A comparison of the effects of heat moisture treatment (HMT) on rheological properties and amylopectin structure in sago (*Metroxylon sago*) and arenga (*Arenga pinnata*) starches

Dede R. Adawiyah¹ · Sayuri Akuzawa² · Tomoko Sasaki³ · Kaoru Kohyama³

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Abstract The objective of this study was to study and compare the impact of HMT on rheology and textural properties observed between sago and arenga starches, and then related to structural change of amylopectin. The HMT were conducted using the autoclaving method at 20% moisture content and heated to 120 °C for 60 min for sago and 90 min for arenga starch as optimum condition. The HMT shifted gelatinization temperature higher and reduced the enthalpy of both starches. The HMT sago starch paste exhibited an exceptionally strong shear thinning behavior as shown by a rapid decrease of viscosity and an increase of shear rate. The HMT clearly made the texture of starch gels more fragile compared to their native form and reduced their breaking point to a lower strain. The HMT effect on the rheological properties and texture of the sago starch was greater than the changes observed with the arenga starch. Major changes in rheological properties after

HMT was not followed by changes in amylopectin structure. The HMT process did not significantly affect the amylopectin chain-length distribution in Arenga starch. In the sago starch, HMT affect to long chain amylopectin with $DP \geq 37$. The HMT effect on rheology and textural properties was higher in sago starch than arenga starch. This study demonstrated that long chain amylopectin with $DP \geq 37$ plays an important role in contributing to the rheological change caused by the HMT.

Keywords Viscosity · Texture · Breaking-point · Gelatinization · Gel-point

Introduction

Heat-moisture treatment (HMT) is defined as the physical modification that involves low moisture levels (<35%) during a certain period and heating at high temperatures (84–120 °C) above the glass transition temperature but below the gelatinization temperature (Gunaratne and Hoover 2002). Zavarese and Dias (2011) compiled results variations in HMT conditions, source of starches, moisture treatments (10–30%), heating temperatures (90–130 °C), and heating times (5 min to 16 h). Sui et al. (2015) stated that the extent of change caused by HMT depends on various parameters, including botanical source, moisture content, temperature, length of treatment, heat source, and cooling process.

The effect of HMT on sago starch has been reported by Purwani et al. (2006) and Pukkahuta and Varavinit (2007). Purwani et al. (2006) used a moisture level of 25% and heating temperature of 110 °C for 16 h in an oven, while Pukkahuta and Varavinit (2007) conducted HMT tests on sago starch by using an autoclave at 100, 110, and 120 °C

✉ Dede R. Adawiyah
dede_adawiyah@ipb.ac.id; dede_adawiyah@yahoo.com

Sayuri Akuzawa
akuzawa@nodai.ac.jp

Tomoko Sasaki
tomokos@affrc.go.jp

Kaoru Kohyama
kaoruk@affrc.go.jp

¹ Department of Food Science and Technology, Faculty of Agricultural Technology, Bogor Agricultural University, Bogor 16002, Indonesia

² Department of Nutritional Science, Faculty of Applied Bioscience, Tokyo University of Agriculture, 1-1-1 Sakuragaoka, Setagaya-ku, Tokyo 156-8502, Japan

³ National Food Research Institute, 2-1-12 Kannondai, Tsukuba 305-8642, Japan

with an adjusted moisture content of 20%. Pukkahuta and Varavinit (2007) also reported that using HMT with a heat treatment of 110 and 120 °C on sago starch altered its pasting temperature and thermal properties, and transformed its crystal type from C-type to A-type.

Sago and arenga starches are classified as palm starches obtained from different genera of palm tree, *Metroxylon sago* and *Arenga pinnata*. Both starches have similar amylose content and peak gelatinization temperature (T_p) (Adawiyah et al. 2013). In this research, we compared the effect of HMT on sago and arenga starches on rheological and textural properties. Most researchers reported that HMT was impact to the physical properties of starch such as swelling power, gelatinization, pasting properties, gel texture, etc. Only view researchers reported the effect of HMT on rheological properties. In this research we evaluated the impact of HMT on rheological properties include viscosity, viscoelasticity and breaking point of gel or textural properties. In structural approach, we evaluated the distribution of amylopectin chain-length of each starches.

