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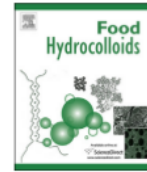*by* Nurul Asiah

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Effect of physical modification on granule morphology, pasting behavior, and functional properties of arrowroot (*Marantha arundinacea* L) starch

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ABSTRACT

The aim of this study was to investigate the effect of physical modifications on granule morphology, pasting behavior and functional properties of arrowroot starch. The methods are including HCl hydrolysis, autoclaving-cooling (at 121 °C for 15 min, cooled at 4 °C for 24 h), and the combination of HCl hydrolysis and autoclaving-cooling in two different cooling times (cooled at 4 °C for 24 h and 72 h). The result showed that all physical modifications applied to the starch did not increase the resistant starch content significantly. In other hand, the same result was obtained by other researches, thus it might be concluded that acid hydrolysis, autoclaving-cooling, and the combination of them did not necessarily change the resistant starch content. In contrast to what was observed with the resistant starch content, acid hydrolysis had an improving effect on solubility and gel hardness of starch without destroying its granule structure, whereas autoclaving-cooling and its combination with acid hydrolysis decreased gel hardness but increased water holding capacities of the modified starches with the damaged starch granules. Furthermore, all viscosity values measured by Rapid Visco Analyzer (RVA) were reduced. This result of this study provides a better understanding of functional characteristics of native and modified arrowroot starches for potential applications in the variety of food products.

1. Introduction

Arrowroot is one of the Indonesian carbohydrate sources, but its use as a food product is still limited. Several researchers have studied the carbohydrate obtained from arrowroot, and mostly focused on the starch (Charles et al., 2015; Erdman, 1986; Faridah, Fardiaz, Andarwulan, & Sunarti, 2010; Faridah, Rahayu, & Apriyadi, 2013; Kooijman, Ganzeveld, Manurung, & Heeres, 2003; Raja & Sindhu, 2000; Villas-Boas & Franco, 2016). In the food industry, starch has been used as a food ingredient to control the structure and texture of many types of food (Chung et al., 2010). Furthermore, starch is often subjected to chemical, physical or enzymatic modifications to get some new characteristics of the

starch including thickening, gelling, consistency and shelf stability to optimize its use in a diverse range of food applications (Reddy, Haripriya, Mohamed, & Suriya, 2014).

Resistant starch type 3 (RS3) is the most type investigated by numerous researchers and food industry due to its lower cost and safety issue (Wang, Wang, Yu, & Wang, 2014), since chemically modified starch may have safety problems for food products (Zhang & Jin, 2011). Faridah et al. (2010) had studied the structure changes of arrowroot starch as influenced by acid hydrolysis, debranching, and autoclaving-cooling cycle modifications using by Gel Permiation Chromatography (GPC), and the result showed that acid modification increased low molecular weight component. Consequently, the amount of degree of polymerization of 6—8 increased in all modified arrowroot starch. Furthermore, Faridah et al. (2013) had modified the arrowroot starch through acid hydrolysis, autoclaving-cooling, and the combination of acid hydrolysis and autoclaving-cooling treatments to produce RS3, and the result showed that the combination of acid hydrolysis and autoclaving-cooling could increase amylose, dietary fiber and RS content. Another research, John, Raja, Rani, Moorthy, and Eliasson (2002)

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investigated the properties of arrowroot starch treated with aqueous HCl at ambient temperature. However, the functional properties of arrowroot starch modified by autoclaving-cooling, and the combination of acid hydrolysis and autoclaving-cooling treatments do not extensively studied yet. Therefore, the aim of this research is to investigate the functional properties of the arrowroot starch modified by acid hydrolysis, autoclaving-cooling, and the combination of acid hydrolysis and autoclaving-cooling treatments.

The physical modification has been widely reported to be depolymerizing starch chains, resulting in the change of functional properties such as a decrease in viscosity, an increase in solubility and water holding capacity (Polesi & Sarmento, 2011). As resistant starch would constitute a food ingredient, this study can provide a better insight into the effect of physical modifications on arrowroot starch in order to find new food applications, since the modifications will change on granule morphology, pasting behavior, and functional properties of arrowroot starch. Moreover, these characteristics will directly influence the end quality of food products.

In this research, arrowroot starch was modified by the physical methods that had been reported by Faridah et al. (2010, 2013), including acid hydrolysis, autoclaving-cooling, and acid hydrolysis combined with autoclaving-cooling (cooling time 24 h). In addition, to investigate the effect of longer cooling time, the starch was also modified by acid-hydrolysis combined with the autoclaving-cooling process with the cooling time 72 h (Dundar & Gocmen, 2013).

