




PARTICLE SIZE MODIFICATION OF BREADFRUIT STARCH (*Artocarpus altilis*) TO NANOPARTICLES USING ACID HYDROLYSIS AND A TOP-DOWN TECHNIQUE

Asri Alfiyah Ningsih Nst¹, Cut Fatimah Zuhra^{2*}, Juliati Br. Tarigan²

¹ Postgraduate School, Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Sumatera Utara, Medan, Indonesia

² Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Sumatera Utara, Medan, Indonesia

ARTICLE INFO	ABSTRACT
<p>Keywords: <i>Breadfruit Starch (Artocarpus altilis)</i>; <i>Nanoparticle</i>; <i>Acid Hydrolysis</i>; <i>Physicochemical</i></p> <p>Article History: Received: 2024-02-14 Accepted: 2024-04-21 Published: 2024-04-25 *Corresponding Author Email: cutfatimah@usu.ac.id doi:10.20961/jkpk.v9i1.85602</p>  <p>© 2024 The Authors. This open-access article is distributed under a (CC-BY-SA License)</p>	<p>Breadfruit (<i>Artocarpus altilis</i>) is a significant starch source, comprising up to 70.25% of its composition, and holds extensive industrial applications. However, the physicochemical properties of natural starch pose several challenges to its direct use as an industrial raw material. These challenges include high viscosity, substantial swelling power, low solubility, significant retrogradation, limited digestibility, and poor thermal stability. To address these issues, modification of the starch particle size to the nanometer scale is proposed, which is anticipated to enhance both functional and physicochemical properties. This study employs a top-down approach through 2.2 N HCl acid hydrolysis at 38°C for 24 hours. This method offers simplicity, efficiency for scale-up in industrial applications, and relatively higher stability than alternative approaches. Particle size analysis using Particle Size Analysis (PSA) revealed an average particle size of 215 nm. Fourier Transform Infrared (FT-IR) spectroscopy showed characteristic bands similar to natural starch, with slight variations in peak intensity, indicating successful acid hydrolysis and structural disruption of the molecular order. Morphological analysis revealed minimal changes in the granules' surface structure, with clumping observed due to acid hydrolysis. The resultant starch nanoparticles exhibited decreased viscosity and swelling while solubility was enhanced. Therefore, nanoparticle starch holds promising applications in food and non-food industries.</p>
<p>How to cite: A. A. Ningsih Nst, C. F. Zuhra, and J. B. Tarigan, "Particle size modification of breadfruit starch (<i>Artocarpus altilis</i>) into nanoparticle size through top down technique using acid hydrolysis," <i>Jurnal Kimia dan Pendidikan Kimia (JKPK)</i>, vol. 9, no. 1, pp. xx-xx, 2024. Available: 10.20961/jkpk.v9i1.85602</p>	

INTRODUCTION

Starch is a renewable biopolymer that can be biodegraded naturally and is abundantly available from various plant sources [1, 2]. *Artocarpus altilis*, commonly known as breadfruit, is highly productive and remains underutilized despite its functional properties and potential health benefits [3]. In Indonesia, breadfruit starch is a popular source, comprising up to 70.25% starch content, thus presenting significant potential

as a raw material [4]. The composition of breadfruit starch includes 22.5% amylopectin and 77.48% amylose, offering superior functionalities compared to wheat, rice, and cassava flours in terms of viscosity, oil and water binding capacities, and expandability [5]. Currently, approximately 60% of starch utilization is in the food industry, with the remaining 40% serving non-food sectors such as pharmaceuticals, chemicals, paper, textiles, and cosmetics [1].

Natural starch presents limitations that can hinder its effectiveness, particularly in the food industry, which demands raw materials that can withstand various processing techniques, including preparation, storage, and distribution. Vulnerabilities of starch include sensitivity to processing conditions such as stirring, acidic environments, high temperatures, unstable viscosity, and low solubility [1, 6-9]. Therefore, starch modification is essential to enhance its utility. Various methods and compounds are employed to physically, chemically, and enzymatically modify starch, aiming to improve its structural and functional properties for diverse industrial applications [10].

Modification of starch to nanoparticle size can address these limitations by reducing the particle size to nanoscale dimensions. Smaller nanoparticles enhance solubility, making them suitable for dispersion or dissolution applications. Additionally, the increased surface area to volume ratio of nanoparticles improves interactions with other molecules and enhances their functional properties. This modification also improves stability against temperature, pH changes, and retrogradation and extends shelf life. Furthermore, starch nanoparticles can enable the controlled release of encapsulated substances such as drugs or nutrients, thus offering enhanced biological properties not present in natural starch [11, 12, 13].

Nanotechnology processes produce starch nanoparticles that generate particles smaller than 1000 nm but larger than a single molecule. The preparation of nanoparticles

can be executed via top-down and bottom-up methods. Top-down methods, including ultrasonication, homogenization, gamma radiation, and acid hydrolysis, are advantageous due to their simplicity, cost-effectiveness, and efficiency at scale, making them suitable for industrial production. They typically produce large quantities of nanoparticles with consistent quality more economically than bottom-up methods, which require specialized precursors and complex synthesis processes [1, 13].

Acid hydrolysis is a prominent top-down method that yields starch nanoparticles with relatively higher crystallinity and stability than other methods. This process involves treating starch with an acid suspension at temperatures below its gelatinization point [8]. The efficacy of acid hydrolysis in nanoparticle formation is influenced by several factors: temperature, which accelerates the hydrolysis reaction by increasing molecular kinetic energy; acid concentration, which dictates the rate and extent of hydrolysis; starch concentration; hydrolysis duration; and agitation [13]. Systematic consideration of these factors and the properties of the resulting nanoparticles is crucial. Optimizing hydrolysis conditions to achieve desired nanoparticle size, morphology, and stability involves experimental design, data analysis, and iterative adjustments. Therefore, this study proposes the preparation of breadfruit (*Artocarpus altilis*) starch nanoparticles using the top-down acid hydrolysis method to explore the characteristics and potential applications of these modified biopolymers

METHODS

1. Material

Breadfruit (*Artocarpus altilis*) with yellowed skin was sourced from Tembung, Deli Serdang, North Sumatra, Indonesia. Chemicals used in this study include distilled water, double-distilled water, and pro-analyst grade reagents from Merck, namely Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH), and Ethanol.