The objective of this study was to study and compare the impact of HMT on rheological properties and distribution of amylopectin chain length observed in sago and arenga starches after HMT using the autoclaving method.

Materials and methods

Materials

The arenga starch was prepared from *Arenga pinnata* cultivated in Banten Province, Indonesia. The crude starch extraction was carried out in local industry in Kebon Manggo village, Gunung guruh district, Sukabumi, West Java, Indonesia. Sago starch was obtained from *Metroxylon sago* produced by local industri in Bogor district, West Java, Indonesia. The starches were purified in laboratory by washing, filtering, decantation, and drying. All reagents for analysis of distribution of amylopectin chain length were analytical grade, water from Milli-Q reagent water system (Millipore Co., Bedford, USA), and isoamylase was purchased from Hayashibara Biochemical Laboratories (Okayama, Japan).

Heat moisture treatment

Heat moisture treatment was carried out by autoclaving method. The starch's moisture content was adjusted to 20% (w/w wet basis) by mixing calculated amounts of water into the starch for 15 min. Next, the mixed starch suspension was placed into a wrapped petri dish for 15 g of starch or Duran glass bottle 250 ml for 100 g starch 1 h before autoclaving at 120 °C for 60 min for sago starch and 90 min for arenga

starch as optimum condition for each starch. Lastly, the petri dishes or bottles were cooled to room temperature and dried overnight at 40–45 °C in a hot-air oven.

Differential scanning calorimetry

Thermal parameters such as onset (T_o), peak (T_p), and conclusion temperatures and enthalpy of gelatinization (ΔH) were determined using differential scanning calorimetry (DSC) (SSC5200H system with a DSC120 module Seiko Instrument, Chiba, Japan) as described by Adawiyah et al. (2013). Approximately 10 mg of dried starch sample was weighed in a 70 μ l silver pan. Distilled water was added to adjust the moisture content to 70% (w/w wet basis). The sealed silver pan containing the starch sample and the reference pan containing distilled water were heated from 30 to 130 °C at rate of 1 °C/min.

Rheological analysis

The starch pastes' flow behavior (viscosity) and viscoelastic properties were measured with a stress-controlled rheometer (AR-G2, TA Instrument, New Castle, USA). A cone and plate geometry (cone angle of 0°58'51" and diameter of 40 mm) was used to determine the viscosity measurement. The shear rates were set as 0.01–10,000 s^{-1} , and measurement time was 2 min. The 3% (w/v) starch paste was prepared by adding water, gentle stirring, then heating to 80–85 °C.

The dynamic viscoelastic properties were measured with frequency and oscillatory stress sweep tests. The frequency sweep test was conducted to determine the native starch's (1–3% w/v) and HMT starch pastes' (4.0–4.5% w/v) transition from sol (liquid state) to gel (solid like). The frequency's range was raised from 0.01 to 100 Hz at a constant temperature of 25 °C and the oscillatory stress was tested within a linear region of 1 Pa. The linear viscoelastic region was determined when the storage or elastic modulus (G') and loss or viscous modulus (G'') plateaued out during the oscillation stress procedure.

Oscillatory stress sweeps were subjected to starch gel (10% (w/v) using 20 mm plate geometry. The oscillatory stress was raised from 1 to 10,000 Pa at a constant temperature of 25 °C and constant frequency of 1 Hz. The value of G' , G'' , $\tan \delta$ (G''/G') and σ_{max} in linear region were measured. The σ_{max} or critical stress value was determined when G' deviated more than 5% from the previous constant (plateau) value.

Texture analysis

The textural properties of the 10% (w/v) starch gel were measured with a Texture Analyzer (TA.XTplus, Stable Micro Systems, UK) equipped with a load cell of

50 N in uniaxial compression test. The starch gels were compressed at a constant speed of 1 mm/s until reaching 90% of strain. The starch gels were prepared according to Adawiyah et al. (2013). The breaking points were determined based on first reduction of force or the first peak on the force-strain curve.

