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Exploration of Breadfruit, Jicama, and Rice Starches as Stabilizer in Food Emulsion

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***Abstract*— The aim of this research was to investigate the ability of three native starches from Indonesia to stabilize oil in water emulsion with and without the addition of lecithin as surfactant. Breadfruit, bengkuang (jicama), and rice starches were extracted from local sources in Banda Aceh - Indonesia. Two variables studied were type of starches and the amount of oil added into emulsion (15 and 25%). Proximate analysis showed that the starch content of breadfruit, jicama and rice were 77.57, 67.41, and 80.51% respectively and the amylose content were 20.50, 16.5, and 13.6%. Results showed that the *emulsification index* (EI) of emulsion prepared with jicama and rice starches were lower than the EI of emulsion stabilized by breadfruit starch. However, the viscosity of breadfruit emulsion was higher than the other two emulsions. Storage stability test in room temperature also demonstrated that oil in water emulsion made from breadfruit starch had the lowest separation rate over storage period compared to jicama and rice emulsions. Overall, stabilization of 25% oil in breadfruit emulsion was slightly better than addition of 15% oil where the visible boundaries or serum layer of the emulsion was in the range of 5-6 ml at the end of storage test. Breadfruit starch was further modified by reacting it with octenyl succinic anhydride (OSA) to produce OSA-modified breadfruit starch. The degree of substitution (DS) of OSA modified breadfruit starch was 0.0231. OSA-modified breadfruit starch is highly potential to be used as food emulsifier and therefore studied further to examine its ability to stabilize oil in water emulsion.**

***Keywords*— breadfruit starch; rice starch; jicama starch; OSA-modified Starch; emulsion stability**

I. Introduction

Starch is the storage energy in plants and has becoming one of the most abundant organic materials for food and industrial resource. Starch is synthesized in amyloplasts of seeds, grains, roots and tubers of many plants and has been used for the main source of carbohydrate for human, animals, and microorganisms [1]. Starch consist of two polymers i.e., amylose and amylopectin which has been applied widely in food industries for many purposes.

One of the most important roles of starch is as stabilizer particularly it functions as texture modifier for various food products. Emulsion is the basis where stabilizer is used to stabilize an immiscible liquid which is dispersed into another liquid. A particle-stabilized emulsion usually referred to as Pickering Emulsion.

Native starch granules can be used as stabilizer in pickering emulsion system. At least three types of starches have successfully tested (rice, waxy maize, and wheat starches) as a sole emulsifier for liquid paraffin emulsion [2]. Base on this previous investigation, this study was conducted to explore the ability of Indonesian native starches i.e., breadfruit, bengkuang (jicama), and rice starches to be used as stabilizer in oil in water (O/W) emulsion.

The starches were characterized before emulsification process. Two levels of oil additions examined were 15% and 25% with and without addition of lecithin as surfactant. Monitoring visible boundaries formed during emulsion storage, accelerated test by centrifugation, measurement of emulsification index, observation of droplet size and distribution microscopically and viscosity analysis were the analytical procedures that were investigated.

II. Materials and Methods

A. Materials

Breadfruit, jicama, and rice as raw materials for starches were purchased from local market in Banda Aceh. The vegetable oil used was palm oil which was bought from supermarket in Banda Aceh, Indonesia. Lecithin, alcohol 96%, ethanol, diethyl ether, chloride acid, NaOH, anthrone, sulfate acid, and pure glucose were all of analytical grade. Double distilled water was used for emulsion preparation as well as for analysis.

B. Methods

1) Preparation of starches: Breadfruit and jicama were sorted, peeled, cleaned with water, and then cut and re-cleaned, whereas rice was washed. Suspension of those starches was produced by grinding them into puree then extracted with distilled water and the slurries left overnight at room temperature. The supernatant was separated and the starches were dried in the oven for 7 hours at 50^{o}C. The dried starches were grounded by hammer mill then sieved using 80 meshes perforated strainer. Three types of starches were analysed for the moisture, ash, and starch contents by the AOAC method [3]. Starch determination was started by hydrolysing the starch with acid, following determination of total reducing sugar and calculating the starch contents by 0.9 Factor. The amylase content of each starch was measured by IRRI method.