2. Tools

The equipment prepared for this study comprised Erlenmeyer flasks, beaker glasses, test tubes (all Pyrex), spatulas, glass funnels, stirring rods, mortars and pestles, mesh sieves, thermometers, a pre-calibrated shake incubator (verification of incubator temperature was performed using a calibrated thermometer to ensure accurate conditions during reactions), an oven (Mettler), a centrifuge, cuvettes, an Ostwald viscometer, rubber bulbs, stopwatches, an analytical balance, and a universal indicator. Analytical instruments used include Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and a Particle Size Analyzer (PSA). Before sample analysis, the surface area of the PSA site was cleaned to prevent interference from contaminants. Preparation of the PSA solution followed specific instructions to ensure proper dilution and mixing.

2. Breadfruit (*Artocarpus altilis*) Starch Isolation

Yellow-skinned breadfruit was peeled, and the stalk was removed. After

peeling, the breadfruit was thoroughly washed to remove any gumminess. It was then chopped into small pieces and mashed, and the slurry was filtered through gauze to separate the starch. The filtrate was left in a beaker glass to settle, allowing the starch to precipitate. This precipitate was washed repeatedly with water until the wash water became clear. The starch was then dried at 45°C for 24 hours—care was taken to avoid temperatures that exceeded the gelatinization point of the starch, as this could degrade its properties. Overly long drying times were avoided to prevent excessive moisture loss and undesirable changes in starch structure and functionality. Finally, the dried starch was pulverized, sieved, and weighed [14, 15].

3. Starch Nanoparticle Preparation

29.4 grams of breadfruit starch was suspended in 150 ml of 2.2 N HCl solution. Previous research indicates that an acid concentration ≤ 2.2 N is optimal and does not produce particles smaller than 1000 nm [8, 13]. The suspension was placed in a shake incubator at 38°C for 24 hours. The reaction was neutralized with 1N NaOH to halt the acid hydrolysis process. The resultant starch suspension was filtered, washed with distilled water and ethanol, and dried at 40 °C for 24 hours. After drying, the material was mashed and sieved [16, 17, 18].

4. Characterization

Following acid hydrolysis, the breadfruit starch undergoes several characterization steps using advanced instrumentation. The Particle Size Analyzer

(PSA) is first employed to determine the nanoparticle size of the treated starch. Subsequent characterization involves Fourier Transform Infrared Spectroscopy (FTIR) to identify any changes in functional groups and to compare the intensity variations of starch nanoparticle peaks against those of natural starch. Scanning Electron Microscopy (SEM) is then used to assess the differences in surface morphology between native breadfruit starch and its nanoparticle counterpart. These analyses are crucial for verifying nanoparticle synthesis's success and observing any alterations in the physicochemical properties of starch, such as viscosity, swelling power, and solubility.

5. Swelling Power and Solubility

Swelling power and solubility tests are conducted according to established methods [19, 15], with natural breadfruit starch as a control for comparing physicochemical properties. A known quantity of starch is suspended in distilled water and heated in a water bath at 85°C for 30 minutes. After cooling to room temperature, the suspension is centrifuged at 5000 rpm for 15 minutes. The supernatant is then dried in an oven at 110°C to a constant weight to measure the soluble starch, indicated by the dry weight of the residue. The residue and the retained water post-centrifugation are weighed to evaluate the swelling capacity.

$$\text{Swelling Power} : \frac{\text{Sediment Left Behind (g)}}{\text{Starch Weight (g)}}$$

$$\text{Solubility (\%)} : \frac{\text{Dried Supernatant (g)}}{\text{Starch Weight (g)}} \times 100\%$$

6. Viscosity Measurement

Viscosity is measured using the Ostwald viscometer method [15]. A sample of 2.5 grams of starch is dissolved in 100 ml of distilled water. This solution is transferred into a 5 ml pycnometer, and repeated measurements determine the precise weight. For viscosity testing, 10 ml of the solution is introduced into the Ostwald viscometer. The solution is drawn up to the upper limit of the viscometer using a rubber bulb to ensure accurate measurement of the time required for the liquid to pass between two marked points. This procedure is critical for determining the flow properties of starch solutions, which are essential for their potential application in various industrial processes.

RESULTS AND DISCUSSION

1. Breadfruit (*Artocarpus altilis*) Starch Isolation

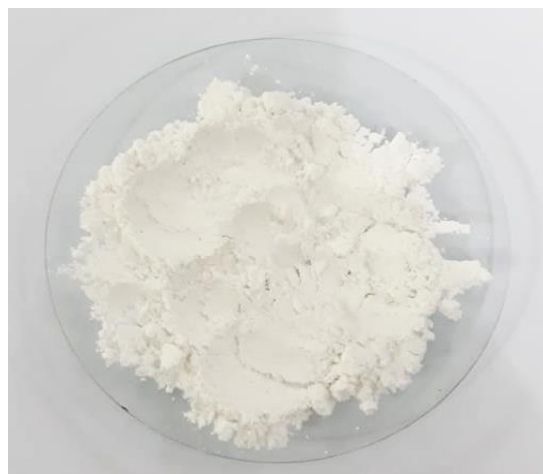


Figure 1. Breadfruit (*Artocarpus altilis*) Starch

The starch isolated in this study was derived from breadfruit (*Artocarpus altilis*) with skin beginning to yellow, sourced from Tembung village, Deli Serdang Regency, North Sumatra Province,

Indonesia. This choice was influenced by the area's abundance and underutilization of breadfruit. From 2 kg of breadfruit, 200 g of starch was obtained, reflecting a yield of 10%. The yield is contingent upon the maturity of the breadfruit; prior studies have shown that young breadfruit yields approximately 4.3%, whereas ripe breadfruit yields about 8.93%. It is noted that the starch content in breadfruit varies with the fruit's maturity [20].

The efficacy of the starch isolation process is influenced by the solubility of the compounds to be extracted, adhering to the principle of 'like dissolves like.' Being a polar substance, starch is extracted using water—a polar solvent—which has been shown to enhance the yield of starch obtained. This aligns with findings from previous research, which indicate that using water as a solvent produces higher yields and proves more cost-effective and practical on a larger scale compared to other chemical solvents [21]. This efficiency makes water an ideal choice for starch isolation in terms of cost, availability, and environmental impact.

