Effect of Temperature and Reaction Time on the Swelling Power and Solubility of Gadung (Dioscorea hispida Dennst) Tuber Starch during Heat Moisture Treatment Process

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Abstract. The starch from Gadung (Dioscorea hispida Dennst) has been underutilized in food and industrial applications due to its instability under harsh processing conditions, especially with high temperature. Gadung starch has a low setback viscosity, retrogrades less and therefore unable to form strong gels. Heat moisture treatment (HMT) may be one of alternatives to improve thermal stability and result in unique properties desired by various end users. In this research, Gadung starch was modified using hydrothermal treatment employing moisture content (MC) of 16 g water/100 g starch (wb) at various temperature (80, 90, 100 and 110°C) and reaction times (2, 4, 6, 8, 10, 12 and 16 h). In general, an increase in temperature from 80 °C up to 100 °C and time during HMT caused a decrease in swelling power (SP) and water solubility (WS) of the starch. However, unique phenomena were observed when the HMT of the starch was carried out at 110 °C as the swelling power and water solubility of the starch were higher than that obtained from HMT at 100 °C. Under this condition, both swelling power and water solubility of the starch increased when HMT was conducted from 2 up to 6 hours. Beyond 6 hours, the swelling power and water solubility of the starch gradually decreased.

1. Introduction

Gadung (Dioscorea hispida Dennst) is a woodbine belonging to the genus of Dioscorea within the Dioscoreaceae family. This plant has a thorny stem twinning to the left, which may reach up to 20 meters in height with a hairy trifoliate leaves and generates small pale yellow flowers [1]. This plant is reported easily found in the shade or near stream of secondary forest of South East Asia and its surrounding archipelagos [2]. Being planted in the beginning of rainy season (October-November), a mature bulky tuber with white to yellow flesh is usually harvested in summer (April-September) [3]. A mature tuber weighs up to 15 kg and contains up to 20 g carbohydrates/100 g yam on wet weight basis (wb). With respect to its high carbohydrate content and superior texture, this tuber has long been served as staple food for people in the rural areas, specifically during World War II. In Indonesia, Thailand, Vietnam, Malaysia and the Philippines, gadung tubers are mostly consumed boiled, steamed, or fried after being detoxified through a complicated cyanogens removal process. With no gluten content, but rich in resistant starch content, gadung tuber can be a potential food source for people in reducing the risk of obesity, diabetes, wheat allergy and the incidence of celiac diseases. At present, numerous person in many Western communities apply a gluten-free diet, keeping away of wheat, rye and barley [4]. The markets for gluten-free products have been increasing rapidly [5].
widening the opportunities for the development of new technologies to create new products using gluten-free ingredients as alternative for traditional manufacturing bakery products [6]. By far, commercial utilization of gadung tubers in industrial applications is limited. The major drawback of most of tuber starches is their instability under conditions of high temperature, shearing, and acidity, which limit many of starch applications in industry [7]. Modification of root and tuber starches can improve their stability and result in the specific characteristics desired for various end uses and market needs. With these encouraging conditions and benefits in mind, an attempt on the processing of gadung tuber into functional food materials was carried out.

Starch can be modified by chemical, physical, enzymatic, and genetic methods; however, the physical methods present a series of advantages [8]. The regulation of chemically modified starch for food (particularly for baby food) is quite strict, in such a way that the demand for physically modified starches is increasing [9]. Physically modified starch is considered safe for use in food products, as it does not involve any chemicals [10, 11]. The physical method of heat-moisture method is particularly favorable for the food applications with novel functional properties [12]. HMT may be an alternative to chemical modification for altering the gelatinization and retrogradation properties of tuber and root starches [13].

Heat-moisture treatment (HMT) is one of hydrothermal modifications in low moisture contents (<35% W/W), and commonly exposure at a temperature above the glass transition temperature (Tg) but below the onset (To) temperature of gelatinization (84 – 120°C) for a certain period of time (15 min – 16 h) [14]. HMT causes the rearrangement of amylose and amyllopectin chains in the starch, and therefore may modify its X-ray pattern, crystallinity, swelling power, amylose leaching, pasting, and gelatinization properties, as well as its susceptibility to enzymatic or acidic hydrolysis, which also affect the starch rheological properties [13 – 15]. The starch pastes formed after gelatinization is useful in many food applications for desirable physicochemical properties [16]. Known reports on the HMT change of several starches are corn, cassava, potato, wheat, waxy corn, amylomaize, oat, and barley and legumes starches. The significance of this impact was related to the moisture levels during heat treatment and starch source [17]. Swelling power (SP) is an indicator of water holding capacity of the starch molecules by hydrogen bonding [18], while water solubility (WS) is defined as the maximum amount of starch that can be obtained in a specific volume of water ([19]). Swelling and solubility index provides the evidence of interactions between the water molecules and the starch chains in the crystalline and amorphous regions ([19]). Based on swelling power at 95°C, Schoch and Maywald [20] classified starches as high swelling (≥ 30), moderate swelling (20 < SP < 30), restricted swelling (16 – 20) or highly restricted swelling (< 16). With SP and WS value of 15.5 and 9.92 (g/g dry starch), gadung starch falls in the highly restricted swelling starch category [21]. Starch with low solubility and stable values are best starch for raw material noodles use. The swelling power of starch, flour, and wholemeal of wheat correlate positively with the eating quality of white salted noodles [22].

