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Effect of Modification Processes on Cassava Starch: Physichochemical Properties and Expansion Ability of Coated Penute

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Abstract. One of popular peanut-based food product in Indonesia is coated peanuts. Coated nuts are peanuts wrapped in a flour batter and then fried until it dry. Coated peanut quality is influenced by the nature and characteristics of the flour used. Tapioca starch used as a coating on coated peanut products are expected to have a crispness and a good baking expansion. Natural starch has some lack, which it requires a long cooking time and pasta is formed loud and unclear. To improve the performance of the starch used, native starch is modified by physical, chemical or enzymatic process into diversified products with better functionality. In this work, modified starch is obtained by three different modification process, namely process of fermentation using Lactic Acid Bacteria, process of hydrolysis using lactic acid and process of esterification using lactid acid and ethanol. The analysis include the analysis of swelling power, solubility, determination of amylose content, crispness and level of dough development. Modified starch is expected to have optimal crispness and optimal baking expansion. From the result shown modification by hydrolysis give better characteristic of modified starch than the result of esterification and fermentation. Adding UV rays during modification give significant impact for starch. After modification is complete, drying under sunlight or drying with oven has their own strenght and weakness. The optimum variable from this research is wet tapioca starch which modified by esterification with adding UV rays and drying using direct sunlight which have swelling power 21,74 g/g, solubility 18,30%, expansion ability 1457,7%, and crispy starch value 345,8 gf.

Keywords: tapioca starch, crispness, UV rays, sunlight, coated peanuts, expansion ability

1. Introduction

Peanut is one of the most common food material in the world. It is widely produced in tropical and subtropical country. Peanut protein has high nutritional values and contains no cholesterol [1]. Peanut based food product is one of the popular snack in Indonesia. Peanuts are typically boiled, fried or roasted before consumed. One of the most popular peanut-based food is coated nuts for its variance in shape and flavor. Starch used as coating for coated peanuts also contributes on the quality of the product.

Starch is a polymer that consists of two major molecular components, the highly branched molecule known as amylopectin and the primarily linear molecule known as amylose [2]. Chemical structure of starch are found to affect the functional properties of starch [3]. Properties of native starch may not be suitable for all applications. To meet its specific desirable functions, starch can be modified physically, chemically or enzymatically to enhance their positive attributes and minimize their defects [4].

Cassava starch is recommended for use in snacks for improved expansion. Cassava starch can perform most of the functions where wheat starch are currently used [5]. However, the starch granule characteristics needs to be modified so that the ability to expand during baking or frying can be enhanced. Acid modification of starch has been widely used to alter granular structure and increase starch solubility. The modified starch is produced by controlled addition of mineral acid in a water-starch suspension under agitation [6]. The use of alcohol during hydrolysis have been investigated with a view to increase the yield process and to minimize the quantity of acid used [7]. Physical modification also has been used in conjunction with chemical modification of starch.

In this research, the focus will be on the combination of the modification process to produce modified tapioca starch. Three different modification process are applied which are fermentation process using lactic acid bacteria, hydrolysis process using lactic acid and esterification process using lactic acid and ethanol. The aforementioned process then combined with radiation process using UV light during modification and drying process. The modified starch are expected to have optimal crispness and high baking expansion level in order for the starch to be used as a coating for coated peanuts.

2. Materials and methods

2.1. Materials

Commercial cassava starch (Gunung Agung) were obtained from a local market in Semarang (Indonesia). The chemical agents (Merck) were all analytical grade.

2.2. Preparation of lactic acid solution and ethyl lactate solution

For the hydrolysis process, lactic acid solution were prepared by mixing lactic acid (98% concentration) and distilled water with total volume of mixture is 1000 ml (1% v/v). For the esterification process, ethyl lactate solution were obtained by mixing lactic acid with ethanol in a 1:1 mixture ratio. The mixture was allowed to stand for 24 hours before diluted in 1000 ml of distilled water.

