Functional properties of hydrothermally modified lesser yam (Dioscorea esculenta) starch

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Abstract. Lesser yam (Dioscorea esculenta L.) is a potential starch source that can be found easily in Indonesia but has limitations in its application due to its characteristics. For this reason, native lesser yam starch was modified to improve its functional properties. The hydrothermal modification was chosen because it is safe and environmentally friendly. The hydrothermal modifications used in this research were Heat Moisture Treatment (HMT) and Annealing (ANN). This work aims to increase the use of local tubers as an alternative starch source and to study the effect of hydrothermal modification on the functional properties of lesser yam starch such as swelling power, solubility, and freeze-thaw stability. HMT was carried out using 3 moisture levels (20%, 25%, 30%) and 3 heating time levels (4h, 8h, 16h). ANN using 3 starch and water ratio levels (1:2; 1:3; 1:5) and 3 heating time levels (6h, 8h, 10h). The results indicated that swelling power and solubility decreased with the increasing moisture level in HMT and ANN in general, but have various effects in syneresis depend on moisture level and heating time. HMT modified starch prepared at 25% moisture level and 4h heating time and ANN modified starch prepared at starch: water ratio 1:3 and heating time 10h is concluded to be the best choice for food product application especially thermally stable need food product.

1. Introduction

The use of tuber starch in food processing has been widely done, including as a substitute for wheat in the manufacture of sweetbreads, as a raw material for making noodles, as a thickening agent for various food products such as vegetable soup products, as well as filler and fat substitution in sausages [1][2][3][4][5]. However, native starch has limitations in pasting properties, heat resistance, swelling and solubility, and freeze-thaw stability so that its use in the food industry is limited. Starch modification can change the functional properties of starch that it can be used in a specific industry so that the use of starch becomes wider.

The modifications of starch are possibly divided into physical, chemical, and enzymatic. Physical modification has recently begun to be looked at, especially in its use in the food industry due to the difficulty of licensing approval for chemical reagents used in chemical modification. One of the physical modifications that can be done is hydrothermal modification. Hydrothermal modification is a modification that involves a limited amount of water and a specific heat temperature. This modification is classified as a safe modification because uses safe materials [6]. Hydrothermal modifications that can be done include heat moisture treatment (HMT) and annealing, HMT and
Annealing can change the physical and chemical properties of starch without destroying the granule structure. In this modification, the things that need to be controlled include the ratio of starch and water, temperature, and heating time. The differences between HMT and annealing are the water added and the temperature used. HMT uses a limited water content (10-30%) with a temperature range of 90-120°C while annealing uses a higher water content (50-60%) with a temperature below the starch gelatinization temperature. HMT and annealing can change the physicochemical properties of starch such as increased thermal stability and decreased retrogradation, making it suitable for use in the canned food and frozen food industries. Besides, HMT and annealing reduce granule swelling properties, reduce amylose leaching, and increase heat stability, making it suitable for application in the noodle industry [7].

Some recent works on hydrothermal modifications have been reported in banana starches [8], bean starch [9], tuber starches such as potato and cassava starch [10], also taro starch [11]. Among tuber starches, information on this modification on lesser yam tuber starch is still limited. The information about the functional properties of hydrothermally modified starches needs to be extended to enhance its applications in the food industry and added its economic value. This study aims to characterize the functional properties of hydrothermally modified starch in terms of swelling power, solubility, and freeze-thaw stability compared to native starch, which affects its performance in food products.

2. Materials and methods

2.1 Materials

The main material in this study was the lesser yam tuber (Dioscorea esculenta L.), collected from a local lesser yam cultivation center in the Banyumas area, Central Java. The study was conducted in July-October 2020. The supporting materials used are distilled water, aluminum foil, Na$_2$S$_2$O$_5$, deionized water.