This study aims to investigate the effect of temperature and reaction time on the swelling power and water solubility of gadung starch during heat moisture treatment process. The results of this study are expected to be one of probing parameters in searching the possible utilizations of gadung starch in the food industry.

2. Materials and Method

2.1. Materials

Matured gadung tubers with approximately 9 month old were collected from Gunungpati district of Semarang City - Indonesia. All of the chemicals used in this study were the products of Sigma-Aldrich (Singapore) and were purchased at analytical grade (≥ 98.99% w/w purity) from an authorized chemicals distributor in Semarang. They were directly used without prior treatments. The demineralized water used in this study was generated using reverse osmosis water purification system in the Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro - Semarang.
2.2. Starch extraction
The method used for extraction of the gadung tuber starch was similar to that prescribed by Hargono et al. [23] with some modification. Gadung tubers were unpeeled, washed with flowing tap water and sliced into thin chips (± 1 cm). The washed gadung chips were soaked in four parts of water for 12 h. They were then disintegrated in a Waring blender, ground in a stone mill, and strained to remove coarse fiber. The suspension obtained was later centrifuged at 3000 × g for 10 min, after which the supernatant was decanted. The sediment was re-suspended in four parts of tap water. The centrifugation step was repeated many times until no further sedimentation was observed. Finally, the sediment was dehydrated in a hot-air electric oven at 40 °C to dryness (moisture content ± 10% w/w), ground, and sieved through a 300 mesh sifter. The starch was stored in zip-lock polyethylene bags and kept in covered plastic containers at 20 °C.

2.3. Heat moisture treatment
The HMT was performed using the method previously used by Franco et al. (1995) [24]. The starch was firstly conditioned by atomizing and mixing a predetermined amount of distilled water to obtain 16% w/w moisture content. The moistened starch samples in glass containers were heated in an air oven at various temperatures (80, 90, 100 and 110 °C) and reaction times (4, 6, 8, 10, 12 and 16 h). After equilibration to room temperature, the glass containers were opened and the heat moisture treated starch samples were dried in an electric oven at 105 °C to moisture content of 10% w/w.

2.4. Swelling power and water solubility measurements
The swelling power and water solubility of the native and heat moisture treated gadung starches were measured using the method of Tattiyakul et al. [21] with slight modifications. A carefully weighed dry starch (m₀ ~ 0.5 g) was dispersed in 50 mL of water to obtain 1% slurry in a centrifugal tube. The starch dispersion was heated under gentle agitation at 95 °C for 30 min. The cooked starch dispersion was then equilibrated to room temperature and was further centrifuged at 3,000×g for 20 min. The supernatant was decanted and dried at 105 °C in a glass Petri dish to a constant weight (mₛ). The swelling power (SP) and water solubility (WS) of the starch were calculated using equations 1 and 2.

\[
SP = \frac{mₛ}{m₀ \cdot \left(1 - \frac{WS}{100}\right)}
\]

\[
WS = \frac{mₛ}{m₀} \times 100
\]

where mₛ is the weight of the swollen starch granules. The measurements were done in duplicates and the reported data were the average or them.

3. Results and Discussion

3.1. Swelling power
The swelling power of starch gives information on the mass of water that can be absorbed by one gram of starch granules in the presence of excess water at high temperature. Coincidentally, swelling power value also indicates the degree of crystallinity of the starch granules. Starch granules with lower crystallinity have a higher tendency to absorb more water and swell to a larger extent. Commonly, tuber starches have lower crystallinity and hence exhibit high swelling power due to their higher amylopectin content. Starch granules with greater swelling power usually show a harmonious higher amylose leaching. The swelling power of native gadung starch and various species Dioscorea starches are tabulated in Table 1, whereas the swelling power values of the native and heat moisture treated
gadung starches at various temperatures and reaction times obtained from this study are presented in Table 2.