2. Breadfruit Starch (*Artocarpus altilis*) Nanoparticles

The reduction in size to nanoparticles enhances their functionality and desired physicochemical properties when used in various industries. Specifically, nanoparticles increase solubility, which is crucial for applications that require dispersion or dissolution. By enhancing the absorption capacity, reducing particle size increases the surface area-to-volume ratio, which in turn improves molecular interactions. This

facilitates the controlled release of encapsulated drugs or nutrients and boosts their functional properties. Additionally, nanoparticle stability is enhanced against factors such as temperature, pH, retrogradation, and it also extends shelf life [11, 12, 18].

The transformation of particles to nanoparticles under specific reaction conditions occurs through a two-stage acid hydrolysis process, as illustrated in Figure 2 [22]. Initially, there is a rapid degradation of the starch granule's amorphous regions containing amylopectin, followed by a more gradual breakdown of both amylose and amylopectin in the crystalline areas [1, 22].

Prior to the hydrolysis of the starch crystal's interior, the acidic environment generates hydrogen ions that react with oxygen atoms within the glycosidic bonds of starch. These bonds are subsequently hydrolyzed. Amylose molecules, being more readily cleaved than amylopectin molecules, result in a reduction of the amylose fraction and the production of shorter amylose chains with lower molecular weights, thus reducing the degree of polymerization. The length of the amylopectin chains significantly influences the functional properties of starch nanoparticles, such as the binding capacity for active ingredients when used as a matrix [23]. Refer to Figure 3 for a depiction of the acid hydrolysis reaction mechanism [8].

The process of acid hydrolysis used to produce breadfruit starch nanoparticles has previously been conducted at a temperature of 33°C for 6 hours. This procedure resulted in an average particle size of ≥ 1000 nm. To optimize the reaction

conditions, the temperature was increased to 35°C for the same duration; however, this adjustment did not significantly reduce the particle size. Subsequently, the hydrolysis time was extended to 12 hours at 35°C, which led to a notable reduction in particle size, although the average still remained above 1000 nm. Therefore, to achieve the desired nanoparticle size, both the temperature and duration were further increased to 38°C for 24 hours, resulting in an average particle size of ≤1000 nm. These reaction conditions differ from those found in previous studies [8, 13, 16, 17, 18, 24].

In this study, lower temperatures were employed to prevent the gelatinization

or breakdown of the crystalline structure of the starch. The selection of temperatures below the gelatinization threshold is strategic, as acid molecules preferentially attack the amorphous regions of the granule, leading to a more rapid hydrolysis in these areas compared to the crystalline regions [1]. While extending the hydrolysis time can decrease particle size, excessively prolonged hydrolysis may lead to the dissolution of starch in the acidic medium, thereby reducing the yield of starch nanoparticles [25]. The results of these adjustments are documented in Table 1 and illustrated in Figure 4.

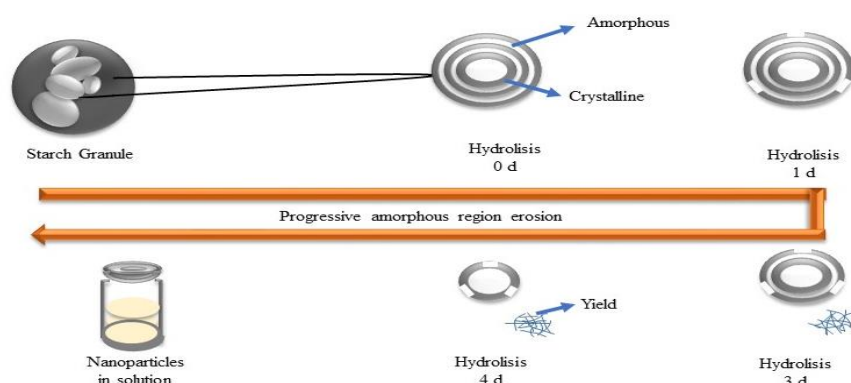


Figure 2. Scheme of Acid Hydrolysis Method

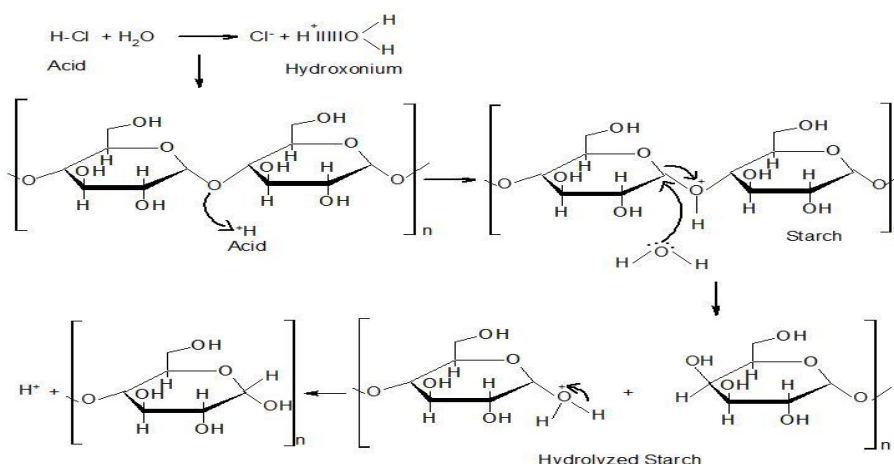


Figure 3. Mechanism of Acid Hydrolysis Reaction on Starch

3. Characterization Particle Size Analyzer (PSA)

The particle size distribution was determined using a Particle Size Analyzer (PSA). This instrument operates on the principle of dynamic light scattering, also known as photon correlation spectroscopy (PCS). Measurements with the PSA are generally more precise than those obtained through a Scanning Electron Microscope (SEM), especially for analyzing nanometer and submicron size particles that are prone to agglomeration. The particle size measured represents the size of a single particle due to the dispersion of the particle into the medium. The outcome is a distribution of particle sizes, which provides a comprehensive view of the sample's state. Thus, this method is more accurate than particle measurement techniques that use image analysis for small samples [26].