2.3. Acid modification and acid – alcohol modification

Cassava starch sample of 1000 g were dispersed in a lactic acid solution/ ethyl lactate solution and then stirred using a magnetic stirrer for 25 minutes (steering speed of 8 scales). For treatment using UV radiation, the mixture were exposed under UV lamp (25 watt) while being stirred. The mixture then filtered with a filter cloth before oven dried or sun dried (9 h).

2.4. Fermentation

Lactic acid bacteria solution for fermentation were obtained by diluting 15 ml lactic acid bacteria starter in 10000 ml of distilled water. Cassava starch sample of 1000 g were dispersed in a lactic acid bacteria solutions and then immersed for 3, 5 and 7 days. The product was filtered with a filter cloth, then placed on a portable solar dryer and dried for 9 hours.

2.5. Swelling Power

Modified starch (0.1 g) was dissolved in 10 ml distilled water in a centrifuge tube. The suspension was heated using a water bath at 60^0C for 30 minutes. The supernatant was separated by using a centrifuge at a speed of 2500 rpm for 15 minutes. Swelling power were determined by using Eqs 1.

$$\text{Swelling power}\left({}^{gr}/_{gr}\right) = \frac{supernatant\ weight}{dry\ sarch\ weight} \tag{1}$$

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2.6. Dough development level

The dough development level was calculated by measuring the volume of dough before and after frying. Dough was prepared by mixing 10 g of starch sample with warm water. Dough diameter was measured before frying (D1) and after frying (D2) to calculate the volume with assumption that expansion is perfectly spherical. Dough development level was calculated using Eqs 2.

$$\text{Volume expansion}(\%) = \frac{V_1}{V_2} \times 100\% \tag{2}$$

V1 = dough volume before frying
V2 = dough volume after frying

2.7. Solubility

Modified starch (0.1 g) was dissolved in 10 ml distilled water in a centrifuge tube. The suspension was heated using a water bath at 60^{0}C for 30 minutes. The supernatant was separated by using a centrifuge at a speed of 3000 rpm for 20 minutes. The percent solubility was calculated using Eqs 3.

$$\%\, Solubility = \frac{dry\ starch\ weight}{supernatant\ volume} \times 100\% \tag{3}$$

2.8. Amylose Content

The amylose contents of the starch samples were determined using colorimetric method.

2.9. SEM

Starch surface characteristics were observed by using scanning electron microscopy (SEM - *JSM-6510 series-JEOL Products*). Starch samples were coated in platinum and examined with magnification of 3000x to determine the surface starch modified photography, cracks, and surface starch films.

2.10. Fracture ability

Fractureability was obtained by *Texture Analyzer* TA.Xt*plus* with *probe* 5 *Blade Kramer Shear Cell*. The data accuired will be in force (gf)

3. Result and Discussion

3.1. Swelling Power

The swelling power for each modified starch and native starch sample are presented in Table 1. In general, native starch has lower swelling power than modified starch [8]. In this experiment, there are some variabels that resulted in modified starch with lower swelling power than native starch. Table 1 shows that swelling power of native starch is 13.21 g/g. There are nine variables which have swelling power content higher than native starch. As example for sixth variable which has swelling power 14.23 g/g after it was modified by hydrolysis method and drying under sun ray. While six other variables have swelling power content lower than native starch. As example, the second variable has swelling power of 11.80 g/g after it was modified with esterification method and drying under sun ray.

Table 1 shown that there is no significant impact of the tapioca starch condition (dry starch and wet starch) on swelling power. For the same modification process, swelling power of the dry starch is 11.09 g/g, while for wet starch it is 15.02 g/g. On the other hand, based on modification process, swelling power of hydrolysis starch is higher than esterification starch. The swelling power of the 8th variable (15,02g/g) is higher than the 4th variable (13.91g/g).