2. Material and methods

2.1. Materials

The tubers of arrowroot (*Marantha arundinaceae* L.) were acquired from the local supplier and the obtained starch contained $25.64 \pm 1.32\%$ amylose. Porcine pancreatic α-amylase (catalog no. P7545) and amyloglucosidase (catalog no. A7095) were purchased from Sigma-Aldrich Chemical Co. Hydrochloric acid (HCl), sodium hydroxide (NaOH), dinitrosalicylic acid (DNS) and other analytical grade solvents and reagents were used in all the experiments.

2.2. Isolation of starch

The starch was isolated from arrowroot (*Marantha arundinaceae* L.) according to the method of Faridah et al. (2013). The tuber was peeled, cut into small pieces, and washed. Then, the sample was grounded and immediately suspended in water (ratio 1:3.5 w/v). The slurry was filtered through a nylon cloth and the filtrate was precipitated. The obtained precipitate (starch) was then oven dried at 50 °C. The recovered white colored starch was homogenized with warring blender and filtered through a 100 μm sieve. This procedure was repeated for three times. This starch was used as a control and namely control.

2.3. Physical modification of arrowroot starch

2.3.1. Acid hydrolysis

Acid hydrolysis of arrowroot starch was performed by using the procedure used by Aparicio-Saguilan et al. (2005). Arrowroot starch was suspended in 2.2 M HCl (1:1 w/v) for 2 h at 35 °C. The pH was adjusted to 6.0 by adding 1.2 M NaOH. The acid-treated starch (namely AH) was then oven dried at 50 °C, grounded, and sifted through 100 mesh sieve for further analysis.

2.3.2. Autoclaving-cooling

Modification by autoclaving-cooling was performed according

to the method of Lehmann, Rossler, Schmiedl, and Jacobash (2003). Starch sample was autoclaved at 121 °C for 15 min, cooled and kept at 4 °C for 24 h. This procedure was repeated for three times (3 cycles). The starch (namely AC) was oven dried at 50 °C and grounded, sifted through 100 mesh sieve for further analysis.

2.3.3. Acid hydrolysis and autoclaving-cooling

This modification method was performed using the combination of procedure used by Aparicio-Saguilan et al. (2005) and Lehmann et al. (2003). Briefly, the starch was hydrolyzed, and then subjected to autoclaving-cooling cycle treatment. The obtained starch (namely AH-AC 24) was oven dried at 50 °C and grounded, sifted through 100 mesh sieve for further analysis.

2.3.4. Acid hydrolysis and cooling-autoclaving with cooling time of 72 h

Starch sample was hydrolyzed by HCl and then subjected to autoclaving-cooling cycle treatment according to the procedure by Aparicio-Saguilan et al. (2005) and Lehmann et al. (2003) with extended cooling for 72 h (Dundar & Gocmen, 2013). The obtained starch (namely AH-AC 72) was oven dried at 50 °C and grounded, sifted through 100 mesh sieve for further analysis.

2.4. Determination of resistant starch (RS) content

The resistant starch content was determined according to the procedure of Englyst, Kingman, and Cumming (1992) with slight modification. Briefly, the starch sample of 1 g was suspended in 0.1 M pH 5.2 sodium acetate buffer (1:20 w/v). The sample was incubated in a 90 °C water bath for 30 min, and allowed to cool until 37 °C. 5 mL of enzyme solution (pancreatin and amyloglucosidase) was added to the sample, incubated at 37 °C for 120 min, and then centrifuged at 1789×g for 10 min 2 mL of DNS was added to 1 mL of the supernatant. The solution was incubated in a 95 °C shaking water bath for 10 min, cooled to room temperature, and then diluted using 10 mL distilled water. Absorbance was measured using a spectrophotometer at 550 nm. Hydrolyzed starch was determined as the amount of glucose x 0.9. Resistant starch was calculated as: RS (%) = total starch (%) − hydrolyzed starch (%). The total starch was determined using AOAC (1999) method, in which it was determined as the amount of free glucose obtained by acid hydrolysis. Briefly, the starch sample was hydrolyzed with HCl 25% and distilled water for 2.5 h. The sample was neutralized by NaOH, filtered and added with distilled water. 1 mL of the sample was added with DNS, incubated in water bath at 100 °C for 10 min, and then added with 10 mL of distilled water. The sample was measured by spectrophotometer at 550 nm. The amount of free glucose in the sample was calculated using the standard curve. Each sample was analyzed in triplicates. Total starch (%) = (the amount of free glucose/weight of dry sample) x 0.9×100.

