

# Preparation of Indonesian taro starch particles via precipitation process

**Reynaldi Januar Wantar, Dave Mangindaan\***

<sup>1</sup> Food Technology Department, Faculty of Engineering, Bina Nusantara University, Jakarta, Indonesia 11480

\*dmangindaan@binus.edu

**Abstract.** Indonesia is one of tropical agricultural countries with abundant food sources. One of the unexplored food sources is taro, which acts as promising starch sources for further studies in the fields of food science and also nanotechnology. Starch is a combination of amylose and amylopectin that forms polysaccharide (a type of carbohydrate), found in several tuber plants, with a competitive market share of 48.5 million tonnes, equals to 15 billion euro globally. Furthermore, there are a lot of potential of starch in the biotechnology and pharmacy fields, which are still employing starch in forms of nanoparticles as the supporting materials for the applications in tissue engineering, as excipients for tablets and drug delivery, along with possibility as a candidate for fat replacer. In this research starch particles were prepared via nanoprecipitation method by using NaOH, urea and ethanol. The precipitated starch particles were then dried via two different processes, which are inside a Petri dish (in an opened and a closed dish), in an atmospheric oven at 45°C for 16 h. The produced starch particles were characterized by using SEM (scanning electron microscopy) and FTIR (Fourier transform infrared spectroscopy). From this study, we have fabricated starch nanoparticles with the characteristic diameters of 203-596  $\mu\text{m}$  (based on SEM analysis) via nanoprecipitation using NaOH, urea, and ethanol, which were dried in a closed Petri dish. Chemical characterization of that particular starch particles has shown that it is a hydrolyzed starch, having non-amorphous structure, with finger prints at wavenumbers of 3350  $\text{cm}^{-1}$  and 1002  $\text{cm}^{-1}$  based on FTIR analysis.

**Keywords:** taro, starch, nanoparticles, nanoprecipitation, non-amorphous

## 1. Introduction

Starch is a combination between amylose and amylopectin to form polysaccharide [1]. Starch is also found in the root, stem, and seed of cereal plants such as rice, corn, wheat, tapioca, and potato. Globally, the main source of starch is from maize or corn (82%), wheat (8%), potato (5%), and cassava (5%) [2]. In the early 2000s, the market share of starch is forecasted to reach 48.5 million tonnes, equals to 15 billion euro, which is very interesting not just financially, but also for research and development [3]. The applications of starch in the biotechnology and pharmacy fields are wide open. Those fields are still employing starch nanoparticles as the supporting materials for the applications in tissue engineering [4], as excipients for tablets and drug delivery [5]. There is also a possibility for starch, especially the Indonesian native taro starch, as a candidate of fat replacer for the application in the food technology field. Indonesia as a agricultural tropical is a producer of those



aforementioned starch sources. However, there are quite some alternative starch sources that have not been fully studied (underutilized starches), where one of them is Indonesian taro starch.

There are some methods for preparing Indonesian taro starch nanoparticles, with several losses in the aspects of quantity, quality, or both. Starch nanoparticles with diameter of 20-50 nm have been synthesized via fabrication of starch-butanol complex, followed by enzymatic hydrolysis [6], but there is a product loss in the hydrolysis step, up to 90%. As an alternative of this procedure, there is also a physical treatment method, by using high pressure homogenization with 100% yield of nanoparticles [7]. However, the diameter of the homogenized starch nanoparticles is not uniform. With those aforementioned limitations, then it is required to have a reliable starch nanoparticles fabrication method, with adequate yield, homogeneous diameter, and also take an important consideration of the biocompatibility of the nanoparticles in the food applications. A promising procedure for production of Indonesian taro starch nanoparticles is nanoprecipitation method, from sago starch [8]. In this study, we employed the nanoprecipitation process, with some modifications, in order to fabricate Indonesian taro starch nanoparticles.

