

Synthesis and Characterization of Nanomaterials from Porang (*Amorphophallus muelleri*) and Its Application for Bioplastic: Preliminary

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Submitted: September 24, 2022; Revised: November 24, 2022; Accepted: December 13, 2022;

Published: November 30, 2023

ABSTRACT

The increase in plastic waste caused by population growth and human activities is capable of leading to negative consequences for the environment. The substantial accumulation contributes to environmental pollution since its resilience against microbial degradation poses a significant challenge. Furthermore, the utilization of bioplastics as a biodegradable substitute presents a viable strategy for diminishing reliance on synthetic plastics. Starch emerges as a prevalent primary component in the fabrication of bioplastics, owing to its array of merits including renewability, cost-effectiveness, non-toxicity, and facile degradability. The application of nanomaterials to bioplastics is believed to accelerate the degradation of bioplastics. Therefore, this study aimed to identify the characteristics of nanomaterial from porang (*Amorphophallus muelleri*) and bioplastic. The method included the extraction of porang nanomaterial through a specified water-to-porang ratio (2.5:1) followed by sonication (50 W, 75 minutes). The formulation of bioplastics involved the amalgamation of corn starch, porang nanomaterial, and glycerol. In addition, the chemical properties of porang nanomaterials included 41.41% starch content, 13.49% amylose, 7.87% ash, and 2.52% calcium oxalate. The particle size of porang nanomaterials was distributed from 603.7-952.1 nm with an average 722.6 nm crystalline structure containing calcium oxalate. The bioplastic had the form of a thin brown layer with a thickness value ranging from 0.23-0.39 mm. This research was expected to provide new information related to the essential characteristics of nanomaterials from porang and its potential application in solving environmental issues caused by synthetic plastics.

Keywords: Bioplastic; nanomaterials; particle size test; porang

INTRODUCTION

The utilization of plastic materials in Indonesia is consistently increasing every year, in line with the simultaneous growth of the population. This phenomenon is primarily attributed to the widespread adoption of plastic for purposes of packaging and as utensils, including items such as straws, spoons, and forks, owing to their favorable attributes of convenience, lightweight

nature, impermeability to water, adaptability, and cost-effectiveness. Meanwhile, the unwarranted proliferation has imparted a substantial and detrimental imprint on the environment. Condorferries.co.uk estimations propose an annual generation of approximately 381 million tons of plastic waste due to human activity, a figure that may be doubled in 2034. In the year 2015, the global employment of plastic eclipsed the 300 million ton mark. Indonesia stands as the second-

largest contributor to this predicament, ranking only behind China, which contributes 187.2 million tons of plastic waste into its waters (Jambeck et al. 2015). The surge in waste production equates to a staggering 38 million tons per annum, with 30% of this quantum constituting plastic materials (Hendiarti, 2018). Plastic exerts negative effects on the environment by reducing soil fertility and polluting the sea, hence endangering the survival of marine life. Burning plastic waste also causes air pollution and global warming, as well as produces CO₂ and HCN gas (Purwaningrum, 2016).

The next problem is the length of time for the decomposition of plastic waste by microorganisms found in the soil. Consequently, to curb the generation of this waste, it is imperative to drive innovation by developing plastics derived from natural materials, a category commonly known as bioplastics. Starch, a prevalent natural polymer, stands out as a key candidate for the fundamental material used in bioplastics production. The widespread utilization across various industries underscores its significance in this context. In addition, the industrial demand peaked at 25 million tons in 2012 to fulfill diverse industrial requirements (Schrijver & Homburg, 2013). The main application is currently around 60% used for the food processing industry, and 40% for applications in non-food industries, such as chemical, pharmaceutical, paper, textile, cosmetic, and other industries. Starch as a biomaterial has attracted much attention due to the following advantages, easy to obtain, renewable, inexpensive, non-toxic, and easily degraded (Mahmood et al., 2017). As a raw material for bioplastics, natural starch has weaknesses, and modifications need to be made to have better characteristics.

An alternative effort to improve the characteristics of starch and increase its added value is to modify it in nanoparticle size. Irawan et al. (2014) reported that nanotechnology is a cutting-edge technological approach for several fields. Starch nanoparticles are in the range of 1-1000 nanometers and the technology can significantly improve the characteristics. Therefore, it has a low suspension viscosity at relatively high concentrations with high binding strength due to its large active surface area (Maryam et al., 2018). The production has been widely reported from various agricultural commodities, including breadfruit starch (Afriani, 2019), corn starch (Palupi et al., 2020), and cassava starch (Hedayati et al., 2020).