As previously discussed, the particle sizes analyzed with the PSA varied according to the different temperatures and durations used during the acid hydrolysis process. The modification of nanoparticle size through acid hydrolysis is influenced by several factors, including temperature, acid concentration, starch concentration, hydrolysis time, and agitation, which are crucial in achieving the desired nanoparticle size [8, 25]. The results are presented in Table 1 and Figure 4.

The acid hydrolysis conditions employed in this study used 2.2 N HCl at 38°C for 24 hours, resulting in an average particle size of 215 nm. This outcome is

superior to previous conditions, as in Table 1, where the average particle sizes did not reach the nanometer scale. Previous research conducted at a temperature of 35°C over 7 and 10 days yielded particle sizes ranging from 20-420 nm and 30-300 nm, respectively [24]. The results obtained using 2.2N HCl are more effective than those achieved with HCl concentrations ≤ 2.2 N at a temperature of 40°C for 4 hours and 24 hours, which did not produce nanoparticle sizes ≤ 1000 nm. The optimal conditions for using HCl at a concentration of 2.2 N have been validated by prior researchers [8, 13]. With an average particle size of 215 nm, these nanoparticles can significantly alter the physicochemical properties of starch to meet specific industrial requirements in the processing of starch nanoparticles. The smaller particle size increases solubility, which is advantageous for applications necessitating dispersion or dissolution. Moreover, the increased surface area to volume ratio of nanoparticles enhances their interaction with other molecules, facilitating the controlled release of encapsulated substances. While the acid hydrolysis process is commonly used for producing starch nanoparticles, it is also noted to be energy-intensive [1].

Table 1. Average Particle Size at different reaction conditions

Temperature (°C)	Time (Hour)	Average Particle Size
33°C	6 hour	2.342 nm
35°C	6 hour	2.158 nm
35°C	12 hour	1.190 nm
38°C	24 hour	215 nm

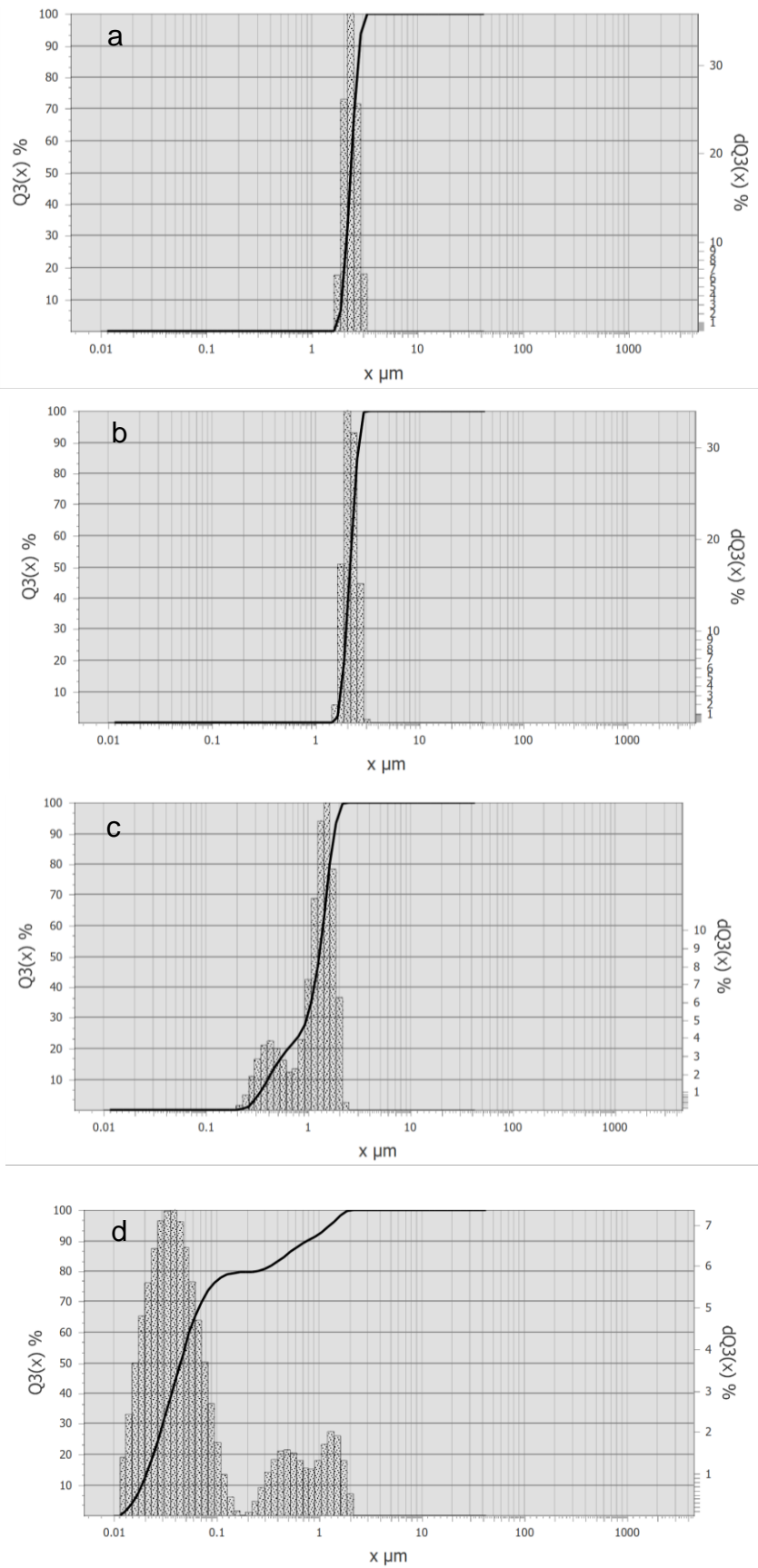


Figure 4. PSA Characterization of Breadfruit Starch Nanoparticles under Temperature and Time conditions (a) 33°C;6h, (b) 35°C;6h (c) 36°C;12h, and (d) 38°C;24h

4. Characterization FT-IR

The FTIR spectroscopy results show structural changes in starch granules due to acid hydrolysis. Spectra displaying vibrational peaks in the wavenumber range of 3400-3200 cm^{-1} indicate the presence of hydroxyl groups (OH). In nanoparticle starch, the stretching peak of OH groups shifts to higher wavelengths [27]. The absorption at wavenumbers 2923-2929 cm^{-1} corresponds to the stretching vibrations of the alkane C-H group (CH_3) [9], and the absorption at wavenumber 1148 cm^{-1} signifies the presence of the CO ester group. The absorption band at 1080 cm^{-1} indicates the CO glycosidic functional group [28], and the peak at 1645 cm^{-1} is attributed to water bonds within the starch granules.