2.2 Methods

2.2.1 Extraction of lesser yam starch [12]. The extraction of lesser yam starch was carried out using a 0.02% (b/v) Na$_2$S$_2$O$_5$ solution. First, the outer shell of the lesser yam is peeled, the damaged parts are removed, and cut into cubes with a size of about 3x3x3 cm. Then, weigh 1000 g before immersing in 4 L of Na$_2$S$_2$O$_5$ solution with a concentration of 0.02% (b/v) for 10 minutes with a ratio of 1:4 (lesser yam: Na$_2$S$_2$O$_5$). Lesser yam has been soaked for 10 minutes then ground using a blender for 2 minutes. The slurry was separated using a filter cloth to obtain suspended starch in the filtrate. The filtrate obtained is allowed to stand at room temperature for 5 hours for the precipitation process before being rinsed twice with demineralized water and separated from the excess solvent. Then, the solid was dried in an oven (50°C) for 18 hours and ground dry using a blender until a fine powder was formed. The fine powder is sieved with a 60 mesh sieve to obtain lesser yam starch powder.

2.2.2 Modification of heat moisture treatment (HMT)[13]. The lesser yam starch was adjusted to its moisture content by spraying distilled water while stirring until the moisture content was 20%, 25%, and 30%, before heating treatment. The starch was then incubated in the refrigerator at 10°C for 12 hours and then thawed at room temperature. The starch was tightly packed using aluminum foil, then heated in an oven at 110°C for 4, 10, and 16 hours. The starch obtained was dried using a cabinet dryer at 50°C until the moisture content is about 10-12% then ground using a grinder and sieved using a 100 mesh sieve.

2.2.3 Modified annealing (ANN)[14]. Modification of annealing (ANN) was carried out using 100 g lesser yam starch suspended in deionized water with a ratio of starch: deionized water, among others 1:2, 1:3, 1:5 (w/w) and placed in a 1 L glass container and closed with aluminum foil and incubated
in an oven at 50°C for 6, 8, and 10 hours. At the end of the incubation period, the starch suspension was filtered using filter paper, washed twice with water, before drying in an oven at 40°C overnight. The sample obtained was then ground for further analysis.

2.2.4 Analysis of physical properties of starch. The modified starch obtained was analyzed for swelling power and solubility [15], and freeze-thaw stability [16] to obtain selected modified starch at once compared to native starch.

2.2.5 Data analysis. Data were analyzed using one-way ANOVA, Duncan’s multiple range test, to enable posthoc comparisons for the means and correlations (p < 0.05). The ANOVA and Duncan’s multiple range tests were performed using SPSS 11.

3. Results and discussion

3.1 Heat moisture treatment starch

3.1.1 Swelling power. The HMT treatment reduces the swelling power of native lesser yam starch (Table 1). This is in line with [17] who reported that HMT treatment can reduce swelling and breakdown of unpolished red rice starch granules. Swelling power is reduced with HMT treatment because this treatment can increase crystallinity, reduce hydration in starch, increase the interaction between amylose and amylopectin molecules so that it can strengthen intramolecular bonds [7]. The higher the water content used, the lower the granule to swelled, except for the 16 hours of HMT treatment. This shows that water content affects the swelling power decreasing of the HMT starch.

3.1.2 Solubility. In general, HMT treatment reduces solubility compared to native starch, this is in line with research conducted by [17] and [18]. According to [18] during the HMT process, a complex is formed between amylose and amylose, amylose with amylopectin, and amylose with large amounts of fat. The complex formed makes the starch have a stronger and more compact bond so that the amount of amylose leaching during heating is lower [19,20]. The solubility of HMT starch increases with increasing heating time. Whereas in the swelling power, the higher the water content was used, the lower was the solubility. This shows that the water content in HMT modification affects decreasing the solubility of the starch produced.

Table 1. Functional properties of native and modified HMT starch.

| Treatments | Swelling Power (g/g) | Solubility (%) | Syneresis (%) |
|------------|----------------------|----------------|--------------|
| Native     | 12.76e               | 44.43e         | 22.34bc      |
| 4H20%      | 9.89bc               | 5.93a          | 21.13bc      |
| 4H25%      | 7.94a                | 5.42a          | 29.24cde     |
| 4H30%      | 9.21b                | 6.21ab         | 35.3e        |
| 10H20%     | 11.28d               | 12.47d         | 34.48e       |
| 10H25%     | 9.32b                | 9.57c          | 22.83bc      |
| 10H30%     | 9.33b                | 8.72bc         | 24.37bcd     |
| 16H20%     | 10.19bc              | 10.19cd        | 18.81b       |
| 16H25%     | 10.63cd              | 9.28c          | 3.98a        |
| 16H30%     | 9.69bc               | 4.39a          | 31.53de      |

