1990), a metal compound such as Ca<sup>2+</sup> could act as an acid or electron acceptor that is capable of binding donor electrons of glucose -OH from amylose and amylopectin molecules.

Figure 1a-c shows that in normal rice the peak viscosity which indicates granule breakdown look clear. In calcium-fortified rice types, those peaks seemed flatter and even less clear. The granule breakdown temperature of calcium-fortified rice of LA and HA was not detected. Bryant and Hamaker (1997) stated that increasing the Ca(OH)<sub>2</sub> could eliminate the granule breakdown peak. This condition showed that fewer swollen granules broke down or granule swelling was low. Moreover, heating during the processing of calcium-fortified rice caused starch gelatinization which meant that most of the granules had already been broken. According to Tester *et al.* (2004), gelatinization caused granule swelling and breakage. Therefore, the temperature of granule breakdown of calcium-fortified rice of LA and HA was not detected. The swelling and breaking of

Table 2. Visco-amylograph of normal and Ca-fortified rice

Varieties	t <sub>i</sub> minutes	T <sub>i</sub> (°C)	Ca <sup>2+</sup> mg/100 g- dry matter	Gelatinization		Granules breakdown		Viscosity (cp)		
				t <sub>G</sub> minutes	T <sub>G</sub> (°C)	t minutes	T	Peak (93°C)	50°C	Setback
Normal LA	-	-	6.13	9.0	63.00	19.0	93.30	3891.20	5427.2	1536.0
Ca-fortified LA	10	80	93.98	11.0	69.90	+	+	3372.80	6342.4	2969.6
	25	90	119.01	11.0	68.90	+	+	2892.80	5651.2	3148.8
		80	111.58	11.0	69.70	+	+	2502.40	6176.0	3283.2
		90	119.54	11.0	66.10	+	+	1203.20	4147.2	2944.0
Normal MA	-	-	5.40	11.0	72.50	18.0	93.40	4070.40	4256.0	185.6
Ca-fortified MA	10	80	96.16	13.0	78.00	19.0	93.00	3193.60	4819.2	1625.6
	25	90	117.81	13.0	76.70	20.0	93.20	2982.40	5030.4	2048.0
		80	121.41	13.0	78.70	20.0	93.70	2457.60	4588.8	2131.2
		90	128.37	11.0	71.70	20.0	93.50	2457.60	5030.4	2355.2
Normal HA	-	-	6.24	9.0	63.40	19.0	93.40	3059.20	4691.2	1632.0
Ca-fortified- HA	10	80	103.88	11.0	70.60	+	+	2617.60	4729.6	2496.0
	25	90	109.66	12.0	72.20	+	+	2412.80	5113.6	2316.8
		80	121.55	12.0	70.70	+	+	716.80	2438.4	1721.6
		90	123.61	12.0	70.90	+	+	320.00	1318.4	998.4

\* + : not detected

t<sub>i</sub> : infusion timeT<sub>i</sub> : infusion temperature

granules depended on the gelatinization temperature of the rice starch, the highest gelatinization temperature being MA (72.5°C), therefore the granule breaking temperature was detected at the same heating temperature.

Table 2 shows the paste viscosity and peak viscosity change of normal LA, MA and HA and calcium-fortified rice. Based on the apparent viscosity, the peak viscosity of calcium-fortified rice was lower and seemed even flatter than that of normal rice. Lee *et al.* (1995), found that the peak viscosity of rice fortified with Ca-lactate was lower than that of normal rice. This condition was caused by gelatinization of the starch during the fortification process which led to the breakage of a large proportion of the starch granules. This in turn lowered the granules ability to swell. Moreover, interaction between starch molecules and Ca<sup>2+</sup> could decrease starch solubility (Bryant and Hamaker, 1997). Based on the rice variety, the higher the amylose content, the lower the paste viscosity. Lii *et al.* (1996) showed that the straight chain amylose had low water binding capacity or the swelling of the starch granules was lower than amylopectin. Therefore the higher the amylose content, the lower the viscosity. Wariyah *et al.* (2008) found that calcium-fortified rice processed by infusion at a temperature of 80°C for 10 - 15 minutes had a high acceptability, despite the texture being harder than that of normal rice.

## Conclusion

Calcium fortification of rice by the infusion method at temperatures of 80 - 90°C for a period of 10 minutes resulted in calcium-fortified rice with a gelatinization temperature higher than that of normal

rice, but with lower granule swelling ability and paste viscosity. Based on the amylose content, the higher the amylose content, the higher the gelatinization temperature, the lower the paste viscosity. Those data indicated that the cooking quality of calcium-fortified rice was not as good as that of normal rice.

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