2.5. Granule morphology

The surface of starch granules was examined using scanning electron microscope (SEM, ZEISS, type of EVOMA10). A dried sample was attached to double-sided adhesive carbons disc, which was pressed on a specimen stub. Gold was used to coat the sample using a sputter coater (Quorum, type Q150R ES). The sample was examined using an accelerating voltage of 16 kV and working distance = 9 mm at the magnification of 1000x, 2000x, and 10.000x.

2.6. Pasting properties

The pasting viscosity of modified starches was measured according to the method of Charles et al. (2015) with minor

modification. The viscoamylographic properties of the samples were performed with Rapid Visco Analyzer (RVA, Tecmaster Perten USA) using 3 g of sample in 25 mL of distilled water. Starch slurries were heated to 95 °C at a rate of 6 °C/min, held at 95 °C for 5 min, cooled to 50 °C at 6 °C/min, and held at 50 °C for 2 min. The following parameters: peak, holding, breakdown, final and setback viscosities were obtained from the viscoamylographs.

2.7. Functional properties

2.7.1. Gel texture properties

Gel texture properties were analyzed using Wang, White, and Pollak (1992) and Kaur, Singh, McCarthy, and Singh (2007) methods with slight modification. Starch paste (starch:water 1:8) was heated in water bath at 95 °C for 30 min. The starch paste was poured into a plastic tube and then stored 4 °C for various periods of time (6, 20, 24, 72, and 168 h). The texture profile analysis was performed on the samples in tubes at room temperature using texture analyzer XT2. Each gel sample in the tube was penetrated to a depth 6 mm with a p5 cylindrical probe (5 mm in diameter) at a speed of 1 mm/s. The force (g) was recorded as the firmness of the gel, and the force-time curve was obtained. The test was performed in triplicates and after five different times of storage to study the retrogradation of the starches.

2.7.2. Swelling power (SP) and water solubility index (WSI)

The swelling power of the samples was analyzed using the method previously described by Ikegwu, Okechukwu, and Ekumankana (2010). The starch was dispersed in distilled water (1:50 w/v) to form a suspension. The suspension was incubated in a 95 °C water bath for 30 min and then cooled to 28 - 30 °C. The starch was then centrifuged at 541 ×g for 12 min. The supernatant was dried and weighed to measure the amount of dissolved starch in the supernatant (solubility). The water solubility index was determined as: WSI = (weight of dry solids in supernatant/weight of dry sample) x 100. The weight of the precipitate was used to calculate the swelling power. The swelling power was determined as follows: SP = [(weight of precipitate − weight of dry sample)/weight of dry sample] x 100.

2.7.3. Freeze-thaw stability

Freeze-thaw stability was analyzed using Charles et al. (2015) method. Starch paste (starch:water 1:9 w/v) was incubated in a 95 °C water bath for 30 min and then allowed to cool to room temperature. The starch paste was frozen at −18 °C for 24 h, and then allowed to thaw at 30 °C for 1.5 h. This procedure was repeated four times (4 cycles). The sample was then centrifuged at 1006×g for 10 min and obtained supernatant was weighed. The freeze-thaw stability was determined as: syneresis (%) = (weight of supernatant/weight of sample) x 100.

2.7.4. Water holding capacity (WHC) and oil holding capacity (OHC)

The WHC and OHC of the samples were analyzed according to the procedure described by Chau, Cheung, and Wong (1997). Briefly, a sample was vortexed with distilled water or cooking oil (1:10 w/v) for 1 min and centrifuged at 541 ×g for 30 min. The wet precipitate was weighed to calculate the WHC or OHC. The WHC or OHC was determined as: WHC or OHC = [(weight of wet precipitate − weight of dry sample)/weight of dry sample] x 100.

2.7.5. The color of fine powder starch and its paste

The color of starch and its paste were analyzed using chromameter. Measurement of L^* = lightness (where 0 = black, 100 = white), a^* ($+a^*$ = redness and $−a^*$ = greenness) and b^*

($+b^*$ = yellowness and $−b^*$ = blueness). Whiteness was calculated, based on the following equation (Yang, Wang, Wang, & Ye, 2014): Whiteness $= 100 − [(100 − L^*)^2 + a^{*2} + b^{*2}]^{1/2}$

2.8. Statistical analysis

All experimental data were statistically analyzed using Analysis of Variance (ANOVA) on SPSS version 20.0 software. The significance of the difference between means was determined by the Duncan test at 5% significance level.

3. Result and discussion

3.1. Effect of physical modifications on the yield of resistant starch

In this study, all physical modifications applied to the starch did not increase the resistant starch significantly (Table 1). In other hand, Faridah et al. (2013) reported the increasing resistant starch content under autoclaving-cooling process and the combination of acid hydrolysis and autoclaving-cooling, but they reported similar result for resistant starch content under acid hydrolysis treatment.