2) Preparation of emulsion: Each 1000 ml emulsion was made by 60% water and 40% total solids [4]. First, emulsion was initially made by homogenizing 337 gram of breadfruit, rice and jicama starch into 600 ml water, followed by addition of 15% of palm oil, and 5% of emulsifier from the total oils (lecithin). The mixture was homogenized until the starch was completely dispersed. The second emulsion is fine mixture of 295 gram of each starch dispersed into 600 ml water, continuing with addition of 25% palm oil, and 5% of lecithin from the total oils. Finally, each emulsion was mixed in a 2L beaker glass, homogenized with T25 Digital Ultra Turrax for 18,000 rpm for 3 minutes in room temperature.

For emulsion without emulsifier (lecithin), all preparation was the same as above procedures except for the addition of lecithin as surfactant. Emulsions stability were analysed by monitoring the visible boundaries formed during storage at room temperature, measuring the emulsification index after accelerated test by centrifugation, observing emulsion droplet size and distribution by light microscope, and viscosity analysis.

3) Emulsification Index: Measurement of emulsification index (EI) was based on the emulsion separation after accelerated test by centrifugation. Briefly, 10 ml of emulsion was centrifuged at 5000 rpm for 5 minutes. Emulsification index was calculated from Eqs. (1), where *Vo* was volume of emulsion and *V* was volume of cream phase separated in the centrifuge tube [5] in [6].

$$Emulsification\ Index = \left(\frac{V}{Vo}\right) x\ 100\% \qquad (1)$$

4) Droplet size of o/w emulsion: Some droplet sizes and distribution were observed microscopically to see their uniformity in emulsion. One droplet of emulsion sample was place on the object glass and covered. Digital Microscope Olympus BX41 DP12 was used for the droplet evaluation with 40x magnification.

5) Viscosity: This analysis was followed the AOAC method (1995) using Brookfield viscometer. One hundred ml of each emulsion was poured into a beaker glass then the viscosity was measured by stirring the spindle at 100 rpm until the value was stable [7].

6) Monitoring visible boundaries during storage: The visible boundaries of emulsions were observed following the method developed by [8]. Each emulsion sample was filled into a glass cylinder (3/4 of the glass height) then the separation of serum layer, cream layer, and sedimentation of starch were recorded over a period of time (48 hours). The glass cylinders were covered, stored in room temperature and monitored periodically for emulsion separation.

7) Breadfruit Starch Modification: Modification process was following the method described by [9]. One hundred and twenty five gram of breadfruit starch was dissolved in 475 ml distilled water and pH was adjusted using NaOH to 8.5. OSA solution (97%) was added dropwise into the mixture which was continuously stirred. The process was continuing for two hours and stopped by decreasing pH by addition of HCl solution. The mixture washed thrice and dried at 40°C for 24 hours.

III. Results and Discussions

A. Starch Characteristics

The characteristics of three starches are provided in Table 1. Rice starch has a higher starch content (80.51%) compared to jicama and breadfruit starch (67.41% and 77.57% respectively), but its amylose content is the lowest. The differences in starch and amylose contents might be caused by differences in the varieties, genetics, plant age, and environmental growth conditions [10].

B. Emulsification Index

Calculation of emulsification index (EI) was done to measure emulsion stability. This test was actually the acceleration examination using centrifugal method. Centrifugation time and speed weaken the emulsifier protection toward the dispersion of oil droplets and cause the droplets to coalesce thus forming larger particles. As a result, the emulsion can be separated into two distinct phases, a layer of cream and transparent layer which usually called serum layer. Furthermore, emulsification index was measured by comparing the volume of cream layer to the volume of initial emulsion before centrifugation.

TABLE I
THE CHARACTERISTICS OF RICE, JICAMA AND BREADFRUIT STARCHES

Starch Type	Color	Moisture (%)	Mineral Content (%)	Starch Content (%)	Amylose Content (%)
Rice Starch	White	7.49	0.10	80.51	13.6
Jicama Starch	White	7.79	0.08	67.41	16.5
Bread-fruit starch	Very light yellow	11.37	0.19	77.57	20.5

The result of emulsification index (Figure 1) shows that emulsions with 25% added oil had higher emulsification index compared to emulsions with addition of 15% oil. Breadfruit starch emulsion with 25% added oil exhibited the highest emulsification index (18%). Interestingly, the EI of breadfruit emulsions prepared without lecithin (Table 2) were lower than the values in Figure 1.