Porang (*Amorphophallus muelleri*) is a rising commodity in Lampung, currently getting attention from industry practitioners due to glucomannan content. The production of glucomannan from porang also yields starch as a by-product and has the potential to be used

as bioplastic. In addition, no reports or studies have produced and reported the characteristics of starch nanoparticles from porang tubers and their application as bioplastics for food packaging. The specific objective was to ascertain the existence of starch nanoparticles derived from porang tubers, subsequently employed in the development of a prototype bioplastic. The process of generating starch nanoparticles elevates the intrinsic value and utilization potential of these tubers, as well as serves as a proactive measure to safeguard the environment against the negative effects of plastic waste. Therefore, this study aimed to identify the characteristics of nanomaterials from porang and their application for bioplastic.

METHODS

Materials

The main material used in this study was yellow porang tubers, harvested on April 2022 after 7 months. Subsequently, the porang was transported from Metro (Lampung) packed with gunny sacks. Other materials used were maize starch (Maizenaku, food grade, West Jakarta, Indonesia), glycerol (RP Chemicals, food grade, Malaysia), aquadest, and other chemicals for analysis.

The equipment used were digital ultrasonic cleaner with ultrasonic power 50 watt (DADI-628A, China), particle size analyzer (Beckmen Coulter LS 13 320 XR, nano type, US), scanning electron microscopy (SEM-EDX Zeiss Evo ® MA 10, Germany), X-Ray Diffractometer (X'Pert PRO MPD PW3040/60, PANalytical, Netherland), blender (Phillips HR2115, Indonesia), digital caliper (RoHS, China), and other chemical glassware for other preparations.

Preparation of Porang Nanomaterial

The preparation of nanomaterial from porang was carried out through extraction and sonication processes. The extraction method was consistent with Istiqomah (2021) where porang was peeled off and washed with clean water to remove any contaminants. Furthermore, it was soaked in water for 1 hour, then homogenized using a blender with a ratio of water:porang 2.5:1, and then filtered and precipitated. After the precipitation process, the precipitated part was separated and oven-dried at 50 °C for 12 hours. The material was then filtered and sieved at 100-mesh to obtain a flour form. The sonication process was carried out according to Bel-Haaj et al. (2013) with a modification of sonication temperature. The flour was placed in a 50 mL beaker glass with 1.5% concentration and immersed in an ultrasonic bath at room temperature (25 °C), operating at a frequency of

40 kHz, and a power setting of 50 W for 75 minutes. Subsequently, the suspension was dried in a drying oven at 50°C for 2 hours and proceeded to particle size analysis (PSA). The dried form proceeded to chemical properties analysis (ash, moisture, starch, and amylose) (AOAC, 2015), calcium oxalate content (Utaminingsih & Muhtadi, 2021), micrograph with Scanning Electron Microscopy (SEM), and identification of material phase and composition with X-Ray Diffraction (XRD).

Preparation of Bioplastic

The bioplastic was prepared by the application of the solution casting method according to Abotbina et al. (2021) with modification, containing a mixture of corn starch, porang nanomaterial, and glycerol. Corn starch (10%), porang nanomaterial (5%), and 5 mL of glycerol were mixed in a beaker glass and then 100 mL aquadest was added. The mixture was heated in a hot magnetic stirrer at 70-80 °C and stirred until the solution became viscous, before casting in a glass plate. Subsequently, the glass plate was placed at room temperature until the film was formed and released to proceed with thickness measurement. The thickness of the bioplastic was measured on five different spots using a digital micrometer under three replications and the obtained data were analyzed descriptively.

RESULTS AND DISCUSSION

Chemical Properties of Porang Nanomaterials

The chemical properties of porang nanomaterials were investigated, including starch, amylose, ash, and protein contents, as shown in Table 1. The porang nanomaterials had starch, amylose, water, ash, and calcium contents of 41.41%, 13.49%, 7.32%, 7.87%, and 2.52%, respectively. The starch content of porang starch flour was higher than in another study reported by Istiqomah (2021), resulting in a starch content of 12%. Aryanti & Abidin (2015) stated that the starch content of porang is also affected by the type or variety of plants. The results showed white and yellow starch contents of 7.554% and 5.958%, respectively. Higher starch content also affected the rate of biodegradation of bioplastics. According to Shafqat et al. (2020), the higher the starch content of the material used in bioplastic, the faster the rate of biodegradation. Aryanti & Abidin (2015) also reported that the amylose content of white and yellow porang is 17.536% and 16.948%, higher than in this study. Furthermore, Nisah (2017) reported that amylose content affected the properties of bioplastic, where the higher amylose content increases the strength and elongation of bioplastic.

