Water Solubility, Swelling and Gelatinization Properties of Raw and Ginger Oil Modified Gadung (Dioscorea hispida Dennst) Flour

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Abstract: The aim of this study was to study the modification of gadung (Dioscorea hispida Dennst) flour using ginger oil as cross-linking agent following dispersion method to meet the standard physicochemical properties of wheat flour. For this purpose, effect of gadung starch: ginger oil molar ratio (2 and 3), reaction time (30, 60, 90 and 120 min) and temperatures (30, 40 and 50ºC) on the water solubility, swelling and gelatinization properties of the modified gadung flour were investigated. Best modification condition was obtained at modification using gadung starch:ginger oil ratio of 3 at 30ºC and 60 min, where the modified gadung flour obtained has a very similar water solubility, swelling and gelatinization properties with American wheat flour, which were 7.28 (g/100g), 7.9 (g/g) and 56.2ºC, respectively. One of the drawbacks of the modified gadung flour obtained was only the presence of the remaining ginger aroma.

Keywords: Cross-linking, gadung flour, gelatinization, ginger oil, swelling power, water solubility

INTRODUCTION

Gadung (Dioscorea hispida Dennst.) is one of unpopular member of tubers which is available in almost all parts of Indonesia’s archipelago, Malay Peninsula, Thailand and Malaysia (Burkill, 1935). This tuber crop is an important source of carbohydrates and has been used as staple foods, especially by people in the tropical and subtropical regions during WW II but rarely eaten by natives these days because it requires a lot of time and effort to prepare (Liu et al., 2006). A mature gadung tuber weighs up to 15 kg and every 100 g of the tuber (wet basis) contains up to 20 g carbohydrates, 78 g water, 1.81 g protein, 0.16 g fat, 0.93 g fibre and 0.69 g ash (Coursey, 1967). The resistant starch contained in this food source has been related with a slow digestion in the lower parts of the human gastrointestinal tract, resulting in slow liberation and absorption of glucose. This tuber’s digestive property has suggested the utilization of gadung tuber in reducing the risk of obesity, diabetes and other related diseases (Aprianita et al., 2009). In addition, as carbohydrate source, gadung tuber does not contain any gluten, which makes gadung tuber becomes an important substance in the reduction in the incidence of Celiac Disease (CD) or other allergic reactions (Rekha and Padmaja, 2002). With these benefits in mind, an effort on gadung processing into edible food materials was undertaken.

The major problems related to the limitation of gadung tuber utilization as a food source for human are its high content of toxic substances, i.e. alkaloids and hydrogen cyanide in both free and bound forms (Edijala et al., 1999) and its relatively high moisture content and vulnerability to gradual physiological deterioration after harvesting. Bhandari and Kawabata (2005) reported their successful efforts to reduce the bitter and toxic compounds of Nepali wild yam tubers to a safe level. Indeed, the susceptibility of gadung tuber to gradual physiological deterioration can be overcome by processing gadung tubers into less perishable products such as gadung flour through a drying process. However, like other tuber flours, the starch contained in the flour is quite fragile and tend to be fragmented by prolonged heating or agitation. This starch is also very sensitive to acid, which results in a rapid breakdown in viscosity. These shortcomings can be overcome by starch modification through cross-linking that prevents starch granule rupture and loss of viscosity under acidic conditions. Low level of cross-linking can eliminate the rubbery, cohesive, stringy texture of cooked native starch, particularly waxy and root or tuber starches. During cross-linking process, the starch molecules can be interconnected by reactions of their two types of hydroxyls, primary (6-OH) and secondary (2-OH and 3-OH) with trace amounts of a multifunctional reagent (Seib, 1996). The reagents permitted by FDA for making cross-linking food grade starch are phosphoryl chloride, sodium trimetaphosphate, adipic acetic mixed anhydride, and mixtures of sodium trimetaphosphate and tripolyphosphates. Epichlorohydrin is no longer used by
starch manufacturers in the U.S. because chlorohydrins are carcinogens (Seib, 1996). Therefore, the searches for new safer cross-linking agents are important, especially those available in the natural resources.