In Table 1, starch sample with the highest swelling power is starch that has gone through modification with addition of UV radiation. It shows in Table 1 on the 9th variable (21.39 g/g), 10th variable (21.74 g/g), 11th variable (20.55 g/g) and 12th variable (21.56 g/g). UV rays radiation have a big influence for swelling power. Then based on drying process, swelling power of oven dried starch is higher than sun dried starch. It shown in the third variable (13.6 g/g) that is higher than the fifth variable (11.36 g/g). For fermentation process, the longest fermentation time results in the highest swelling power among the other fermented starch. Fermentation in seven days give higher swelling power among the other fermented starch, it is 15,00 g/g.

The differences on swelling power is because of the difference of each amylose and amylopectin content on the modified starch. There is negative correlation between amylose content and swelling power because amylose can make lipid complex in the starch, so it will inhibit swelling [9, 10]. Since amylopectin is primarily responsible for granule swelling [11], higher amylose content would reduce the concentration of swelling fraction of starch and thus decrease the viscosity. In summary, swelling of starch is mainly a property of amylopectin, while amylose acts as a diluent.

Table 1. Swelling power, solubility and expansion ability of modified starch

Variable	Swelling Power (g/g)	Solubility (%)	Dough Level (%)
Dry starch, esterification, sunray drying	11.09	15.63	1064.8
Wet starch, esterification, sunray drying	11.80	16.20	1023.8
Dry starch, esterification, oven drying	13.06	14.37	766.0
Wet starch, esterification, oven drying	13.91	14.39	984.0
Dry starch, hydrolisis, sunray drying	11.36	15.90	1262.6
Wet starch, hydrolisis, sunray drying	14.23	16.94	1044.1
Dry starch, hydrolisis, oven drying	14.85	14.93	749.6
Wet starch, hydrolisis, oven drying	15.02	16.75	888.8
Dry starch, esterification + UV, sunray drying	21.39	17.40	834.7
Wet starch, esterification + UV, sunray drying	21.74	18.30	1457.7
Dry starch, hydrolisis + UV, sunray drying	20.55	16.85	1106.8
Wet starch, hydrolisis + UV, sunray drying	21.56	16.20	1171.9
Dry starch, 3 days fermentation	13.21	13.00	185.4
Dry starch, 5 days fermentation	13.26	17.00	250.0
Dry starch, 7 days fermentation	15.00	22.00	569.0
Native starch	13.28	13.45	179.0

3.2. Amylose Content

The result of amylose content in the modified starch is shown in table 2. The native starch have the highest amilose content, 18,90%. Modified starch has lower amylose content than native starch [12]. The fermented starch has the lowest amylose content, it is 14,25%. Fermented starch has the lowest amylose content because in fermentation the starch granule will be hydrolised by microba to produce organic acid. The organic acid mainly lactic acid plays a major role in degrading the amylose. Amylose content and proportion of outside chains of amylopectin are thought to be major players in the water retention capacity of gel [13]. This amylose present in the starch is responsible for the film forming capacity [14]. Because, the formation of starch based edible films involves two process namely, gelatinization (swelling, disruption and leaching of soluble components (amylose) of the starch) and retrogradation (reduction in the solubility of dissolved starch). Positive and negative significant correlations have been reported between swelling power with amylopectin unit chain ratio and amylose content respectively [15].