The swelling power of gadung starch showed a relatively low value of 15.76 g swollen starch/g dry starch, which is very close to that reported by Tattiyakul and her coworkers [21], but far below the swelling power data reported by Ashri et al. [3]. In this regard, gadung starch falls within highly restricted swelling starch category [20]. As clearly shown in Table 1, the swelling power of gadung starch was comparable to those of D. alata Linn., D. cayenensis-rotundata and D. esculenta starches. Some even lower swelling power values were reported for D. bulbifera Linn., D. opposita Thunb. and D. septemloba Thunb starches [25, 26]. In contrast, D. trifida exhibits highest swelling power value. The low swelling power value could be associated to high amylose content of the starch and the linear arrangement of the amylose molecules in the starch granules that thwarts water molecules to diffuse into the starch granules [28]. In addition, amylose can also interact with lipid and the linear part of amylopectin to form complexes, which potentially prevent amylose leaching and starch granule swelling.

### Table 1. Swelling power (g/g dry starch) and water solubility (%) of various dioscorea tuber starches at 95 °C

| Species                  | Swelling power | Solubility | References |
|--------------------------|----------------|------------|------------|
| D. hispida Dennst        | 15.76 ± 1.20   | 9.97 ± 0.30| This work  |
| D. hispida Dennst        | 15.60 ± 0.80   | 9.90 ± 0.50| [21]       |
| D. hispida Dennst        | 18.25          | 20.00      | [3]        |
| D. alata Linn.           | 16.92 ± 1.61   | 30.04 ± 2.70 | [25]     |
| D. bulbifera Linn.       | 12.79 ± 3.00   | 10.46 ± 3.86 | [25]     |
| D. cayenensis-rotundata  | 13.90 ± 1.70   | 8.70 ± 1.70| [26]       |
| D. dumetorum             | 13.70          | 12.40      | [26]       |
| D. esculenta             | 14.3 ± 1.40    | 10.50 ± 2.50 | [26]     |
| D. opposita Thunb.       | 12.42 ± 0.48   | 16.27 ± 3.64 | [25]     |
| D. septemloba Thunb.     | 12.14 ± 0.03   | 14.40 ± 0.25 | [25]     |
| D. trifida               | 20.90 ± 0.70   | 4.30 ± 0.30| [27]       |

### Table 2. Swelling power (g/g dry starch) and water solubility (%) of HMT treated gadung starch

| Time (hour) | 80°C | 90°C | 100°C | 110°C |
|-------------|------|------|-------|-------|
|             | SP   | WS   | SP    | WS    | SP    | WS    | SP    | WS    |
| 0           | 15.76| 9.97 | 15.76 | 9.97  | 15.76 | 9.97  | 15.76 | 9.97  |
| 2           | 15.56| 6.86 | 15.51 | 4.81  | 14.69 | 5.25  | 15.23 | 6.07  |
| 4           | 15.45| 6.48 | 14.31 | 4.64  | 14.87 | 5.54  | 15.10 | 6.45  |
| 6           | 15.41| 6.38 | 14.14 | 4.24  | 15.21 | 4.74  | 15.33 | 6.80  |
| 8           | 15.28| 6.16 | 13.74 | 4.15  | 13.37 | 3.88  | 14.76 | 6.36  |
| 12          | 14.84| 5.45 | 13.72 | 3.98  | 12.33 | 3.48  | 14.43 | 5.74  |
| 16          | 14.43| 4.84 | 12.91 | 3.84  | 12.24 | 3.33  | 14.26 | 5.65  |

The swelling power of gadung starch gradually decreased as HMT temperatures increased from 80 °C to 100 °C. However, swelling power of gadung starch increased as the HMT temperature was further increased to 110 °C. Similarly, the swelling power of gadung starch also gradually decreased with the increase of HMT duration. Pranoto et al. [29] also observed a reduction of swelling power with longer HMT duration for sweet potato starch of four selected Indonesian cultivars after HMT at 110 °C. In addition, Sun et al. [30] reported that the swelling power of early indica rice starch decreased with the increasing HMT temperature (90 to 100 °C) and duration (3 to 7 hours). However, no further alteration in swelling power of early indica rice starch when HMT temperature was
increased to 100 °C. Kong et al. [31] also found that the swelling power of normal rice starch was lower for when it is subjected to a longer HMT duration (4 to 16 hours).