Distribution of amylopectin chain length

Analysis of the distribution of amylopectin chain-length was conducted based on the Koizumi et al. (1991), and Akuzawa and Kawabata (2003). A high-performance anion exchange chromatography (HPAEC) using a DX-500 system (Dionex, CA, USA) equipped with an ED-40 pulsed amperometric detector was utilized. A Dionex CarboPac PA1 column (250 mm $\times$ 4 mm ID) with a guard column (25 mm $\times$ 3 mm ID) was used to evaluate the amylopectin chain-length distribution of each sample. Samples were dissolved in a 50 mM sodium acetate buffer at pH 3.5 and debranched with isoamylase from *Pseudomonas* for 12 h at 40 °C before being injected into a 25 μ l sample loop. We used gradient elution from an aqueous solution of 150 mM sodium hydroxide (eluent A) to 150 mM sodium hydroxide containing of sodium acetate up to 500 mM (eluent B). The pulse potentials and durations used was described in Akuzawa and Kawabata (2003).

Data analysis

A statistical analysis was conducted using *t* test for paired sample (Microsoft Excel) to study the impact of HMT on sago and arenga starches at significant levels of 5% ($p = 0.05$).

Results and discussion

Gelatinization properties

Figure 1 shows the the effect of heating time on the gelatinization temperature of starch while keeping the temperature at 120 °C and the moisture content at 20%. The gelatinization endotherm of HMT starches shifted to higher temperatures commensurate with the increase in heating time. The T_o , T_p , and T_c also shifted to higher temperatures as increasing of heating time during heat moisture treatment. Increasing of T_o , T_p , and T_c of arenga and sago starches have been attributed to structural change in crystalline and amorphous region which involve amylose–amylopectin within starch granule. HMT reduced mobility of amorphous region, and require higher temperature to swelling and disrupt the crystalline region.

The HMT reduced the gelatinization enthalpy ΔH in both the sago and arenga starches. The ratio of reduction in the sago starch was higher than in the arenga starch. As compared to the native sago starch ΔH value of 16.36 J/g, the HMT sago starch ΔH value was approximately 10 J/g or 39% less. The ΔH value of native arenga starch was approximately 15.40 J/g whereas the ΔH of HMT arenga starch was 11 J/g, or 28% less. High temperature during HMT caused disruption of hydrogen bonding in crystalline region and may caused decreasing of ΔH of HMT starch. Gunaratne and Hoover (2002) stated the decrease in ΔH after the heat moisture treatment suggest that some of the double helices present in crystalline and in non-crystalline regions of the granule may be disrupted when subjected to the prevailing conditions of heat-moisture treatment. This difference of ΔH between native and HMT was reported by Pukkahuta and Varavinit (2007) in sago starch, and also in other starches such as potato, yam, and cassava (Gunaratne and Hoover 2002; Adebowale et al. 2009); potato (Varatharajan et al. 2010); corn (Takaya et al. 2000; Chung et al. 2009); and rice (Hormdok and Noomhorn 2007). Other researchers reported different results. Li et al. (2011) reported that HMT increased the ΔH of mung bean starch, whereas Hoover and Manuel (1996) reported that the ΔH of pea and lentil starches remained unchanged after HMT.

Some endothermic curves for HMT arenga for 30 and 60 min and for HMT sago for 30 min showed temperature transition after T_p . Pukkahuta and Varavinit (2007) observed biphasic broadening of T_p for HMT sago, which can be explained by an inhomogeneous heat transfer during the HMT process or can be caused by un-gelatinized granules that were melted at higher temperature. Biliaderis (1990) explained that at low temperature there are two transitions M_1 (similar to T_p) and M_2 as in the typical DSC thermal profile of rice starch. Granules containing the least stable crystallites melt first at M_1 and the un-gelatinized granules will melt at higher temperatures at M_2 transition. Based on this finding, we chose 60 min for the optimum autoclaving period of sago starch and 90 min for that of arenga starch to prevent damage of starch and energy loss. Rheological, textural and amylopectin structure were tested using the optimum HMT starches and native starches.