As illustrated in Figure 5, the FTIR spectra of both natural starch and nanoparticle starch display similar band characteristics, albeit with slight variations in the intensity of peaks. The nanoparticle starch shows a decrease in the absorption ratio compared to native starch, suggesting a

reduction in starch crystallinity. This reduction occurs during the acid hydrolysis reaction, which targets starch granules' crystalline and amorphous regions.

At wavenumbers 950-1050 cm^{-1} , a high peak intensity indicates starch's characteristic amorphous and crystalline order [27]. The intensity at these wavenumbers decreases in starch nanoparticles due to structural disruptions of the inner molecular order during acid hydrolysis, distinguishing it from natural breadfruit starch [29]. This structural change indicates that acid hydrolysis has reduced the amylose content, resulting in a short-chain amylose fraction with a lower molecular weight.

The length of the amylopectin chain influences the functional properties of starch nanoparticles, such as their ability to bind active ingredients when used as a matrix. Starch nanoparticles offer significant advantages for their application as functional ingredients in food, including excellent air permeability, small size, and high biocompatibility [30].

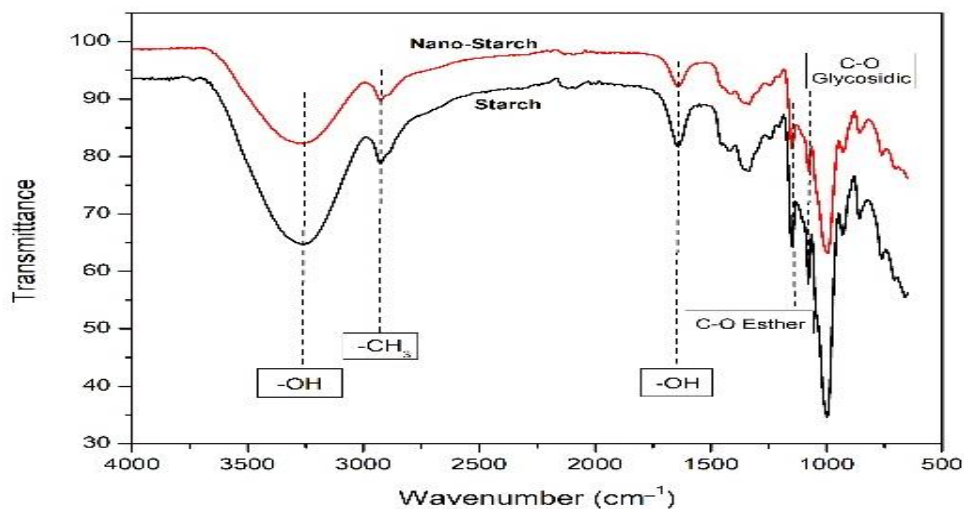


Figure 5. FTIR Spectra of Sukun Starch and Sukun Starch Nanoparticles

5. Characterization SEM

SEM images, presented in Figure 6, illustrate the morphology of breadfruit starch granules both before and after acid hydrolysis. The granules exhibit various shapes—polyhedral, elliptical, and round—with sizes ranging from 3.0 to 7.9 μm [5]. During the short-duration acid hydrolysis process, as depicted in the schematic in Figure 1, the morphology of the starch granules undergoes minimal change. This limited alteration is attributed to the acid's selective action on the amorphous regions of the starch. At the same time, the crystalline areas remain intact, thus preserving the overall shape of the granules [31, 32].

However, the surface morphology of the starch nanoparticles appears clumpy due to the agglomeration of damaged granules. This agglomeration results from the disruption of hydrogen bonds during acid

hydrolysis, which causes granules to adhere, forming clumps. Such changes impact the physicochemical properties of the starch nanoparticles, including viscosity, swelling, and solubility [33]. Previous research indicates that these nanoparticles are particularly suited for specific applications, such as drug delivery matrices [29].

The agglomerated surface morphology of starch nanoparticles enhances their encapsulation efficiency, differing significantly from that of natural starch. This efficiency improvement is due to the altered physicochemical properties resulting from the nanoparticle formation, which optimally affects particle size reduction to the nanometer scale. The higher encapsulation efficiency observed in nanoparticle starch samples underscores their potential advantages over natural starch in pharmaceutical and other applications.

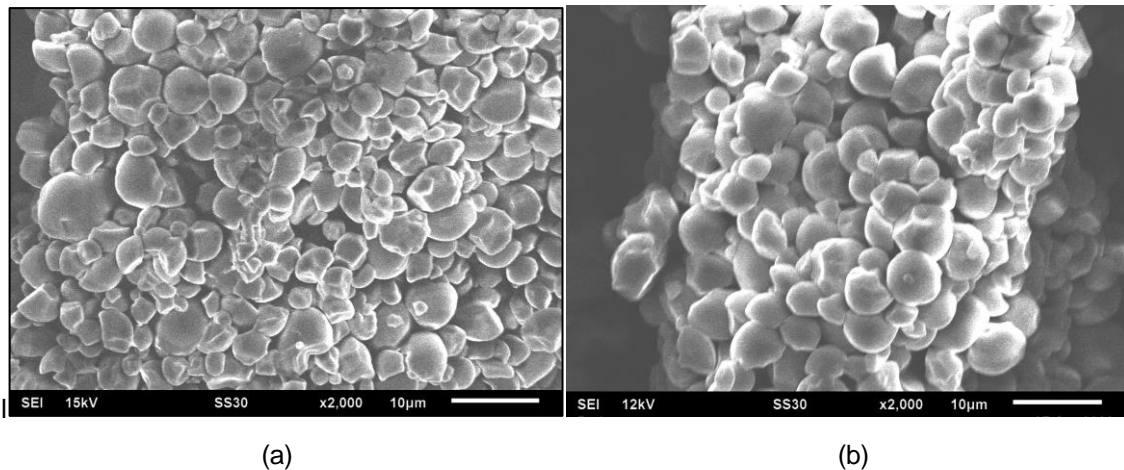


Figure 6. Granule Morphology of (a) Breadfruit Starch; (b) Breadfruit Starch Nanoparticles