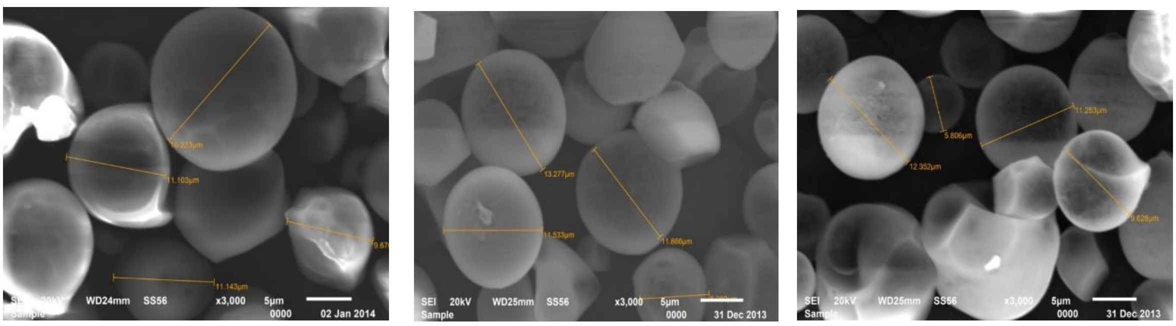
Amylose content increased after the starch was modified. This result is in contrast with our result where modified starch has lower amylose than native starch. A high amylose content has usually been linked to a greater tendency to retrogradation in starches, showing higher peak viscousities with consequently greater breakdown [16].

Table 2. Amylose content of modified starch

No	Variable	Amylose content (%)
1	Native Starch	18.90
2	Wet starch, esterification + UV, sunray drying	17.18
3	Dry starch, hydrolisis, sunray drying	16.03
4	Wet starch, hydrolisis + UV, sunray drying	15.13
5	Wet starch, esterification, oven drying	14.86
6	Dry starch, 7 days fermentation	14.25

3.3. SEM

Scanning electron microscopy has been used to observe the surface granule morphology of starch with a magnification of 3000 times. The sample used in the SEM analysis is unmodified cassava starch (native starch), starch after esterification process (starch ester), and starch after hydrolysis process (hydrolyzed starch). Fig 1 shows the surface structure of native starch (a), starch esters (b), and hydrolyzed starch (c).



(a) (b) (c)

Figure 1. Surface morfology of starch (3000x) for native starch (a), starch esters (b), and hydrolised starch (c)

Fig 1 shows that the cassava starch after and before modification has not changed since the modifications performed under the gelatinization temperature. Both have a structure that is round and have irregular pieces at the ends. The size of both types of particles varies. Native starch has a particle size averaging between 9,670 - 16,223 µm, while the starch ester having an average particle size smaller than native starch which is between 8,080 - 13,277µm and the hydrolise starch having average particle size between 5,806 - 12,352 µm.

From the result, granule size of esterified starch is bigger than hydrolysis starch. Starch particle size and the structure of starch depend on water absorption and gelatinization. In general, the acid modification leads to an increase in the crystallinity of amilodextrin because the amorphous region is hydrolyzed. Similarly, in the presence of alcohol the degradation probably occurs primarily in the amorphous areas of starch granules [17]. The rate of water absorption increases with decreasing particle size because relative surface area increases when volume is reduced. During the gelatinization of the starch granules, the released amylose and amylopectin molecules interact mainly through hydrogen bonds. Modified starch disturbed the formation of double helices of amylose with amylopectin branches, and then reduced the interaction between amylose and amylopectin molecules making the starch film flexible. The interaction between the amylose and amylopectin molecules contributed to the film formation, but were so strong that the starch films were readily brittle and rigid [18].

3.4. Dough development level

The dough development level for each modified starch and native starch sample are presented in Table 1. Baking expansion ability can be correlated with the dough development level. The good baking expansion ability of modified starch was also associated with high swelling power and solubility [19].

Table 1 shows that the highest expansion volume is starch that has gone through esterification process which has expansion of 1457.7 %, whereas the lowest expansion volume is 3 days fermented starch which has expansion 185.4%, native starch as comparator has expansion volume of 179 %. The modified starch with esterification and hydrolysis process are not significantly different, each modified starch have expansion volume of 1066.8% and 1044.1% respectively.

Expansion ability of modified starch are influenced by its amylose content. Amylose can binds water so that higher amylose content on starch the better it will be since it will increase expansion volume [20]. Expansion ability level and snack texture are influenced by amylose and amylopectin ratio [21]. Starch with higher amylopectin content results on the fragile structure, whereas amylose content make a more rigid structure and hard to crack .