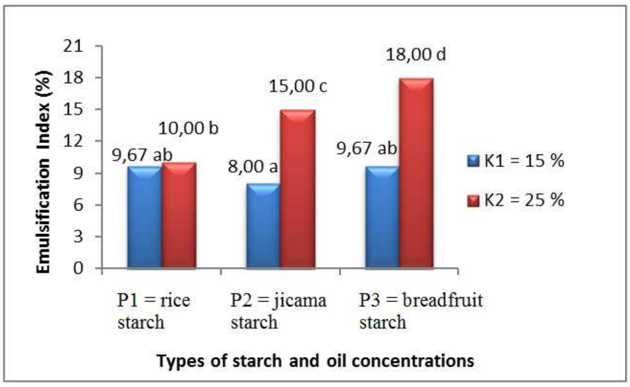

Fig. 1 Emulsification index (CI) of emulsions with addition of lecithin measured by centrifugal method

TABLE II
EMULSIFICATION INDEX OF EMULSION WITHOUT LECITHIN

Starch Type	Oil Concentration	
	15%	25%
Rice Starch	5%	18%
Jicama Starch	10%	15%
Breadfruit starch	5%	6%

On the other hand, the lowest emulsification index in Figure 1 was 8% which obtained from 15% jicama emulsion and this value was lower compared to the same emulsion but without lecithin (10%). As the percentage of emulsification index increases, the emulsion stability decreases. Increasing emulsification index indicates high separation between the dispersed phase and the external phase, which also shows less stable emulsion.

McClements (2007) explained that the accelerated stability test by centrifugation usually conducted to predict the long term creaming stability of emulsion in a short time. However, the author also added that the results should always be treated cautiously because the factors that determine droplets movement in gravitational field (normal storage condition) may be different from those that are involved in centrifugal field. These mean that emulsion stability from the centrifugal test results can be different from the real stability when emulsion stored at room temperature for a period of time.

C. Emulsion droplet size and distribution

This analysis was done just to evaluate the approximate droplets sizes and their distribution in emulsion. Therefore, only two figures from microscope observation are provided. Theoretically, the smaller oil droplets lead to the better spread in the continuous phase.

Figure 2 shows that the round yellow images are the oil droplets while the black particles are the starch granules. The droplet sizes are varied ranging from less than 5 µm to about 28 µm. The figure clearly indicates that the starch granules surrounding the oil droplets thus stabilize the emulsion.

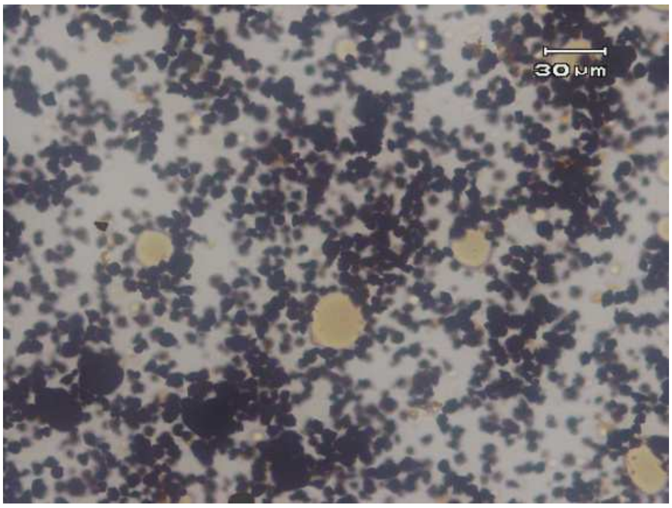

Fig. 2 Rice Starch Emulsion with 15% oil concentration

Figure 3 illustrates the emulsion system prepared by adding 25% oil into breadfruit starch dispersion. Compared to previous Fig 2, the average oil droplets are smaller (±15 µm) and the droplets are distributed more evenly in the system. However, the starch granules are bigger than the rice starch granules. Figure 3 confirms the storage stability test of breadfruit emulsion and explains why this emulsion was quite stable compared to other emulsions.

Emulsion system with an average droplet diameter of 5 µm has good stability if supported by the high viscosity of the external phase. The results show that the emulsions with the addition of 25% oil produce larger oil droplets particularly for emulsions made from rice and jicama starches (figures are not shown). This finding might be caused by the amount of lecithin (emulsifier) added was not enough to arrange themselves onto interfacial region of the oil droplets that formed after homogenization.