This reduction in swelling power has been reported to be caused by the enhancement of crystallinity, the reduction of hydration or the formation of amylose–lipid complexes [32]. Gunaratne and Hoover [12] found that the decrease of swelling power of HMT starches can be the result of enhanced interactions during HMT treatment, such as amylose–amylose and amylose–amylopectin chains. It may be due to formation of new molecular rearrangement of starch chains after HMT [14]. This is found to be similar with the results obtained by Horndork and Noomhorm [33] where swelling power of rice starch decreased after HMT. Moreover, similar result was established by Zavareze et al. [34] for pinhao starches. During hydrothermal treatment, the added water acted as a plasticizer and promoted additional interactions between amylose – amylose or amylose and linear branches of amylopectin [7, 13]. In addition, Zavareze and Dias [15] proposed that the decrease in swelling power may also be due to stronger intermolecular connection, development of complexes of amylose–lipid, or can be due to alteration of the crystalline arrangement of starch. This resulted in a denser granule structure that is partially responsible for the decrease in swelling power. HMT promotes formation of ordered double helices, and in doing so, limits starch swelling and solubility, as suggested by Lawal [35].

3.2. Water solubility

Solubility of starch is the result of the leaching of amylose when the starch is heated under excess amount of water [36]. As the starch granules imbibe more water and swell, the amylose dissociates from and diffuses out of them. The water solubility of various starches extracted from tubers and bulbils of dioscorea family in comparison to gadung starch is presented in Table 1. The water solubility of gadung starch is relatively low (9.97%), which is closely similar to that reported by Tattiyakul and her coworkers [21]. Surprisingly, this value is only about a half of water solubility data of gadung starch reported by Ashri et al. [3]. It is also obvious that the swelling power of gadung starch was comparable to those of D. bulbifera Linn., D. cayenensis-rotundata and D. esculenta starches. Higher swelling power values were reported for D. alata Linn., D. dumetorum, D. opposita Thunb. and D. septemloba Thunb starches [25, 26]. In contrary, D. trifida starch exhibits the lowest swelling power value. The low water solubility value could be associated to high amylose content of the starch and the linear arrangement of the amylose molecules in the starch granules that retards water molecules to diffuse into the starch granules [28]. In addition, amylose can also interact with lipid and the linear part of amylopectin to form complexes, which substantially impede amylose leaching and starch solubilization.

The water solubility of native and heat moisture treated gadung starches are shown in Table 2. Table 2 shows that the solubility of gadung starch decreased with increasing HMT temperature up to 100 °C. The decrease in water solubility could be explained that the starch granules become more rigid during HMT [37], which could be correlated to the internal rearrangement/reassociation of starch granules during HMT [38], which provide more advanced interactions between starch functional groups within amylose–amylopectin and/or amylopectin–amylopectin chains, formation of more ordered amylopectin clusters, and the establishment of amylose-lipid complexes within starch granules [15]. HMT was reported to promote the formation of ordered double helices, and in doing so restricts starch solubility, as proposed by Lawal [35].

However, HMT at higher temperatures (110 °C) resulted in higher water solubility of gadung starch. However, their values were all below those of native gadung starch. Having compared their solubility and amylose leaching data of gadung starch before and after HMT at 110 °C, Tattiyakul et al. [21] proposed that the increase in solubility of gadung starch treated at higher HMT temperature could probably triggered by physical weathering of the more crystalline starch granules and not being a result of molecular leaching of amylose.

The water solubility of gadung starch gradually decreased when it was subjected to a longer HMT duration. Pranoto et al. [29] also found a reduction of solubility of sweet potato starch of four selected
Indonesian cultivars after HMT at 110 °C. However, they also reported that the solubility of sweet potato gradually increased with HMT duration. This result is in good agreement with Sun et al. [30] who reported a gradual decrease in the solubility of early indica rice starch with the increase HMT temperature (90 to 100 °C) and duration (3 to 7 hours). However, no further alteration in swelling power of early indica rice starch when HMT temperature was increased to 100 °C. Kong et al. [31] also found that the swelling power of normal rice starch was lower when it is subjected to a longer HMT duration.

4. Conclusion
Gadung starch was modified using hydrothermal treatment employing moisture content (MC) of 16 g water/100 g starch (wb) at various temperature (80, 90, 100 and 110 °C) and reaction times (4, 6, 8, 10, 12 and 16 h). In general, an increase in temperature and time during HMT caused a decrease in swelling power and water solubility of the starch. Unique phenomena were observed when the HMT of the starch was carried out at 110 °C as the swelling power and water solubility of the starch were higher than that obtained from HMT at 100 °C. Both swelling power and water solubility of the starch increased when HMT was conducted from 2 up to 6 hours. Beyond 6 hours, the swelling power and water solubility of the starch gradually decreased.

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