Also, recent return to research at finding substitutes for wheat flour, either in part or in whole, in the manufacture of pan loaf bread for economic and health reasons has brought to fore the evaluation of other flours, including gadung flour, for this purpose. This article reports the water solubility, swelling and gelatinization properties of raw and cross-linked gadung flour using ginger oil as cross-linking agent towards evaluating their application in food and other uses.

MATERIALS AND METHODS

All experiments in this study were conducted in the Food Processing Technology Research Laboratory of Diponegoro University, Semarang-Indonesia for the period of May to October 2011.

Materials: Matured gadung tubers of 8 month age were harvested in June 2011 and were of a uniform medium size and free from mechanical or pathological injuries. The ginger oil was prepared by atmospheric hydrodistillation of fresh ginger rhizomes. All chemical reagents of analytical grade (minimum 99.99 % purity) were purchased from Sigma-Aldrich Pte. Ltd. (Singapore) and used directly without further purification.

Preparation of gadung flour: The matured tuber of gadung was used to prepare gadung flours at the Department of Chemical Engineering, Diponegoro University, Semarang-Indonesia. Tubers were washed using tap water to remove surface soil. The tubers were then hand-peeled and trimmed to remove the skin and defective parts. After peeling and trimming, the tubers were cut into smaller pieces before slicing with a Cuisinart food processor equipped with a 0.1 cm ultra thin blade. The thin slices were then soaked in brine to remove substances which causes dizziness. The slices were further leached in an agitated tank using flowing tap water to remove the cyanides content to reach a safe level before dried on perforated trays by using an electrical convection oven (60°C for 24 h). The dried slices were ground into flour using a Cross-Beater mill (Glen Mill Corp., Maywood, NJ) equipped with a 0.5 mm screen. The flour was then packed and heat-sealed in laminated bags of about 100 g each. The bags were stored prior to starch isolation and for physical and chemical analyses.

Analysis of starch content in the gadung flour: Starch content in the gadung flour was determined using the method developed by Jane et al. (1992a). Gadung flour (about 50 mg, dsb) was suspended in 90% dimethyl sulfoxide (3 mL) and boiled in a water bath at 96°C for 1 h. After cooling, methanol (10’) was added to precipitate the solid. The mixture was centrifuged and the supernatant was discarded. A phosphate buffer solution (pH 6.9, 0.1M, 3 mL) and porcine pancreatic α-amylase (91,330 units) were added to solid residues. The mixture was incubated in a shaker water bath (Versa-Bath, model 236, Fischer Scientific, Pittsburgh, PA) at 35°C for 4 h. At the end of the incubation, glucoamylase (25 units) in an acetate buffer solution (pH 4.3, 0.1M, 0.55 mL) was added into the digestion mixture and the pH of the mixture was 4.5. The digestion mixture was then incubated in the same shaker water bath at 55°C for 4 h. Glucose produced in the digest was quantitatively analyzed by measuring the absorbance at 520 nm using mixture hexokinase and glucose-phosphate dehydrogenase coupled with chemical reduction of iodonitrotetrazolium (glucose diagnostic kist no. 115, Sigma) (Carroll et al., 1970).

Modification of gadung flour: Gadung tuber flour was modified using ginger oil following dispersion method under atmospheric condition (Seib, 1996). A predetermined mass of gadung flour was mixed with 200 mL of aquaest in a 500 mL Erlenmeyer flask for 10 minutes to get gadung flour dispersion. At the same time, a predetermined amount of ginger oil was dispersed in 100 mL aquaest by mixing both substances in a 250 mL Erlenmeyer flask for 10 min. The ginger oil-water dispersion was then transferred into gadung flour dispersion and mixed by continuous stirring at 100 rpm to perform modification. The suspension was then decanted to separate the modified flour and the dispersant water. The modified flour was then transferred to a Petri dish and dried in a vacuum oven at 40°C before milled and sieved as fine powder modified flour. Effect of gadung flour:ginger oil molar ratio (2 and 3), reaction time (30, 60, 90 and 120 min) and temperatures (30, 40 and 50°C) on the water solubility, swelling and gelatinization properties of the modified gadung flour were investigated.