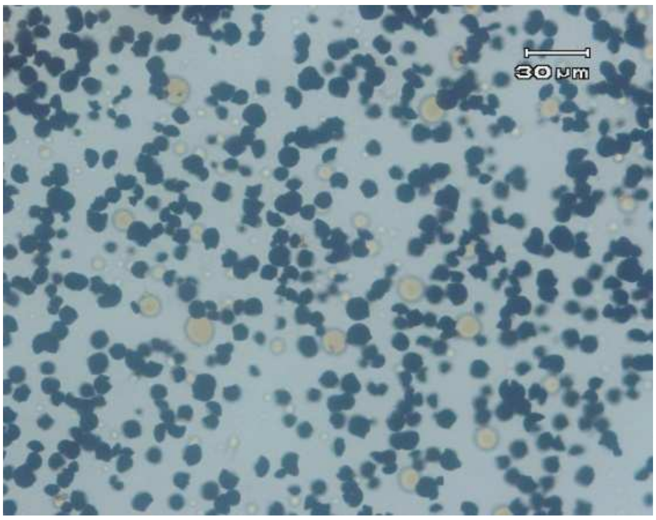

Fig. 3 Breadfruit Starch Emulsion with 25% oil concentration

In addition, low solubility of native starches in water also influenced the stability. Such emulsion systems are not able to maintain droplet dispersion for a long time, resulting in the aggregation of oil droplets which in turn accelerate the process of coalescence and flocculation.

D. Viscosity Measurement

Viscosity is a value that indicates the viscosity level of the dispersing medium of an emulsion system. In the o/w emulsion system, the addition of lecithin will increase the viscosity to form a more stable emulsion. The result of viscosity analysis showed that starch types affect the emulsion viscosity (Figure 4).

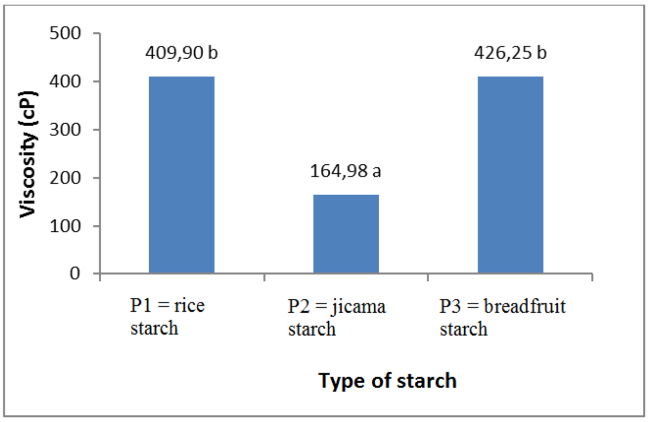

Fig 4 Effect of starch types on the emulsions viscosity

Figure 4 indicates that the viscosities of breadfruit and rice starches are significantly higher than jicama starch. The higher number of hydroxyl groups within starch molecules will increase the starch's ability to absorb water therefore the viscosity of the continuous phase will also increase. In general, starches with high amylose content would highly soluble in water. Amylose has a greater ability to form hydrogen bonds than amylopectin [11]. The breadfruit starch has a higher amylose content compared to other two starches. Therefore, it exhibited a higher viscosity than jicama and rice starches. High viscosity emulsion increases the stability of o/w emulsion during storage.

E. Storage Stability Test

Figure 5 shows the changes of emulsions stability during storage for up to 48 hours. Emulsions were stable right after homogenization process and started to separate few hours after that.

(a) (b)

Fig. 5 Emulsion stability during storage: a). 0 hours; b). 48 hours

Figure 6 shows that for emulsion with 15% added oil, rice starch emulsion was separated faster where visible layers was 16.67 ml after 3 hours, followed by jicama starch. In comparison, Fig. 7 shows that emulsion prepared with rice starch and 25% added oil was creamed slower than the 15% added oil. The breadfruit starch emulsion considered as the most stable emulsion for both 15% and 25% oil concentration where the visible layers formed only 5-6 ml after more than 48 hours storage.