In this study, acid hydrolysis did not change the RS content as compared to control, similar to Faridah et al. (2013). Similar result was reported by Ozturk, Koksel, and Ng (2011) who found that resistant starch content of acid hydrolyzed samples did not differ from those of native corn starch, and Nasrin and Anal (2014) who reported that there was no significant difference in resistant starch content among native and modified culled banana starches under combination of acid hydrolysis and autoclaving-cooling treatment. From these researches, it may be concluded that acid hydrolysis and other physical modifications such as autoclaving-cooling and the combination of acid hydrolysis and autoclaving-cooling are not necessarily followed by a change of resistant starch content. Resistant starch yield of food depends on the botanical source of the starch, climatic and soil condition (Sandhu, Singh, & Malhi, 2005), age of the plant (Jane et al., 1999), as well as the season of harvesting should be taking into account (Tester & Karkalas, 2001; Teixeira et al., 2016). In contrast to what was observed with the RS content, the modified arrowroot starches showed the different physicochemical characteristics compared to unmodified arrowroot starch (control).

3.2. Granule morphology

The morphology of the different arrowroot starch granules scanned by SEM is shown in Fig. 1. Unmodified arrowroot starch (control) was observed to be composed of spherical to the elliptical shape of granules with the size range from 7 to 16 μm, and the surface of all starch granules appeared to be smooth. This result was in agreement with the granule shape of arrowroot starch reported by Charles et al. (2015). Acid hydrolysis applied to AH sample made the granule surfaces were found to be slightly rougher and bigger in size (11−22 μm) than control without destroying its granule

Table 1
Total and resistant starch contents of unmodified and modified arrowroot starch.

Samples	Total starch (%)	Resistant starch (%)
Control	$23.16 \pm 0.45^{a,b}$	22.56 ± 0.43^{a}
AH	$24.43 \pm 1.06^{a,b}$	23.83 ± 1.12^{a}
AC	25.17 ± 1.55^{b}	24.21 ± 2.14^{a}
AH-AC 24	22.54 ± 0.17^{a}	21.96 ± 0.08^{a}
AH-AC 72	$23.11 \pm 0.17^{a,b}$	22.03 ± 0.40^{a}

Values are means ± SD of triplicates. Values with different superscripts within each column showed significantly different (p ≤ 0.05).
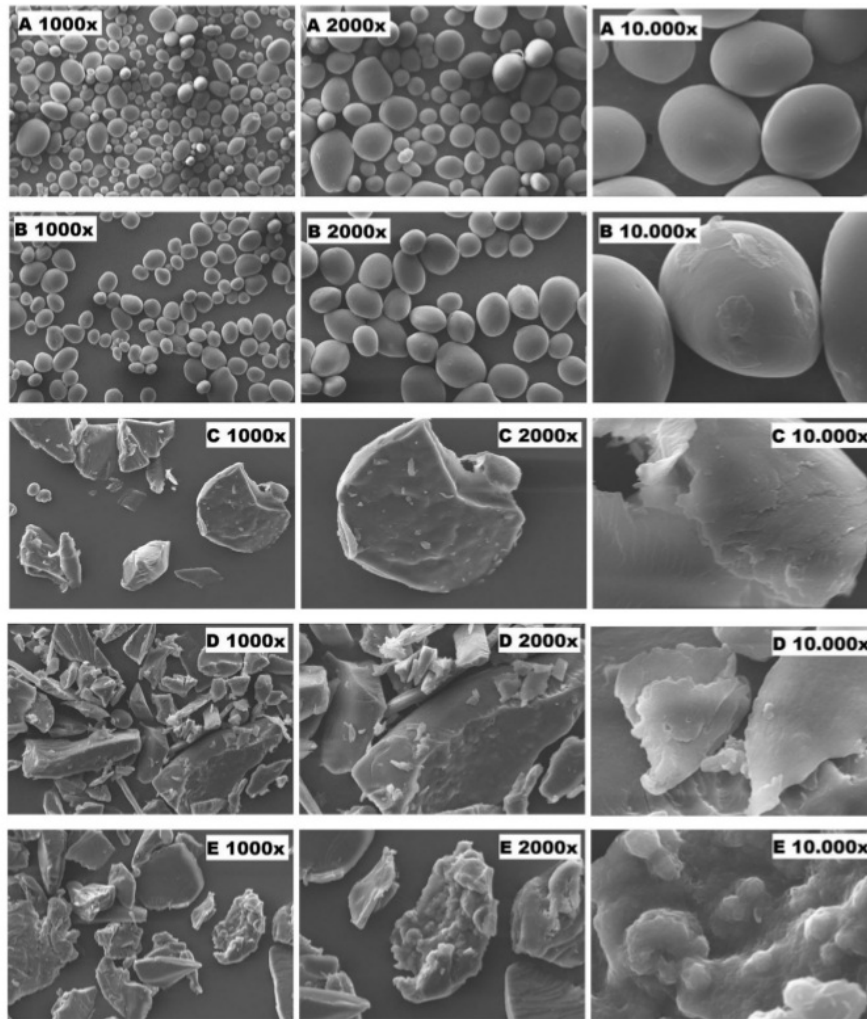
Fig. 1. Scanning electron micrograph (magnification 1000x, 2000x and 10.000x) of (A) control (unmodified arrowroot strach), and modified arrowroot starch by: (B) acid hydrolysis — AH, (C) autoclaving-cooling — AC, (D) combination of acid hydrolysis and autoclaving cooling with storing time 24 h — AH-AC 24, and (E) combination of acid hydrolysis and autoclaving cooling with storing time 72 h - AH-AC 72.