## 2. Methodology

The process of fabrication of Indonesian taro starch particles based on methods by Chin et al [8] who utilized several materials such as Indonesia taro starch, distilled water, ethanol (AR grade), NaOH, urea, and surfactant Tween 80. Firstly, starch 10 g, urea 10 g, and NaOH 8 g were prepared. Afterwards, those were dissolved in 97.2 mL distilled water. A 20 mL aliquot of the prepared starch solution was then taken and put into 400 mL ethanol or 800 mL ethanol to form Indonesian taro starch precipitates. The starch precipitates solutions were then separated by using centrifuge (3000 rpm, 15 mins), to remove the supernatant and to recover the suspended Indonesian taro starch particles.

The recovered particles were washed three times by using AR grade ethanol to remove the residues of NaOH and urea. The suspended Indonesian taro starch particles were then transferred dropwise into 50 mL ethanol containing 5 mL surfactant, under constant stirring for 30 mins. The solution containing Indonesian taro starch was filtered by using Whatman 41 filter paper, and put into the Petri dishes. The Indonesian taro starch particles inside those Petri dishes were then dried in an oven, with conditions tabulated in Table 1. The reason for using atmospheric oven is to widen the possibility for low-educated, or poorly-educated people in Indonesia to use inexpensive apparatus to fabricate Indonesian-based starch nanoparticles. The evaluation of particles size was conducted by using digital micrograph, and SEM (scanning electron microscopy) with magnification of 100× to 1000×. Furthermore, chemical characterization was also carried out by using FTIR (Fourier transform Infrared Spectroscopy).

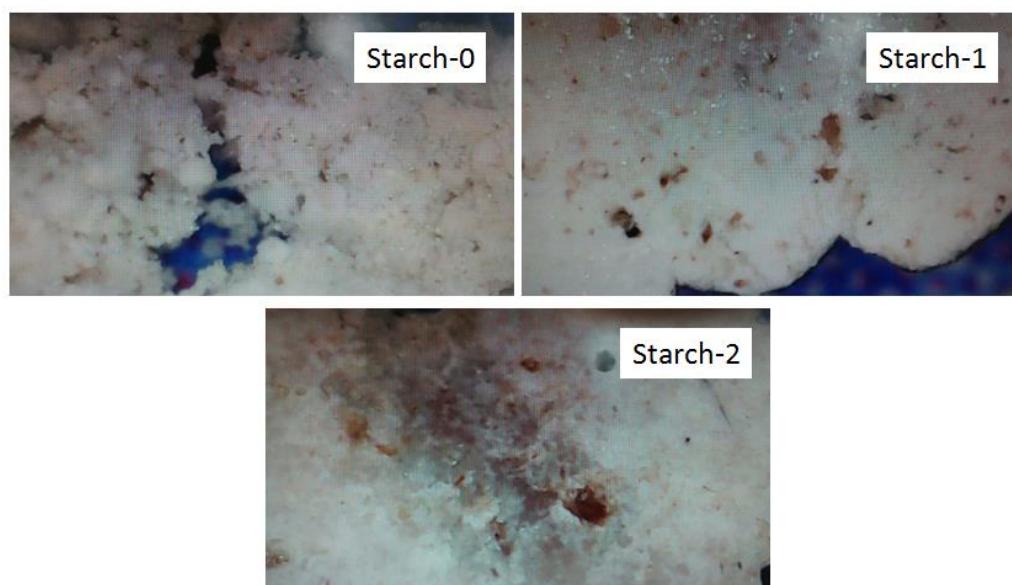
**Table 1. Conditions of drying of Indonesian taro starch particles**

Name	Condition
Starch-0	Native starch without treatment of immersion in ethanol+urea+NaOH
Starch-1	Starch with treatment of immersion in ethanol+urea+NaOH, dried in an atmospheric oven at 45°C for 16 h, in an opened Petri dish (covered with manually perforated aluminum foil)
Starch-2	Starch with treatment of immersion in ethanol+urea+NaOH, dried in an atmospheric oven at 45°C for 16 h, in a closed Petri dish (with glass cover)