6. Viscosity

Viscosity was measured using an Ostwald viscometer, a widely utilized type due to its minimal sample requirements compared to other viscometers [34]. The viscosity of the starch samples, both before

and after undergoing the acid hydrolysis process, demonstrated a decrease in the viscosity of the starch nanoparticles. Lower viscosity is advantageous for encapsulation matrix materials and food ingredients

applications. Nano starch exhibits superior performance when used as an encapsulation material due to its low viscosity, even at high concentrations [13]. The relatively modest change in viscosity, as depicted in Figure 7, can be attributed to the limited duration of the acid hydrolysis process, which did not exceed 24 hours, resulting in only minor variations in viscosity values [31, 23].

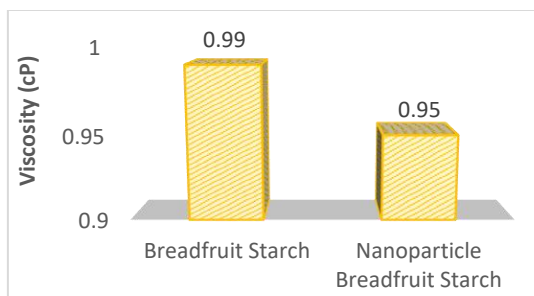


Figure 7. Viscosity Bar Chart of Breadfruit Starch and Breadfruit Starch Nanoparticles

7. Swelling and Solubility

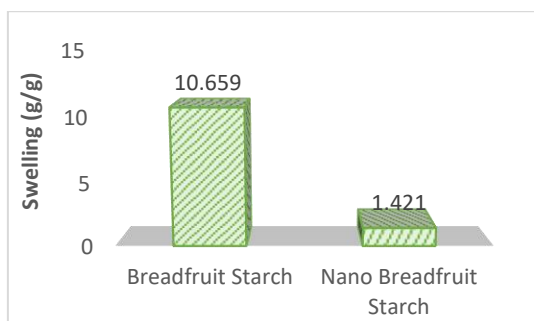


Figure 8. Bar Diagram of Swelling Power of Breadfruit Starch and Breadfruit Starch Nanoparticles

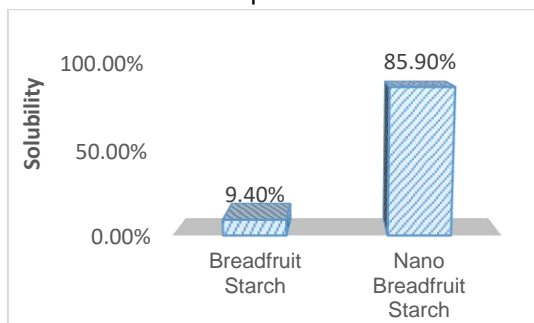


Figure 9. Bar Diagram of Solubility of Breadfruit Starch and Breadfruit Starch Nanoparticles

The analysis of solubility and swelling power revealed that starch subjected to the acid hydrolysis process exhibited a decrease in swelling power and a notable increase in solubility. The tests were conducted at 85°C, where the swelling behavior of starch is influenced by heat. The granules absorb water if starch is heated in excess water above 55°C. Swelling is initially limited and reversible at the gelatinization temperature (around 70°C)—however, continued heating leads to irreversible swelling and eventual rupture of the starch granules [35].

Natural starch demonstrated a solubility of 9.40%, which increased significantly to 85.90% in starch nanoparticles produced through acid hydrolysis. This enhancement in solubility is attributed to the acid-induced degradation of starch granules and the cleavage of starch chains into shorter chains, thus facilitating dissolution. The reduced molecular weight and shorter chains of starch increase its solubility. Furthermore, as starch crystallinity increases, the swelling power decreases. This reduction results from forming hydrogen bonds between the external helix and water molecules. In acid-hydrolyzed starch, the dissolution of amylose and the shortening of amylopectin chains lead to a more branched structure, diminishing the swelling power [31, 23].

Decreased swelling and increased solubility are effects of the disruption of amylopectin side chains. The integrity of amylopectin is crucial for starch's ability to retain water and swell; disrupting these

chains prevents the formation of extensive networks, leading to solubility because the chains can no longer effectively trap water [36]. The high solubility of nanoparticle starch is particularly beneficial for industries requiring dispersive or dissolvable applications. Additionally, encapsulating materials with high solubility enhances the rate of absorption, bioavailability, stability, and bioactivity of compounds, making them attractive for pharmaceutical and food applications. This highlights the growing industrial demand for starch nanoparticles and underscores the challenges in scaling production to meet the physicochemical requirements of various industries [37].

CONCLUSION

The acid hydrolysis process is influenced by temperature and duration to achieve nanoparticle sizes (≤ 1000 nm). Analysis using a particle size analyzer (PSA) under conditions of 38°C for 24 hours yielded an average particle size of 215 nm. Temperature adjustments—ensuring it does not surpass the starch gelatinization threshold—and duration significantly affect particle sizing. Both natural breadfruit starch and its nanoparticle form were analyzed for functional groups using Fourier Transform Infrared Spectroscopy (FT-IR). The results displayed almost identical band characteristics, with minor variations in the intensity of the nanoparticle starch peaks compared to those of the natural starch. These variations indicate that acid hydrolysis disrupted the starch's internal structural order. Surface morphology analysis revealed minimal changes in the starch

granules due to the brief duration of acid hydrolysis. However, the surface of the starch nanoparticle granules exhibited clumping. A comparison of the physicochemical properties between natural breadfruit starch and its nanoparticle form showed a decrease in viscosity from 0.99 cP to 0.95 cP and swelling power from 10.659 g/g to 1.421 g/g. The solubility of the breadfruit starch nanoparticles underwent a substantial increase to 85.90% from the original 9.40%. These changes affirm the potential for application according to industrial needs.