Rheological properties

The HMT significantly changed the flow behavior or viscosities of arenga and sago starch pastes (Fig. 2). HMT starch pastes were significantly less viscous than native starches. The HMT sago starch paste exhibited very strong shear thinning behavior showed by a rapid decrease in viscosity and increase of shear rate. Thus, the HMT sago

Fig. 1 DSC endothermic curves of HMT arenga (a) and sago (b) starches at different heating time

Fig. 2 Viscosity of native and HMT arenga and sago starches (3% w/v) at different shear rates

starch paste was very unstable against a high shear rate. The HMT sago starch paste separated into two phases under high shear, whereas the HMT arenga paste remained homogenous. High shear rate or agitation also was not suitable for pastes of HMT sago starch. This finding suggests that the HMT sago and arenga starches should not be recommended to use as a thickener that often used under high shear conditions in food processing, such as soup, sauces, mayonnaise, etc. HMT starches could be used as an ingredient to make food products with low moisture content and low shear or agitation during processing such as cookies, extruded snack products, etc. Horndok and

Noomhorm (2007) applied HMT rice starch to improve texture quality of noodle. Miyazaki and Morita (2005) used HMT corn starch to replaced wheat flour partially to improve bread quality.

Figure 3 shows frequency dependence of G' (storage modulus) and G'' (loss modulus) of HMT arenga and sago starches to determine the sol–gel transition concentration. The sol behavior exhibited a significant dependency of G' and G'' on frequency. This behavior was evident with the HMT sago starch paste at 4.4% (w/v) and the HMT arenga starch at 4.1% (w/v). The gel behavior exhibited low dependency of G' and G'' on frequency and G' was always higher than G'' . The gel behavior was shown in the HMT sago starch at 4.5% (w/v) and the HMT arenga starch at 4.2% (w/v). Adawiyah et al. (2013) reported that sol–gel concentration or gel point of native sago starch pastes was 1.8% (w/v) and 2.4% (w/v) in native arenga starch. These results suggested that HMT increased the gel point concentration of both starch pastes. HMT starches require higher concentrations to produce a consistency of starch gel similar to those produced by native starches. HMT increased the gel point of sago starch by 2.7%, and arenga starch by 1.8%. The HMT effect of increasing gel point concentration was higher in sago starch than in arenga starch.

Table 1 shows the effect of HMT on the viscoelastic properties of 10% (w/v) sago and arenga starch gels under an oscillatory sweep test. The HMT significantly increased the viscoelastic moduli G' and G'' ($p < 0.05$). The $\tan \sigma$ is a loss factor calculated as ratio G''/G' . The $\tan \sigma$ values of arenga and sago starches (native and HMT) were lower

Fig. 3 Frequency dependence of storage modulus G' (filled square) and loss G'' (open square) of HMT sago (a) and arenga (b) starches

Table 1 Effect of HMT on viscoelastic properties of arenga and sago starch gels at concentration 10% w/w

Viscoelastic properties	Arenga			Sago		
	Native	HMT	p (t test)	Native	HMT	p (t test)
G' (Pa)	1472	4070	0.000	675	1935	0.000
G'' (Pa)	93.02	156.80	0.002	75.30	175.00	0.000
$\tan \delta$	0.060	0.041	0.001	0.100	0.091	0.201
σ_{max} (Pa)	357.2	236.5	0.062	316.2	158.5	0.011

Mean of three replicates

than one, indicating that the starch gels are elastic in nature. The effect of HMT significantly decreased the $\tan \delta$ only in the arenga starch, not in the sago starch.

The other viscoelastic parameter was critical shear stress (σ_{max}). Teng et al. (2011) defined σ_{max} as the extension of linear viscoelastic range of gels, which may be used as an index of gel stability and extensibility. In general, the σ_{max} value of sago starch (native and HMT) was lower than that of arenga starch. HMT decreased the critical shear stress (σ_{max}) of the sago starch significantly ($p = 0.011$). The extensibility of HMT sago starch was lower than arenga starch. HMT sago starch gel was unstable and

weaker than native, indicated as weak gel. Ikeda and Nishinari (2001) stated that linear region of weak gel is narrow if it is compared with that of a true gel. Nishinari (2009) mentioned that a weak gel behavior is structured liquid behavior, whereas true gel (strong gel or elastic gel) is defined when G' is far larger than G'' and both moduli independent of frequency as found for agar gel.

Textural properties

The HMT gave very significant impact on textural or mechanical properties of arenga and sago starch gels.