## 3. Results and Discussion

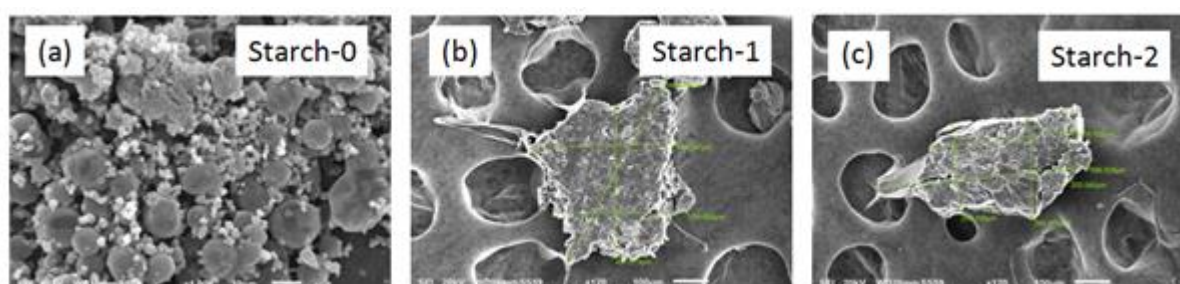
In this section, we will discuss the results of the physical characterizations of the Indonesian taro starch particles by using digital micrograph and SEM, and chemical characterization by using FTIR analysis. The physical appearances of the Indonesian taro starch particles are not significantly different when observed by using digital micrograph, as shown in the Figure 1. The only apparent difference is some spots having color changes from white turned into brown, which were suspected as the side

effect of oxidation during the drying process. Therefore, a further detail analysis by using SEM characterization must be carried out.



**Figure 1. Physical appearance of Indonesian taro starch particles by using digital micrograph**

Based on the morphology analysis by using SEM shown in Figure 2, it could be observed that the particles of Starch-0 (native, no treatment) do not attain agglomeration, while Starch-1 and Starch-2 get granulated, resulting in much larger particle size of samples Starch-1 and Starch-2, compared to that of Starch-0. This phenomenon is could be possibly caused by the atmospheric drying process (not in the vacuum condition), impacting negative effect of the ambient humidity to agglomerate Starch-1 and Starch-2.



**Figure 2. SEM characterizations of Indonesian taro starch particles, at various magnifications, (a) Starch-0, at 1000 $\times$ , (b) Starch-1, at 120 $\times$ , (c) Starch-2, at 120 $\times$ .**

To further recognize the effect of the drying conditions, we must pay attention to the morphology of the SEM analysis for Starch-1 and Starch-2. Generally, the condition of the Indonesian taro starch dried inside a closed Petri dish (Starch-2, size 203-596  $\mu\text{m}$ ) is smaller than the starch dried inside an opened Petri dish (Starch-1, size 376-581  $\mu\text{m}$ ). This finding indirectly suggests that the drying of the Indonesian taro starch particles inside a Petri dish should be conducted in a closed condition, in order to avoid physical, chemical, and biological contamination inside the oven or dryer. Thus, the Indonesian taro starch particles which were dried in closed compartment provide smaller particle size, compared to that of opened Petri dish. This result is useful to be identified as a preliminary step for the optimization of the preparation process for nanosized Indonesian taro starch particles in the future.

To obtain more comprehensive perspective on the effect of the preparation process of the Indonesian taro starch particles (involving immersion in urea, NaOH, and ethanol), the produced

Indonesian taro starch particles were chemically characterized by using FTIR analysis, as shown in Figure 3.