structure. It indicated that acid hydrolysis did not induce significant changes in the granule morphology of the arrowroot starch. The same result was found by Sandhu, Singh, and Lim (2007) for corn starch and Atichokudomchai, Shobsngob, and Varavinit (2000) for tapioca starch. Majzoobi, Kaveh, Blanchard, and Farahnaky (2015) suggested that the increase in the size of the granules might be related to absorption of the acid by the granules, causing some internal changes to the granules.

In contrast to AH, other treatments significantly altered the shape and the surface of granules. As shown in Fig. 1, the granule shapes of AC, AH-AC 24 and AH-AC 72 were totally different from that of control and AH. The complete breakage of AC, AH-AC 24 and AH-AC 72 granules exhibited that the arrowroot starch was likely to be more susceptible to autoclaving-cooling disruption during treatment. Fig. 1C demonstrates that AC after three cycles of autoclaving-cooling treatment (24 h of cooling time) contained an irregular, some large voluminous starch granules with non-uniform morphology and rough surface, and their structures were relatively loose. The combination of acid hydrolysis and autoclaving-cooling cycle with 24 h of cooling time made the granule become irregularly angular and elongated shape with various sizes (Fig. 1D). And the longer cooling time of AH-AC 72 remarkably altered the surface of the starch granules become uneven (Fig. 1E). Excessive degradation of starch granules of AC, AH-AC 24 and AH- AC 72 might cause the granules difficult to swell and reinforce the starch granules to be more thermal and shear resistant which in turn lead to lower viscosities. The change in the structure, size, and shape of starch granule will induce the changes of short-range ordered structure, viscosity, solubility and swelling power (Charles, Huang, & Chang, 2008; Lin et al., 2015; Sokhey & Hanna, 1993).

3.3. Pasting properties

RVA pasting properties of modified and unmodified starches are given in Fig. 2. From RVA analysis, it was observed that the pasting behavior of the starches was remarkably altered by physical

modification, probably caused by excessive degradation of starch granules (Fig. 2 and Table 2). Dundar and Gocmen (2013) and Reddy, Suriya, and Haripriya (2013) reported that the decreasing in the viscosity values could be owed to the destruction of starch granules.

From Table 2 and Fig. 2, it could be seen that the peak viscosity values of all modified starches were found to be significantly lower than control. AC had the highest peak viscosity of the other treated samples, followed by AH, AH-AC 24 and AH-AC 72. From this behavior, acid hydrolysis obviously reduced the viscosity of the starch due to disruption of the amorphous region of the starch granule (Khan, Ali, & Hasnain, 2014). The lack of pasting ability by these physical modifications, particularly in AH-AC 24 and AH-AC 72, also might be corresponded to covalent network formation resulting in more rigid granules which broke up less easily, and consequently the diffusion of water molecules into the starch granules occurred more slowly, thus, in turn, prevented granule swelling (Heyman, De Vos, Depypere, Meeren, & Dewettinck, 2014). However, AH-AC 24 and AH-AC72 had the highest stability to thermal treatment and mechanical shearing during holding period at 95 °C which was showed by the lower values of breakdown. The reduction of breakdown might be attributed by the reorganization within the granule of the modified starches (Sun, Zhu, Si, & Xiong, 2015). Among five samples, AH, AH-AC 24 and AH-AC 72 had the lower setback value which possibly due to the formation of the short chain amylose by acid hydrolysis (Khan et al., 2014) and degradation of longer amylopectin branch chains (Chung et al., 2010). In contrast to treated starches, control had the highest breakdown and setback values of the samples. The higher setback viscosity of control was indicative of the lower stability of cool starch paste or the faster retrogradation of starch paste (Wang et al., 2014). The higher setback of unmodified arrowroot starch was also reported by Hoover (2001).