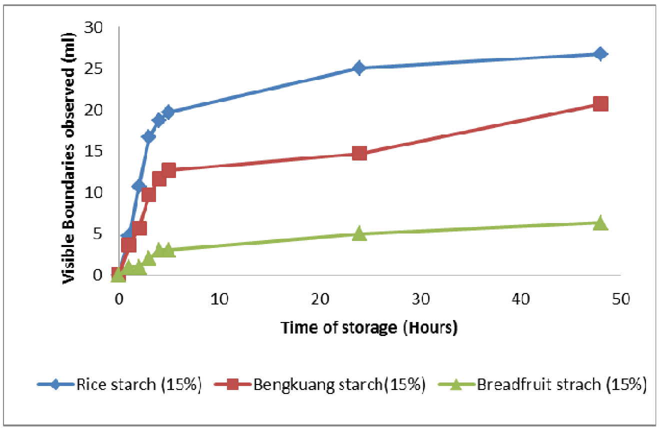

Fig. 6 Changing height of serum layers during 48 hours storage for emulsion with 15% added oil.

Breadfruit starch contains the highest amount of amylose compared to other two starches thus the emulsion viscosity formed also high. Starch granules are able to stabilize emulsion via thickening mechanism i.e., increasing the viscosity of continuous phase (water). Therefore, breadfruit starch was able to maintain the emulsion stability during storage due to its high viscosity.

The high viscosity of breadfruit emulsion successfully controlled the oil droplets movement and prevents droplets coalescence and flocculation. In addition breadfruit starch seems to have natural surfactant such as saponin [12]. Saponin is a type of surfactant from plants which responsible to decrease water surface tension due to its hydrophilic and hydrophobic sides.

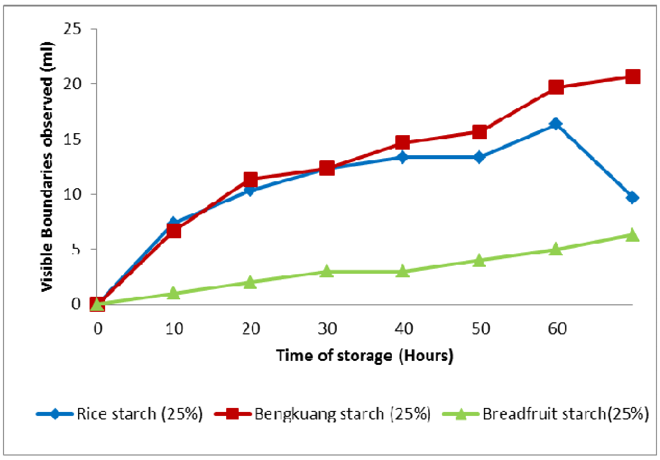

Fig. 7 Changing height of serum layers during 48 hours storage for emulsion with 25% added oil

F. *Breadfruit Starch Modification*

The research results proved that native breadfruit starch is potential to be used as texture modifier to stabilize oil in water emulsion compared to jicama and rice starches. Therefore, to further improve its ability as emulsifier, breadfruit starch was modified using octenyl succinic anhydride (OSA). Starch modification with OSA is chosen because this method has been used widely in food industries.

The modification process resulted the degree of substitution (DS) of OSA-modified breadfruit starch was 0.0231. Chemically, modified starches with OSA are obtained from esterification reaction between starch hydroxyl group and octenyl succinic anhydride. OSA starch allows the hydrophilic sites gain hydrophobic parts in the form of octenyl groups. Therefore the whole molecules of starch will have amphiphilic character [13].

IV. Conclusions

Native rice, jicama and breadfruit starches without addition of lecithin as surfactant are able to be used as stabilizer in O/W emulsion at least for 2 days. Although emulsion separated into two phases (serum layers and emulsion), there were no oiling off in any emulsion made.

Breadfruit starch stabilizes emulsion better than the other two starches as proved by parameters tested. The EI values for breadfruit emulsions without lecithin were only 5% and 6% for 15% and 25% oil addition, respectively. The visible boundaries or serum layer of the emulsions were in the range of 5-6 ml at the end of storage test both for 15% and 25% oil addition.

The stability also supported by observation using light microscope where the droplets size were smaller and distributed evenly in emulsion. Further modification of breadfruit starch resulted OSA-modified breadfruit starch with the DS of 0.0231.

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