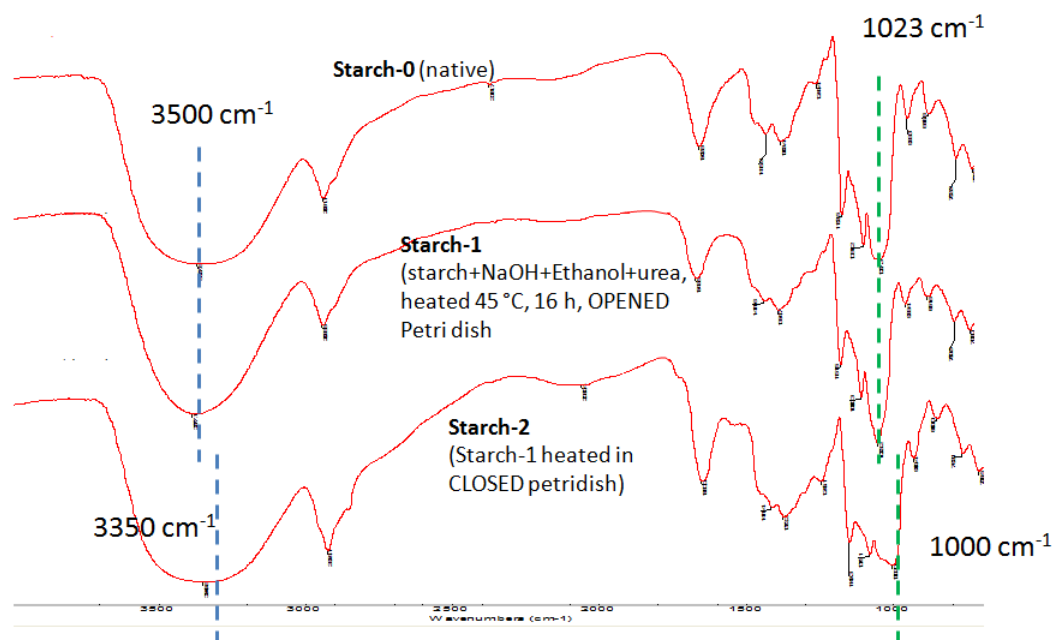


Figure 3. Chemical characterization of Indonesian taro starch particles by using FTIR analysis

A further analysis on the chemical groups for the Starch-0, Starch-1, and Starch-2 using FTIR as shown in Figure 3 demonstrates that there are some obvious changes observed for Starch-2, while the chemical characteristics of Starch-1 is virtually similar to that of Starch-0. At the wavenumber between 3500 to 3000  $\text{cm}^{-1}$ , Starch-2 has a broadened valley (peaked at 3350  $\text{cm}^{-1}$ ), while that of Starch-0 and Starch-1 are not too wide, and peaked at 3500  $\text{cm}^{-1}$ . The widened valley of Starch-2 at 3350  $\text{cm}^{-1}$  is suspected to be caused by stretching vibration of  $\text{-OH}$  [9] that is more dominant in Starch-2, compared to that of Starch-0 and Starch-1. It is highly believed that a more intensive drying process (located in a closed Petri dish) could cause this phenomenon.

Moreover, the peak at 1023  $\text{cm}^{-1}$  of Starch-0 and Starch-1 seems to be shifted to 1002  $\text{cm}^{-1}$  for Starch-2. The group located at wavenumber 1023  $\text{cm}^{-1}$  corresponds with the amorphous phase of the starch, while that of at 1000  $\text{cm}^{-1}$  is related with both lintnerized starch, or granulated starch, which were the product of hydrolysis reaction [10, 11]. Therefore, the preparation of Starch-2 (oven 1 atm, 45 °C, 16 h, in a closed Petri dish) is quite a suitable process to produce Indonesian taro starch particles, which is an appropriate candidate for production of fat replacer products. This candidacy is taken because the preparation process of the Indonesian taro starch particles of Starch-2 resulted in non-amorphous molecular structure (different with the amorphous Starch-0 and Starch-1, not crystalline). As a note, lintnerized starch is a type of starch resulted from Lintner process [12], that is process involving acid hydrolysis of starch (with 2.2 N HCl) at elevated temperature (30-40°C) [11].