Fig. 4 Uniaxial compression curves of HMT and native arenga (a) and sago (b) starch gels

Table 2 Amylopectin chain-length distribution of arenga and sago starches (native and HMT)

Starch	DP 6–12		DP 13–24		DP 25–36		DP ≥ 37	
	%	<i>p</i> (<i>t</i> test)	%	<i>p</i> (<i>t</i> test)	%	<i>p</i> (<i>t</i> test)	%	<i>p</i> (<i>t</i> test)
Sago native	21.17 $\pm$ 0.35	0.094	54.65 $\pm$ 1.87	0.411	13.82 $\pm$ 0.50	0.052	9.51 $\pm$ 0.52	0.044*
HMT sago	23.11 $\pm$ 0.64		56.92 $\pm$ 2.43		11.28 $\pm$ 0.64		7.23 $\pm$ 0.40	
Arenga native	23.68 $\pm$ 0.64	0.400	54.93 $\pm$ 1.21	0.173	13.43 $\pm$ 0.66	0.121	7.95 $\pm$ 1.20	0.250
HMT arenga	22.39 $\pm$ 1.40		51.70 $\pm$ 1.22		15.02 $\pm$ 0.48		10.70 $\pm$ 1.92	

Mean and standard deviation of 2 replicates

* Significant different at α risk 5%

Figure 4 shows the differences of textural properties between the native and HMT arenga (a) and sago (b) starches. HMT clearly shifted the breaking point to a lower strain. Breaking point of native arenga starch was 60.12% strain, whereas breaking point of HMT arenga starch was detected at 53.05% strain as reported previously (Adawiyah et al. 2013). For sago starch, the breaking properties of HMT starch were significantly different. Deformation point in native sago starch was determined in form of shoulder point at 59.96%, meanwhile in HMT sago starch showed a breaking point at 33.51% strain. Table 2 shows the recapitulation of mechanical properties of native and HMT arenga and sago starches. At low strain (before breaking point), the compression stress of HMT arenga and HMT sago starches was significantly higher than that of native starches. These results suggest that the HMT starch gels were more rigid, but more fragile (easier to break or fracture) than that of the native starches. In general, the compression force of the HMT starch was lower than that of the native starch. There was no significant difference in compression force between the native and HMT starches at the targeted strain point (90% strain), but the compression force up to 90% strain in the HMT sago starch was significantly lower than that of native. When comparing the arenga and sago starches, the effect of HMT on the overall compression work or energy up to 90% strain shows dissimilar patterns. The overall compression work of the HMT arenga starch gel was higher than that of the native starch. In contrast, the HMT sago starch gel showed smaller overall compression energy than that of the native starch.

Distribution of amylopectin chain length

The amylopectin chain-length distributions of the sago and arenga starches (both native and HMT) show a similar pattern. The highest distribution of amylopectin chain length was DP (degree of polymerization) 13–24 at 51–57% distribution (Table 2). The peak of chain lengths found in the distribution of chain-length amylopectin can

be used to identify a starch's crystal type. A-type starches peak at shorter chain lengths (first peak at DP 12–14, second peak at DP 41–51) as compared to B-type starches (first peak at DP 14–16, second peak at DP 48–53) (Jane et al. 1999). The first peak of sago (native and HMT) was found at DP 13, and the second peak at DP 42–45. For arenga (native and HMT), the first peak was found at DP 12 and the second peak at DP 42–44. Sago and arenga starches (native and HMT) have characteristics of A-type starches.

Statistically, HMT did not affect the distribution of amylopectin chain-length in arenga starch ($p > 0.05$). However, in sago starch HMT significantly affect the long chain amylopectin with DP ≥ 37 ($p = 0.044$) though the effect was weak. Long chain of amylopectin were important for gel formation. Gel containing amylopectin with longer average branch length were stronger than those containing shorter average branch length (Bertoft et al. 2016). The significant effect of HMT on long chain amylopectin with DP ≥ 37 attributed to significant effect on rheological and textural properties of starch gels.

Conclusion

HMT altered the physical properties of both the sago and arenga starches. The HMT shifted the gelatinization peak to higher temperatures and reduced gelatinization enthalpy, reduced swelling power, reduced viscosity of starch pastes, increased gel point concentration, increased hardness (G'), and decreased the breaking strain. The HMT effect on the rheological properties and texture of the sago starch was greater than the changes observed with the arenga starch. This is likely related to a significant change in the long chain amylopectin (DP ≥ 37). The long-chain portion of amylopectin structure is a contributing factor in regulating a starch's physical properties.

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