Swelling power and solubility: Swelling behaviors were determined by modifying the method of Li and Yeh (2001). Swelling power and solubility of gadung flour were determined by heating flour-water slurry (0.35 g flour in 12.5 mL distilled water) in a water bath at 60°C for 30 min, with constant mixing (Crosbie, 1991). The slurries were centrifuged at 100 × g for 15 min in a Superspeed centrifuge (Sorvall® RC-6, Kendro laboratory products, NC, USA). The supernatant was separated and swollen starch as the precipitate was weighted. Total carbohydrate content of the dissolved material in the supernatant was estimated by phenol-sulfuric assay (Dubois et al., 1956). Solubilized Starch (SS) was reported as the ratio of total carbohydrate in the supernatant to the weight of dry matter starch. To calculate the swelling power, the weight of residue was divided by the original
weight after solubility subtraction (Osunadahunsi et al., 2003). Swelling power (SP, g/g) was calculated as follows: SP = (precipitate weight × 100)/ [(dry matter starch weight × (100-%SS)]. Analysis was conducted in triplicate.

**Amylose content determination:** Amylose content of the isolated starches from gadung flour was determined by colorimetric method (AACC, 2000). The starch sample (20 mg, db) was dispersed in 10 mL KOH (0.5M) and made up to 100 mL with distilled water. To an aliquot (10 mL) of the dispersion, 5 mL of HCl (0.1M) and 0.5 mL of iodine solution (0.1%) were added and made up to 50 mL. Absorbance was measured at 625 nm using a Helios spectrophotometer (Pye Unicam, Germany). The concentration was read on a standard amylose (AK Scientific, Inc., USA) curve plotted from solutions with concentrations of 0-100 mg amylose per 100 mL water. The amylopectin content was calculated by difference (100-amylose %). The absorbance was read on three replications per sample and averaged.

**Differential scanning calorimetry:** Gelatinization temperature of gadung flour samples were determined with Differential Scanning Calorimetry (DSC) (DSC-7, Perkin-Elmer, Norwalk, CT) using the method of Fan and Marks (1998). Gadung flour samples (3 mg, dry basis) were placed in aluminium DSC pans and distilled water was added to give a water-to-flour ratio of 2.5:1. The samples were sealed and allowed to equilibrate overnight before DSC analysis. The sample pans were heated at 10ºC/min from 40 to 120ºC. The DSC analyzer was calibrated using indium; an empty pan was used as a reference. An average of at least three thermograms was used for each starch.

The effect of gadung starch:ginger oil molar ratio (SGOR = 2 and 3), reaction time (30, 60, 90 and 120 minutes) and temperatures (30, 40 and 50ºC) on the water solubility, swelling and gelatinization properties of the modified gadung flour were investigated.

### RESULTS AND DISCUSSION

**Effect of SGORs, time and temperatures on swelling power and water solubility:** The most important property of starch in a commercial application is its ability to swell and produce a viscous paste when heated with water (Leach, 1965). The swelling power of starch gives information on the ability of 1 gram of starch granules to absorb a certain amount of water in presence of excess water at high temperature. This parameter also reflects the degree of crystallinity of the starch granule. Starch granules with lower crystallinity tend to imbibe more water and swell to a greater extent. In contrast, starch granules with greater crystalline areas and with strong bonds in the crystalline regions swell less in cold water or when heated into paste, forming low viscosity paste with high tendency towards retrogradation because of the bonds. Commonly, tuber starches have high swelling power due to their higher amylopectin content and, hence, lower crystallinity. With greater swelling power, starches show harmonious higher water solubility. The swelling power and water solubility of the native and modified gadung flour, gadung starch (Tattiyakul et al., 2006) and American and Korean wheat flours (Chung et al., 2010) are tabulated in Table 1.

The data on swelling power and water solubility of gadung starch at 90ºC reported in the literature are 15.6 (g/g) and 15.8 (g/100g), respectively (Tattiyakul et al., 2006). The lower native gadung flour’s swelling power and water solubility values reported in this study compared with the reported data were due to the lower temperature at which solubility was determined (60ºC), at which temperature the starch granules were swollen, but not disrupted. Increased disruption of crystalline structure occurs during the heating of starch in excess water, leading to increased granule swelling and solubility at higher temperatures.