#### 4. Conclusions

Based on the results from this preliminary research, it could be concluded that we have fabricated Indonesian taro starch particles (sample Starch-2) having characteristics of size around 203-596  $\mu\text{m}$ , from the modified nanoprecipitation method utilizing NaOH, urea, and ethanol. The sample Starch-2 is prepared by drying in a closed Petri dish, heated in an atmospheric oven at 45°C for 16 h. The chemical characteristics of the Starch-2 Indonesian taro starch particles are granulated and non-amorphous starch resulted from hydrolyzed particles, which is a potential candidate for fat replacer products. Further research for the nanosized Indonesian taro starch particles is still currently ongoing.

with emphasis on the optimization of the preparation conditions (e.g. concentration of NaOH, urea, ethanol, surfactant, as well as temperature, drying conditions, preparation time, etc.)

## 5. Acknowledgement

The authors would like to thanks Bina Nusantara University for Hibah Penelitian Terapan for this study.

## References

- [1] S.C. Pang, S.F. Chin, S.H. Tay and F.M. Tchong, (2011), "Starch–maleate–polyvinyl alcohol hydrogels with controllable swelling behaviors", *Carbohydrate Polym.* Vol. **84** pp. 424-429
- [2] H. Angellier, L. Choisnard, S. Molina-Boisseau, P. Ozil and A. Dufresne, (2004), "Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology", *Biomacromolecules* Vol. **5** pp. 1545-1551
- [3] D. Le Corre, J. Bras and A. Dufresne, (2010), "Starch Nanoparticles: A Review", *Biomacromolecules* Vol. **11** pp. 1139-1153
- [4] M.E. Gomes, J.S. Godinho, D. Tchalamov, A.M. Chunha and R.L. Reis, (2002), "Alternative tissue engineering scaffolds based on starch: Processing methodologies, morphology, degradation and mechanical properties.", *Mater. Sci. Eng. C* Vol. **20** pp. 19-26
- [5] M. Mahkam, (2010), "Starch-based polymeric carriers for oral-insulin delivery", *J. Biomed. Mater. Res. A* Vol. **92A** pp. 1392-1397
- [6] J.Y. Kim and S.T. Lim, (2009), "Preparation of nano-sized starch particles by complex formation with n-butanol", *Carbohydrate Polym.* Vol. **76** pp. 110-116
- [7] D. Liu, Q. Wu, H. Chen and P.R. Chang, (2009), "Transitional properties of starch colloid with particle size reduction from micro- to nano-meter. ", *J. Coll. and Interface Sci.* Vol. **339** pp. 117-124
- [8] S.F. Chin, S.C. Pang and S.H. Tay, (2011), "Size controlled synthesis of starch nanoparticles by a simple nanoprecipitation method", *Carbohydrate Polym.* Vol. **86** pp. 1817-1819
- [9] D. Demirgöz, C. Elvira, J.F. Mano, A.M. Cunha, E. Piskin and R.L. Reis, (2000), "Chemical modification of starch based biodegradable polymeric blends: Effects on water uptake, degradation behaviour and mechanical properties", *Polym. Degrad. Stab.* Vol. **70** pp. 161-170
- [10] N. Wellner, M.L. Parker, D.M.R. Georget and V.J. Morris 2012 *Gums and stabilisers for the food industry 16*, ed P A Williams and G O Phillips (Great Britain, UK: RSC)
- [11] L. Jayakody and R. Hoover, (2012), "The effect of lintnerization on cereal starch granules", *Food Res. Int.* Vol. **35** pp. 665-680
- [12] C.J. Lintner, (1886), "Studien uber diastase", *J. Prakt. Chem.* Vol. **34** pp. 378-386