Autoclaving-cooling treatment caused a significant reduction in pasting temperature, while acid hydrolysis, either alone or in combination with autoclaving-cooling, made the pasting temperature is not detectable. It was noteworthy that acid hydrolysis could decrease the ability of starch granules to swell.

Although the modified starch caused a decreasing in viscosity, AC could improve the smoothness of its gel (Fig. 3C), since control had a too rigid gel that limited its use in the industrial application. In the other hand, it has been demonstrated that AH had a more liquid paste, followed by AH-AC 24 and AH-AC 72 respectively (Fig. 3B, D, 3E). This result showed that these modifications made arrowroot starch can be applied to various types of food products.

3.4. Functional properties

3.4.1. Gel texture properties

The data on the gel strength as measured by the texture analyzer after aging for 6–168 h at 4 °C are presented in Fig. 4. From Fig. 4, it can be seen that in the longer storing time AH had the harder gel than control, contrasting with its lower viscosity, whereas the other treated starches had softer gels than control, according to RVA results. However, a sharp increase in the gel hardness of all starches was observed in the storing time of 72 h. The gel of AC was softer than AH-AC 24 and Ah-AC 72, contrasting to what was observed with the higher peak viscosity. It could be postulated that autoclaving-cooling treatment did not lead amylose and amylopectin to re-associate, but it caused them to form a gel network that held the water strongly, reflected by the high WHC and freeze-thaw stability (Table 3).

On the contrary, acid hydrolysis on AH preparation made the gel harder than control in the storing time of 20 h onwards which might be associated with the higher content of short chain amylose. When acid treatment was applied to the starch, chain fragmentation occurred, as well as hydrolysis of amylopectin, forming linear polysaccharides like amylose molecules (Dundar & Gocmen, 2013). Chain fragmentation made the granules become weakened, which might allow more water to permeate inside the granules (Chung et al., 2010), but in the longer storing time with low temperature, re-association of the unbranched and lower molecular mass could raise the level retrograded starch by creating new double helices which were stabilized by hydrogen bonding, leading to stronger gelation properties, and thus forming the stiff gels (Lawal, 2004; Morales-Medina, Munio, Guadix, & Guadix, 2014; Reddy et al., 2013). Kim and Ahn (1996) reported that modification by acid hydrolysis increased gel strength but decreased the viscosity of the starch, confirming the result in this study.

3.4.2. SP, WSI, freeze-thaw stability, WHC, OHC, and color

Swelling power (SP), water solubility index (WSI), freeze-thaw stability, water holding capacity (WHC), oil holding capacity (OHC) and color of starch powder and paste are summarized in Table 3. From the table, it can be seen that autoclaving-cooling process applied in AC, AH-AC 24 and AH-AC 72 could decrease the WSI, however, acid hydrolysis process precisely increased the WSI of AH as compared to control. During the process of AH preparation, amylose and amylopectin were hydrolyzed, forming the shorter chains that made it more soluble (Polesi & Sarmento, 2011), however autoclaving-cooling process in AC, AH-AC 24 and
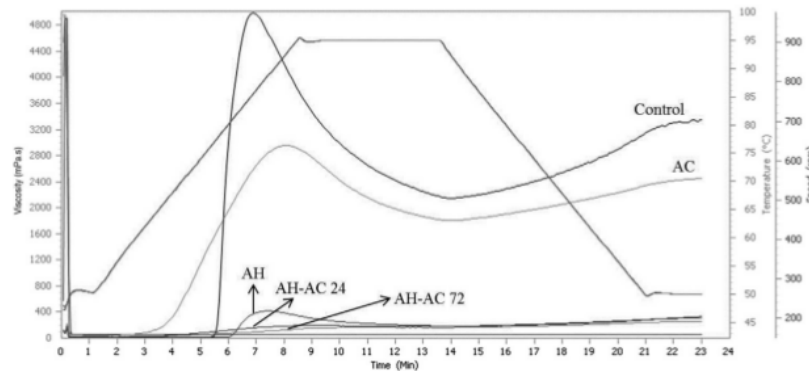

Fig. 2. RVA pasting curves of unmodified arrowroot strach (control), and modified arrowroot starch by acid hydrolysis (AH), autoclaving-cooling (AC), combination of acid hydrolysis and autoclaving-cooling with storing time 24 h (AH-AC 24) and combination of acid hydrolysis and autoclaving-cooling with storing time 72 h (AH-AC 72).

Table 2
RVA pasting properties of unmodified and modified arrowroot starches.