In general, the longer reaction time produced higher swelling power, but reduce water solubility of the modified gadung flour at all temperatures and SGORs. Another interesting phenomenon to note is that the
increase of swelling power and reduction of water solubility was more pronounced when the modification is conducted at lower temperature. The degree of swelling and the amount of solubilization depend on the extent of chemical bonding within the granules, which can be related to reaction time (Tian et al., 1991). The presence of strong intermolecular bonds and high amylose content reduce the extent of swelling by forming an extensive network (Rasper, 1969). Amylose is believed to restrict swelling and starch granules show complete swelling only after amylose has been leached out of the granules (Hermansson and Svegmark, 1996). Commonly, cross-linking occurs as an endothermic reaction, which takes place faster at higher temperature (Lu and Hsieh, 2009).

Therefore, as the cross-linking reaction went by to a longer duration and at higher temperatures, more networks/cross-links was formed during cross-linking and thereby imposed constraints on the swelling behavior of the modified gadung flour. In addition, amylose can also form a complex with lipid and the linear part of amyllopectin and, hence, inhibit amylose leaching and starch granule swelling (Jin et al., 1994). Furthermore, the influence on swelling power and water solubility also depends on the characteristics of amylose and amyllopectin in terms of properties and intensity of the three-dimensional network of micelles in starch granule, bonding degrees at the molecular level, molecular weight distribution, degree and length of branching and conformation (Tester and Morrison, 1990; Hoover, 2001; Brunnschweiler et al., 2005). Other factors that may affect solubility of starches include: source, inter-associative forces within the amorphous and crystalline regions, swelling power and presence of other components, e.g., phosphorous compounds (Moorthy, 2002).

The effort to obtain modified gadung flours with equal swelling power and water solubility values with wheat flour was successful as some results fulfilled the American and Korean wheat flour swelling power and water solubility standards (Chung et al., 2010). The swelling power and water solubility values of modified gadung flours obtained from modification at $SGOR = 2$, temperature $40 ^\circ C$ in $30$ and $60$ min and $SGOR = 3$, temperature $30 ^\circ C$ in $60$ min were in the range of those parameters for American wheat flour. While swelling power and water solubility values of modified gadung flours obtained from modification at $SGOR = 2$, temperature $30 ^\circ C$ in $60$ min and $SGOR = 3$, temperature $40 ^\circ C$ in $120$ min were on par with those Korean wheat flour. One of the drawbacks of the modified gadung flour obtained was only the presence of the remaining ginger aroma.

**Effect of SGORs, time and temperatures on gelatinization temperature**: Table 2 shows thermodynamic properties of gelatinization of native and modified gadung flour, gadung starch (Tattiyakul et al., 2010) and American and Korean wheat flours (Grant, 1998) for comparison. Differential scanning calorimetric studies of gadung flours and starches showed that the gelatinization temperatures of the flours ($85 ^\circ C$) were higher than those of the starches ($71.30 ^\circ C$) (Tattiyakul et al., 2010). The difference could be attributed to the presence of mucilage in the flours. In addition to protein, the mucilage also contains complex polysaccharides such as mannan-like polysaccharides (Tsukui, 2003). The polysaccharide could compete with starch for moisture and result in a higher onset starch gelatinization temperature in the flour.

The onset temperature of gelatinization ($To$) of native gadung flour is also higher than that of American and Korean wheat flour, which is $56.20 ^\circ C$ and $56.40 ^\circ C$, respectively (Grant, 1998). This finding is consistent with Jane et al. (1999) where wheat starch which is grouped as A type-granule starch has lower gelatinization temperature than gadung starch (B type-granule starch). The A type-granule starches consist of larger proportions of short chains amyllopectin and smaller proportions of long chains amyllopectin than B type-granule starches, which results in lower gelatinization temperature. Gelatinization temperature is an indicator of the overall crystallinity of amyllopectin, which is directly related to the structure of amyllopectin (Fredriksson et al., 1998). Yuan et al. (1993) demonstrated that starch with greater amounts of long branched chains of amyllopectin

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<tr>
<th>Starch/ginger oil molar ratio</th>
<th>Temperature (ºC)</th>
<th>Time (minute)</th>
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<th>AC (%)</th>
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<td>Native gadung flour</td>
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<td>Starch</td>
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<td>American wheat (AW)</td>
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<td>Korean wheat (KW)</td>
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\(^{1}\) Tattiyakul et al. (2010); \(^{2}\) Grant (1998)
exhibited higher To than starch with fewer long branched chains. This is because the longer chains have a greater ability to form double helices, which required greater thermal energy to dissociate. Thus, it can be hypothesized from these results that native gadung flour, with higher To contain more long branched amylopectin chains and that gadung flour flours, which had lower values of To had a lower content of long branched chains.