ACKNOWLEDGEMEN

The author would like to thank the Ministry of Education, Culture, Research and Technology of the Republic of Indonesia for funding this research. DRTPM program for fiscal year 2023 with contract No. 75/UN5.2.3.1/PPM/KP-DRTPM/B/2023.

REFERENCES

- [1] Maryam, Kasim A., Novelina, and Emriadi, "Review: Technology for the preparation of starch nanoparticles and its application in the development of bioplastic composites," *Maj. Ilm. Teknol. Ind.*, vol. 15, pp. 36–56, 2018, doi: [10.52759/sainti.v15i2.160](https://doi.org/10.52759/sainti.v15i2.160).
- [2] B. S. Sivamaruthi, P. Kumar Nallasamy, N. Suganthy, P. Kesika, and C. Chaiyasut, "Pharmaceutical and biomedical applications of starch-based drug delivery systems: A review," *J. Drug Deliv. Sci. Technol.*, vol. 77, 103890, 2022. doi:[10.1016/j.jddst.2022.103890](https://doi.org/10.1016/j.jddst.2022.103890).
- [3] S. Nanti, R. H. Yafizah, C. Nilda, and N. Sfriani, "Opportunities and potential of breadfruit (*Artocarpus altilis*) as a

- food ingredient," *J. Ilm. Mhs. Pertan.*, vol. 8, pp. 221–229, 2023.
- [4] J. Eke-Ejiofor and U. B. Friday, "Physicochemical, functional and pasting properties of starch from breadfruit (*Artocarpus altilis*) in gurudi snack production," *J. Biotechnol. Food Sci.*, vol. 7, pp. 38–48, 2019. doi:[10.33495/ijbfs](https://doi.org/10.33495/ijbfs).
- [5] K. A. Mehta, Y. Chin, R. Quek, and C. J. Henry, "Breadfruit (*Artocarpus altilis*): Processing, nutritional quality, and food applications," *Front. Nutr.*, 2023, p. 1–13. doi:[10.3389/fnut.2023.1156155](https://doi.org/10.3389/fnut.2023.1156155).
- [6] Y. Sauyana, "Production of acetate starch using nanocrystalline sago starch," *Dep. Ilmu Pertanian FTP, IPB*, 2014.
- [7] R. R. Maulani, D. Fardiaz, F. Kusnandar, and C. Sunarti, "Functional properties of hydroxypropylated and crosslinked arrowroot starch," *J. Teknol. Ind. Pangan*, vol. 24, no. 1, pp. 60–67, 2013. doi:[10.6066/jtip.2013.24.1.60](https://doi.org/10.6066/jtip.2013.24.1.60).
- [8] Z. Harun, A. Arsad, A. L. Pang, M. A. A. Zaini, M. Abdurrahman, N. Awang, et al., "Acid hydrolysis and optimization techniques for nanoparticles preparation: Current review," *Appl. Biochem. Biotechnol.*, vol. 194, pp. 3779–3801, 2022. doi:[10.1007/s12010-022-03932-6](https://doi.org/10.1007/s12010-022-03932-6).
- [9] N. Nurhaeni, P. Dwiasmukti, and P. Prismawiryanti, "Modification of breadfruit (*Artocarpus altilis*) starch using acetic anhydride and its application in noodle making," *KOVALEN J. Ris. Kim.*, vol. 4, pp. 33–40, 2018. doi:[10.22487/kovalen.2018.v4.i1.10181](https://doi.org/10.22487/kovalen.2018.v4.i1.10181).
- [10] W. A. T., P. I. S., A. Ayucitra, and L. E. K. Setiawan, "Characteristics of sago starch by acetylation and cross-linking methods," *J. Tek. Kim. Indones.*, vol. 7, no. 3, pp. 836, 2008. doi:[10.5614/jtki.2008.7.3.4](https://doi.org/10.5614/jtki.2008.7.3.4).
- [11] S. Y. Cheuk, F. F. Shih, E. T. Champagne, K. W. Daigle, J. A. Patindol, C. P. Mattison, et al., "Nano-encapsulation of coenzyme Q10 using octenyl succinic anhydride modified starch," *Food Chem.*, vol. 174, pp. 585–590, 2015. doi:[10.1016/j.foodchem.2014.11.031](https://doi.org/10.1016/j.foodchem.2014.11.031).
- [12] B. Wang, *Wiley Series in Drug Discovery and Development*, 2022. doi:[10.1002/9781119739883.scard](https://doi.org/10.1002/9781119739883.scard).
- [13] M. Marta, D. I. Rizki, E. Mardawati, M. Djali, M. Mohammad, and Y. Cahyana, "Starch nanoparticles: Preparation, properties and applications," *Polymers (Basel)*, vol. 15, pp. 19–25, 2023. Doi:[10.3390/polym15051167](https://doi.org/10.3390/polym15051167).
- [14] C. F. Zuhra, M. Ginting, W. F. Az-Zahra, "Synthesis of dual modification breadfruit starch (*Artocarpus communis*) with hydroxypropylation and cross-link," *J. Phys. Conf. Ser.*, vol. 1542, pp. 0–6, 2020. doi:[10.1088/1742-6596/1542/1/012013](https://doi.org/10.1088/1742-6596/1542/1/012013).
- [15] C. F. Zuhra, M. Z. E. Sinaga, S. Suharman, R. A. S. Nasution, S. Nurhadija, "Oxidation of breadfruit starch (*Artocarpus altilis*) using hydrogen peroxide," *AIP Conf. Proc.*, vol. 2626, 2023. doi:[10.1063/5.0136101](https://doi.org/10.1063/5.0136101).
- [16] Maryam, Kasim A., Novelina, and Emriadi, "Preparation and characterization of sago (*Metroxylon sp.*) starch nanoparticles using the hydrolysis-precipitation method," *J. Phys. Conf. Ser.*, vol. 1481, 2020. doi:[10.1088/1742-6596/1481/1/012021](https://doi.org/10.1088/1742-6596/1481/1/012021).
- [17] E. K. Sabdongrum, S. Hidanah, S. Chusniati, and Soeharsono, "Characterization and phytochemical