Samples	Peak viscosity (mPa.s)	Holding (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)	Peak time (min)	Pasting temperature (°C)
Control	4477.5 ± 719.13^c	1920.5 ± 320.32^b	2557 ± 398.81^c	3033 ± 453.9^b	1112.5 ± 133.64^c	6.93 ± 0^a	78.4 ± 2.12^a
AH	302 ± 161.22^a	134 ± 67.88^a	168 ± 93.33^a	238.5 ± 130.81^a	104.5 ± 62.93^a	7.60 ± 0.28^a	ND
AC	3106 ± 210.72^b	2185.5 ± 545.18^b	920.5 ± 334.46^b	2989 ± 765.09^b	803.5 ± 219.91^b	8.37 ± 0.42^a	65.2 ± 0.56^b
AH-AC 24	207 ± 15.56^a	192 ± 15.57^a	14 ± 0^a	320 ± 19.80^a	128 ± 4.24^a	8.24 ± 0.79^a	ND
AH-AC 72	206 ± 60.81^a	201 ± 57.98^a	6 ± 2.83^a	324 ± 98.99^a	123 ± 41.01^a	10.10 ± 1.74^a	ND

Values with different superscripts within each column showed significantly different ($p \leq 0.05$). ND (not detected).
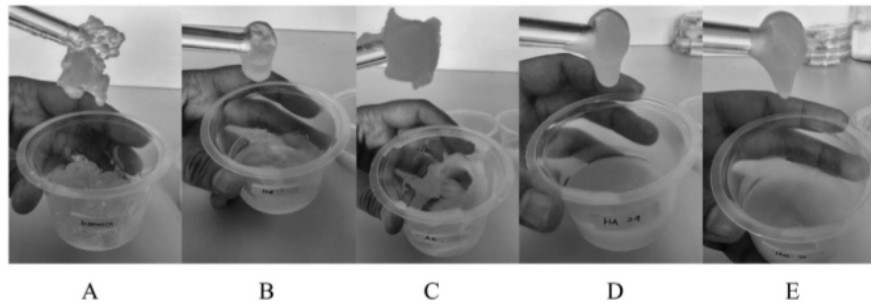

Fig. 3. The paste of (A) control (unmodified arrowroot strach), and modified arrowroot starch by: (B) acid hydrolysis – AH, (C) autoclaving-cooling – AC, (D) combination of acid hydrolysis and autoclaving cooling with storing time 24 h – AH-AC 24, and (E) combination of acid hydrolysis and autoclaving cooling with storing time 72h - AH-AC 72.
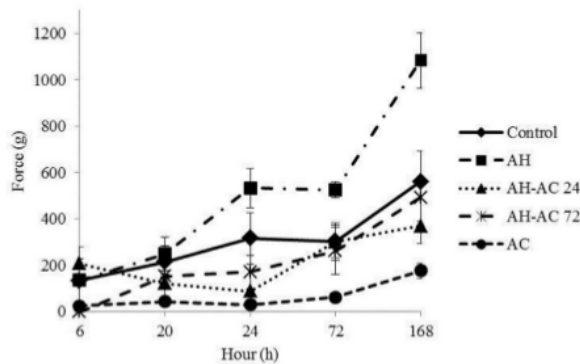

Fig. 4. Gel texture properties of unmodified and modified arrowroot starches.

AH-AC 72 preparations might cause these chains to re-associate to form tightly packed structures stabilized by hydrogen bonding (Haralampu, 2000).

Conversely, AH had the lowest WHC of the treated samples, whereas AC, AH-AC 24 and AH-AC 72 had the higher WHC than control and AH. The possible explanation would be that autoclaving-cooling process could improve the capacity of the starches to hold the water strongly. Nevertheless, the high WHC value of the starch with the combination of acid hydrolysis and autoclaving-cooling treatment did not make the starch had the good freeze-thaw stability. Unmodified arrowroot starch (control) had 0% syneresis, which was in agreement with Charles et al. (2015) who reported similar behavior for arrowroot starch. The lower syneresis of arrowroot starch made it suitable for use in food products involving refrigeration or freezing process (Charles et al., 2015). AH had syneresis of 1.99%, AC had syneresis of 0%, whereas AH-AC 24 and AH-AC 72 had the much higher syneresis than control reaching 77.58% and 123.51% respectively. The results presented in this study provided a valuable indication that acid hydrolysis could drive syneresis but autoclaving-cooling could maintain it. However, the combination of acid hydrolysis and autoclaving-cooling caused syneresis become worse, and the longer cooling time could increase this effect. The higher syneresis on acid hydrolyzed starch was previously reported by Dutta, Kaul, Kalita, & Mahanta (2011) for jackfruit seed starch.

Table 3 also summarizes the OHC that shows the ability of starches to hold the oil. This research revealed that OHC of modified arrowroot starches and control was not different. This functional property is important when the starch will be incorporated in food formulation that involves oil or fat as the ingredient.