Sufficient reaction with UV light causes partial depolymerization of amylose molecules and form hydrogen-bonded network structure. The network structure can absorb and store water during gelatinization process. UV drying gives enough energy to help improve starch properties development. Increases in specific volume is caused of the increases amount of water lost during the frying process. At starch gelatinization due to heating, the water absorbed is evaporated because of the high pressure caused by the expansion of the current driving force [22]. The process of water evaporation during frying process causes volume expansion increased.

3.5. Solubility

As for the percent solubility of each starch sample, native starch as the comparator has percent solubility of 13.45%. Results showed that solubility of modified starch is higher than native starch. This is shown in Table 1, where each variable except for the 13th variable have higher solubility than native starch. As example variable 2 which have solubility of 16,20% after it was modified by esterification method and drying under sunray. These results are in agreement with the other previous report that stated the application of modification process on starch increased levels of swelling and solubility thus resulted in higher value of swelling power and percent solubility than their native counterparts [10]. Higher solubility of starch maybe due to the degradation of starch at higher temperatures. Table 1 shown that there is no significant difference in solubility based on tapioca condition (dry starch and wet starch). For example on fifth variable (15.90%) is lower than sixth variable (16.94%). On the other hand, based on modification process, solubility of hydrolysis starch is higher than esterification starch. It shows that the fifth variable (15.9%) is higher than first variable (15.63%).

In Table 1, addition of UV radiation results in higher solubility than the other variables. It shows on the 9th varibale (17.4%), 10th variable (18.30%), 11th variable (16.85%) and 12th variable (16.2%). UV rays radiation have a big influence for solubility. The treatment of starch using UV light induces change in its functional properties. UV radiation increases water binding capacity and solubility [23]. Those changes can also occurs after treatment with natural sunlight. Based on drying process, solubility of drying under the sun is higher than drying using oven. The second variable (16.20%) is higher than fourth variable (14.39%). For fermentation, the starch with longest fermentation time gives better results than the other fermented starch. Fermentation in seven days give higher solubility among the other fermented starch, it is 22.00%.

The differences on the modified tapioca starch is caused by the differences of each amylose and amylopectin content in the starch. When starch granules are heated in a water suspension, they swell to different degree depending on the temperature and spread off to the outside media [24]. First molecule that leach out is amylose molecule which has shorter chain. There is positive correlation between amylose content and solubility of starch. Higher solubility of starch can be attributed to more solubilizing and leaching of polymers from starch granules with weaker rigidity as heated and broken at high temperature [25].

3.6. Fracture ability

Crispness is textural attributes that associated with the freshness and firmness of food products. Crispness is associated with mechanical force required to compress food until it fractures into smaller pieces, thus it relates to fracture aability of a structure. [26] Instrumental measurements are generally preferred to evaluate the attributes related to crispness. For this experiment, the crispness value measurement is only subjected to the modified starch with the optimum variable. The modified starch that undergo esterification + UV process and dried under sunrays is measured using Texture Analyzer, the result shows that the modified starch has high crispness level that is 345.8 gf.

4. Conclusion

For this research starch condition gives no significant impact on the properties of the modified starch. In general hidrolysis modification results in better phsycochemical, rheology, and expansion ability level characteristic of modified starch. Addition of UV radiation during hydrolisis and esterification process give significant effect on phsycochemical, rheology, and expansion level characteristic starch modified. For drying variabel after modification, drying using natural sunlight and oven have advantage and disadvantage for each process. However, the overall optimum results in variable of the modified starch that has gone through acid – alcohol modification with addition of UV radiation and dried using natural sun rays. The optimum variable results in modified starch with swelling power of 21.74 (g/g) and solubility of 18.3%. The dough development level of the starch is 1457.7% with crispy starch value of 345.8 gf.

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