- screening of Meniran (*Phyllanthus niruri* Linn) extract's nanoparticles used ball mill method," *Pharmacogn. J.*, vol. 13, pp. 1568–1572, 2021. doi:[10.5530/pj.2021.13.200](https://doi.org/10.5530/pj.2021.13.200).
- [18] C. F. Zuhra, M. Z. E. Sinaga, S. Suharman, R. Alvi, S. Nasution, and H. Manullang, "Utilization of breadfruit starch nanoparticle," 2023, doi: [10.1063/5.0136100](https://doi.org/10.1063/5.0136100).
- [19] F. P. dan P. B. R., "Penelitian BIAM," vol. VI, 2010.
- [20] A. Aliyah, L. Rahman, and D. Pratiwi, "Physico-chemical analysis of young and semi-ripe breadfruit (*Artocarpus altilis*) starch from Bone Regency, South Sulawesi as a candidate for excipient in tablet formulations," 2021, vol. 3, pp. 171–178.
- [21] N. D. Sunarya, B. Rusdi, and K. M. Yuliawati, "Library research on starch extraction methods from plant seeds," 2016, doi: [10.29313/v0i0.29214](https://doi.org/10.29313/v0i0.29214).
- [22] O. P. Troncoso and F. G. Torres, "Non-conventional starch nanoparticles for drug delivery applications," *Med. Devices Sensors*, vol. 3, pp. 1–16, 2020. doi:[10.1002/mds3.10111](https://doi.org/10.1002/mds3.10111).
- [23] I. Pudjihastuti, "Development of innovative process combining acid hydrolysis and UV photochemical reaction for production of modified tapioca starch," Master's thesis, *Univ. Diponegoro*, Semarang, 2010, pp. 1–39.
- [24] O. Jeong and M. Shin, "Preparation and stability of resistant starch nanoparticles, using acid hydrolysis and cross-linking of waxy rice starch," *Food Chem.*, 2018. doi: [10.1016/j.foodchem.2018.02.098](https://doi.org/10.1016/j.foodchem.2018.02.098).
- [25] N. A. Hassan, O. M. Darwesh, S. S. Smuda, A. B. Altemimi, A. Hu, and F. Cacciola, "Recent trends in the preparation of nano-starch particles," *Molecules*, vol. 27, pp. 1–24, 2022. doi: [10.3390/molecules27175497](https://doi.org/10.3390/molecules27175497).
- [26] G. Suprobo and D. Rahmi, "The effect of homogenization speed on the physical and chemical properties of nanoparticle creams using the 2015 method," pp. 1–12.
- [27] M. Ahmad, A. Gani, I. Hassan, Q. Huang, and H. Shabbir, "Production and characterization of starch nanoparticles by mild alkali hydrolysis and ultra-sonication process," 2020, pp. 1–11. doi:[10.1038/s41598-020-60380-0](https://doi.org/10.1038/s41598-020-60380-0).
- [28] C. F. Zuhra, G. Mimpin, Marpongahtun, and S. Ayu, "Modification of breadfruit starch using cross-linking method with trisodium trimetaphosphate," *Chim. Nat. Acta*, vol. 4, pp. 142–146, 2016, doi: [10.24198/cna.v4.n3.10925](https://doi.org/10.24198/cna.v4.n3.10925).
- [29] F. Jhan, A. Gani, N. Noor, Z. Ashraf, A. Gani, and A. Shah, "Characterisation and utilisation of nano-reduced starch from underutilised cereals for delivery of folic acid through the human GI tract," *Sci. Rep.*, 2021, pp. 1–15. doi:[10.1038/s41598-021-81623-8](https://doi.org/10.1038/s41598-021-81623-8).
- [30] C. Wang, D. Julian, A. Jiao, J. Wang, Z. Jin, and C. Qiu, "Trends in food science & technology resistant starch and its nanoparticles : Recent advances in their green synthesis and application as functional food ingredients and bioactive delivery systems," *Trends Food Sci. Technol.*, vol. 119, pp. 90–100, 2022. doi: [10.1016/j.tifs.2021.11.025](https://doi.org/10.1016/j.tifs.2021.11.025).
- [31] L. Hidrolisis, I. Pertanian, C. Winarti, N. Richana, D. Mangunwidjaja, and T. C. Sunarti, "Effect of acid hydrolysis duration on the physico-chemical properties of starch," 2014, vol. 24, pp. 218–225.

- [32] R. Zuo, X. Wang, Y. He, S. Deng, X. Zhuang, et al., "Isolation and characterization of natural nano starch from amaranth starch," *Int. J. Biol. Macromol.*, vol. 260, 2024, p. 129525. doi: [10.1016/j.ijbiomac.2024.129525](https://doi.org/10.1016/j.ijbiomac.2024.129525).
- [33] Neelam K., Vijay S., and Lalit S., "Various techniques for the modification of starch and the applications of its derivatives," *Int. Res. J. Pharm.*, vol. 3, pp. 25–31, 2012.
- [34] Regina O., Sudrajad H., and Syaflita D., "Measurement of viscosity uses an alternative viscometer," *J. Geliga Sains J. Pendidik. Fis.*, vol. 6, pp. 127–132, 2019. doi: [10.31258/jgs.6.2.127-132](https://doi.org/10.31258/jgs.6.2.127-132).
- [35] Triwitono P., Marsono Y., Murdiati A., and Marseno D. W., "Isolation and characterization the properties of some Indonesian local varieties mung beans (*Vigna radiata*) starch," 2017, vol. 37, pp. 192–198, doi: [10.22146/agritech.10659](https://doi.org/10.22146/agritech.10659).
- [36] Dyah A. and Lestari N., "Solubility and swelling power of microencapsulated β -carotene encapsulated in a cross-linked starch-chitosan matrix," 2022, vol. 18, pp. 75–83, doi: [10.30862/jn.v18i2.184](https://doi.org/10.30862/jn.v18i2.184).
- [37] Montoya-Yepes D. F., Jiménez-Rodríguez A. A., Aldana-Porrás A. E., Velásquez-Holguín L. F., Méndez-Arteaga J. J., and Murillo-Arango W., "State of the art and research trends," *Polym. Bull.*, vol. 81, pp. 135–163, 2024, doi: [10.1007/s00289-023-04724-6](https://doi.org/10.1007/s00289-023-04724-6).