Table 3
Functional properties of unmodified and modified arrowroot starches.

Samples	WSI (%)	Freeze-thaw stability (syneresis %)	WHC (%)	OHC (%)	SP (%)	Whiteness Starch powder	Starch paste
Control	$1,26 \pm 0,13^c$	$0,00 \pm 0,00^a$	$83,43 \pm 6,55^a$	103.80 ± 27.76^a	$868,71 \pm 80,90^{b,c}$	95.00 ± 0.71^c	47.13 ± 1.45^a
AH	$1,65 \pm 0,18^d$	$1,99 \pm 3,44^a$	$75,39 \pm 3,61^a$	109.01 ± 27.34^a	$555,82 \pm 172,75^a$	96.40 ± 0.81^c	$52.15 \pm 0.91^{b,c}$
AC	$0,35 \pm 0,12^a$	$0,00 \pm 0,00^a$	$275,73 \pm 11,07^c$	95.44 ± 9.98^a	$1016,12 \pm 237,73^c$	87.15 ± 0.32^a	50.05 ± 0.49^b
AH-AC 24	$0,72 \pm 0,03^b$	$77,58 \pm 9,51^b$	$216,34 \pm 2,11^b$	89.79 ± 8.32^a	$668,84 \pm 129,01^{a,b}$	91.55 ± 0.32^b	53.70 ± 1.15^c
AH-AC 72	$0,75 \pm 0,01^b$	$123,51 \pm 57,89^b$	$230,45 \pm 13,24^b$	114.84 ± 21.53^a	$669,75 \pm 10,96^{a,b}$	89.30 ± 2.18^a	$51.33 \pm 0.90^{b,c}$

Values with different superscripts within each column showed significantly different ($p \leq 0.05$).

The swelling power value of AC was not significantly different as compared to control. However, the high swelling power of AC was negatively correlated with the solubility that could be attributed to the changes in the morphological granule shape and size (Singh, Singh, Kaur, Sodhi, & Gill, 2003; Uarrota et al., 2013). Only acid hydrolysis could decrease the swelling power. The causative factors might be that disrupting of hydrogen bonding between adjacent starch polymers and eroding of the amorphous region in starch by acid hydrolysis treatment that lead to higher crystallinity of starch granule and thus restricted its swelling power (Khan et al., 2014; Sun et al., 2015).

The color of the paste was more important than that of the fine white powder because it determined the color quality of end product. From Table 3, it can be seen that all physical modification could enhance the whiteness of the starch paste.

The overall result revealed that AH, AH-AC 24 and AH-AC 72 might suitable for food emulsion products (Ozturk et al., 2011) such as an ingredient for soymilk, thickeners in various aqueous foods, lemon curd manufacture, salad creams and mayonnaises in which neutral tasting and low viscosity were required (Lawal, 2004). Although starch could not form an emulsion on its own because it did not have a capacity for remaining at oil-water interface (Dundar Gocmen, 2013), the starch could give the beneficial effect to emulsion properties of proteins (Herceg, Rezek, Lelas, Kresic, & Franetopic, 2007). Dundar and Gocmen (2013) showed that resistant starch could significantly increase the emulsion capacity and stability values of albumin solution, and Nasrin and Anal (2014) reported that emulsion made from culled banana resistant starch and soy isolate protein could be incorporated into bakery foods like muffin and bread for enhancing its functionality, such as texture, sponginess and targeted delivery of bioactive molecules, and in this case, the modified arrowroot starch might give the same functional properties as the culled banana starch in emulsion system. The proposed mechanism explaining this hypothesis was that the culled banana resistant starch reported by Nasrin and Anal (2014) was produced by a combination of acid hydrolysis and autoclaving treatment in which RVA viscosity values, swelling power, and solubility decreased significantly in the modified culled banana starch. In contrast to AH, AH-AC 24 and AH-AC 72, it is expected that autoclaving-cooling treated arrowroot starch (AC) is suitable for the gelling agent or dessert products such as puddings. Moreover, Altuna, Ribotta, and Tadini (2015) reported that addition of resistant starch could reduce the stickiness of bread dough, and delayed the aging process. Nevertheless, the application of these physically modified starches as a food ingredient still needs further study.

4. Conclusion

It can be concluded that acid hydrolysis has an improving effect on solubility properties of modified arrowroot starch without destroying its granule structure, whereas autoclaving-cooling process can increase water holding capacities of the modified starch compared to unmodified starch (control). Physical modification, especially autoclaving-cooling treatment, causes a degradation of both granule and molecular structure of modified starches, resulting in a decrease in all RVA viscosity values and altering their functional properties, thus giving the interesting possibility of its application in various types of food products with desired characteristics.

Acknowledgments

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