Note: numbers followed by different letters indicate a significant difference at the 5% level.
3.1.3 Freeze-thaw stability. The resistance of modified starch to freezing and thawing conditions can be seen from how much syneresis is. All modification treatments, both heating time and moisture content were not significantly different from native starch except for 4H30%, 10H20%, 16H25%, and 16H30% treatments. Heating treatment for 16 hours with 25% moisture content had the highest freeze-thaw resistance seen from the lowest percentage of syneresis produced. Freeze-thaw stability related to starch retrogradation. The amount of water resulting from syneresis is directly proportional to its tendency to retrograded [21].

3.2 Annealed starch

3.2.1 Swelling power. ANN treatment reduced the swelling power of native lesser yam starch as did HMT treatment (Table 2). However, in the treatment with the highest starch and water ratio (1:5), modified ANN with a duration of 6 and 8 hours had a swelling power that was not significantly different from native starch. According to [22], annealed corn starch has lower swelling power than native starch. Annealing increases the strength between the amylopectin chains which causes the arrangement of the amylose molecules to change. This can prevent amylopectin molecules from developing freely. The longer the duration of ANN is carried out, the lower the swelling power of the starch, indicating that the starch is more resistant to heat. The lowest swelling occurred in the treatment with the lowest water content ratio and the longest ANN time (ANN 10H 1:2). A decrease in swelling can be caused by an increase in starch crystallinity [23].

Table 2. Functional properties of native and ANN modified starch.

| Treatments | Swelling Power (g/g) | Solubility (%) | Syneresis (%) |
|------------|----------------------|----------------|--------------|
| native     | 12.76e               | 44.43e         | 22.34d       |
| 6H1:2      | 11.42c               | 16.91cd        | 21.93d       |
| 6H1:3      | 11.89cd              | 14.52bc        | 15.7cd       |
| 6H1:5      | 12.45de              | 12.33b         | 17.05cd      |
| 8H1:2      | 6.36a                | 15.67cd        | 3.64ab       |
| 8H1:3      | 8.59b                | 12.89b         | 7.25ab       |
| 8H1:5      | 13.06e               | 17.79d         | 1.94a        |
| 10H1:2     | 6.1a                 | 11.79b         | 44.55c       |
| 10H1:3     | 9.28b                | 15.58cd        | 2.3a         |
| 10H1:5     | 11.53c               | 9.18a          | 10.49bc      |

Note: numbers followed by different letters indicate a significant difference at the 5% level

3.2.2 Solubility. ANN treatment on lesser yam starch reduced the solubility compared to its native starch, in line with [23]. This is due to the rearrangement of the starch granule molecular structure. The long heating treatment did not have a significant effect on solubility except for the 10 hour-heating treatment. Heating 10 hours tends to lower solubility than heating 6 and 8 hours. The lowest solubility is in the 10-hour heating treatment with a ratio of starch to water 1:5.

3.2.3 Freeze-thaw stability. Annealing treatment with 6 hours of incubation time and various ratios of water and starch did not show a significant difference in the percentage of starch syneresis but gave a significant difference in the treatment with a heating time of 8 and 10 hours with all ratios of water and starch (Table 2). The highest freeze-thaw stability which was indicated by the lowest percentage of syneresis was shown by 8 hours of heating treatment with a starch: water ratio of 1:5 and 10 hours with 1:3 starch: water ratio. [24] stated that the longer the heating time in annealing will
reduce recrystallization or the tendency to retrograde. The low tendency to retrograde is indicated by a low percentage of syneresis. In other words, it will increase its freeze-thaw stability. The annealing process can increase crystallinity so that the double helix bonds decompose more slowly during gelatinization [25].

4. Conclusion
Native lesser yam starch has functional characteristics in terms of swelling power of 12.76 g/g, solubility of 44.43%, and percent syneresis of 22.34%. HMT and ANN starches have lower swelling power and solubility values than native starch yet have varying percent syneresis values. Hydrothermal modification (HMT and ANN) can increase the stability of starch against heat so that it is suitable for application to food products that require high temperatures in processing.

Acknowledgment
This research was funded by The Directorate of Research and Community Service, Ministry of Research, Technology, and Higher Education, Republic of Indonesia 2020.

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