The gelatinization temperature (To) of the gadung flour decreased from its initial value to certain values corresponded with the SGORs, duration and temperature of cross-linking modification. This finding agreed well with previous study that cross-linking modification caused a decrease in onset temperature of gelatinization (To) of normal rice starch and flour (Liu et al., 1999) and cassava starch (Jyothi et al., 2006). However, in each set of the experiment, the sample with higher degree of cross-linking exhibited higher To values than those with lower degree of cross-linking (shorter reaction time). The chemical and physical properties of the cross-linked starch are finally depending on the chemical nature of the cross-linking agent, the degree of substitution, starch type, reagent concentration, pH, reaction time and temperature (Hirsch and Kokini, 2002). This could most possibly be resulted from the change in crystallinity of the modified starch explained earlier or could be the structure inhomogeneity, which could be expressed by the transition temperature range, resulted from the crystallographic pattern transition. The introduction of oxide, methoxy and other functional groups of the ginger oil at random positions of the starch granule lead to change the orientation of the intra- and inter-molecular hydrogen bonds, resulting in decreased crystallinity in starch granules that promotes gelatinization (Seow and Thevamalar, 1993).

Adverse effects of cross-linking on the gelatinization properties of the cross-linked starches have been reported in the literatures. Xu et al. (1993) reported that cross-linking increased the heat of gelatinization for rice starch. However, according to Yoook et al. (1993) the cross-linked rice starches exhibited a lower value of heat of gelatinization than native rice because cross-linking reduced the portion of starch granules that could be gelatinized. The cross-linked wheat starches (distarch phosphate and aluminum octenyl succinate) were reported to have virtually unchanged To (Wootton and Bamunuarachchi, 1979). From their DSC studies, Woo and Seib (2002) reported that the cross-linked starches showed higher gelatinization temperatures and lower enthalpies than their parent starches. Therefore, according to earlier reports, the effect of cross-linking on gelatinization properties has been found to depend on the nature of the starch source.

The cross-linked wheat starches (distarch phosphate and aluminum octenyl succinate) were reported to have virtually unchanged To than high To contain more long branched amylopectin chains and that gadung flour flours, which had lower values of To had a lower content of long branched chains.

According to Yook, et al. (1999) the cross-linked gadung starch:ginger oil ratio (SGOR) of 3 at 30ºC and 60 min, where the modified gadung flour obtained was only the presence of the remaining ginger aroma.

From the experiments carried out in this work, some conclusions can be drawn: the gadung starch:ginger oil ratio (SGOR), reaction time and temperature affected the water solubility, swelling and gelatinization properties of the cross-linked gadung flour. Best modification condition was obtained at modification using SGOR of 3 at 30ºC and 60 min, where the modified gadung flour obtained has a very similar water solubility, swelling and gelatinization properties with American wheat flour, which were 7.28 (g/100g), 7.9 (g/g) and 56.2ºC, respectively. One of the drawbacks of the modified gadung flour obtained was only the presence of the remaining ginger aroma.

CONCLUSION

Starches with varying amylose content are of interest for food processing because of the potential to modify the texture and quality of the end-use products (Hung et al., 2006). Table 2 shows the changes of amylose content of native gadung flour and gadung flours after modification at different SGORs, time and temperature. As expected, the amylose content of the modified gadung flours is lower than that of native gadung flour, from which means an increase in their digestibility. The decrease in amylose content is followed by reduction in gelatinization temperatures. Starches with high amylose content have high gelatinisation temperature that may not be reached in conventional cooking practices and amylose retrogrades at a faster rate and to more amylose resistant crystalline structures than amylopectin (Venn and Mann, 2004). The amylose content decreased because when granular starch is subjected to cross-linking reaction, amylose will be cross-linked to amylopectin and eluted with amylopectin (Jane et al., 1992b). Like most of other tuber starch, amylose molecules in the starch of gadung flour are isolated from amylopectin molecules and are present at bundles of the amorphous region. Therefore, the amylose molecules should be preferentially cross-linked among themselves at low to moderate degree of cross-linking.

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