Table 1. Chemical properties of porang nanomaterials

Chemical attribute	Result
Starch (%)	41.41±0.02
Amylose (%)	13.49±0.17
Moisture (%)	7.32±0.04
Ash (%)	7.87±0.08
Calcium oxalate (%)	2.52±0.10

Moisture content was lower than in another study reported by Aryanti & Abidin (2015) where the result ranged from 12.32-13.48%. However, it was higher than Istiqomah (2021) which produce a moisture content of around 4.3%, and the difference was mainly affected by the drying method. Elevated temperatures and extended drying durations also yielded reduced moisture content. Soler et al. (2020) elucidated that precise regulation of time and temperature during the drying process was imperative to attain the targeted moisture level. The ash content was higher than in another study reported by Aryanti & Abidin (2015) where the result ranged from 3.9-4.6%. Pasaribu et al. (2018) reported that ash content is related to a mineral presence that is also identical to calcium oxalate, causing itching. In this study, the porang nanomaterials contained 2.52% of calcium oxalate, which was lower than the study by Wardani & Handriato (2019) where the level was 3.94%. This was caused by the removal of the liquid part of the precipitation result containing water-soluble oxalates during the extraction process. Widari & Rasmito (2018) added that the oxalate can be reduced significantly by using boiling in brine method for 30 minutes.

Physical Properties of Porang Nanomaterials

Physical properties of porang nanomaterial were analyzed using Particle Size Analysis (PSA) to determine the particle size distribution, Scanning Electron Microscopy (SEM) to observe the microstructure, and X-Ray Diffraction (XRD) to analyze the phase and composition. The result of particle size distribution, microstructure observation, and XRD diffractogram is shown in Figure 1, Figure 2, and Figure 3.

The particle size analysis (Fig. 1) showed that the porang material had a range distributed from 1187,5-4097,7 nm with an average value of 1404 nm. Moreover, it was bigger than porang nanomaterials with a range of 603,7-952,1 nm (average value of 722,6 nm). This result showed that the sonication treatment can reduce the particle size from Micrometres (µm) to nanometres

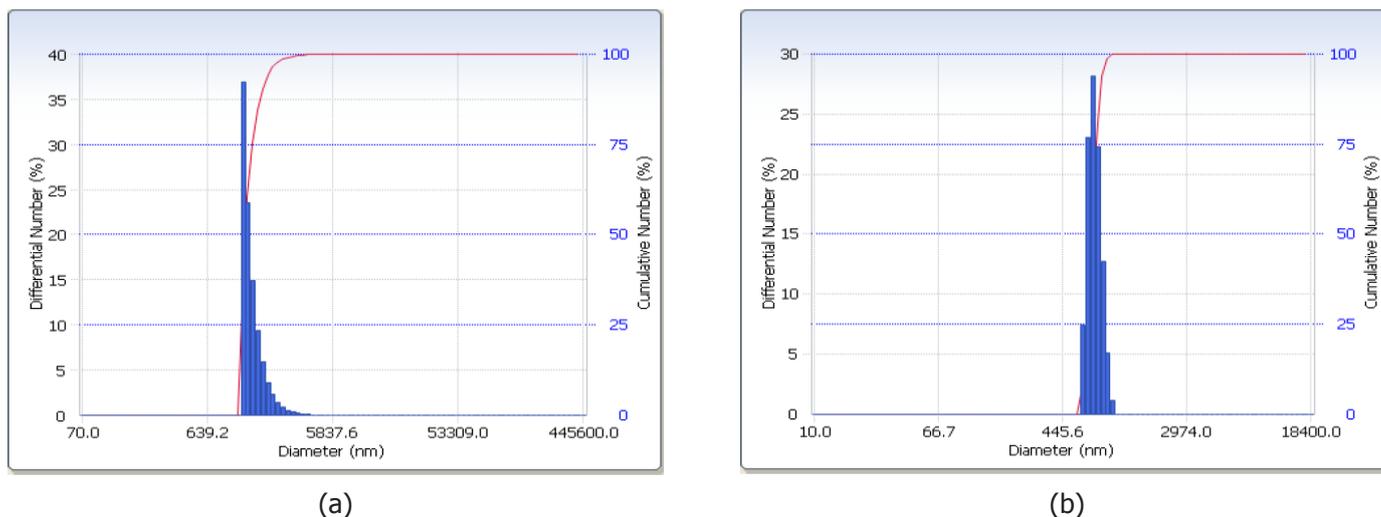


Figure 1. Particle size distribution (a) porang material (b) porang nanomaterial

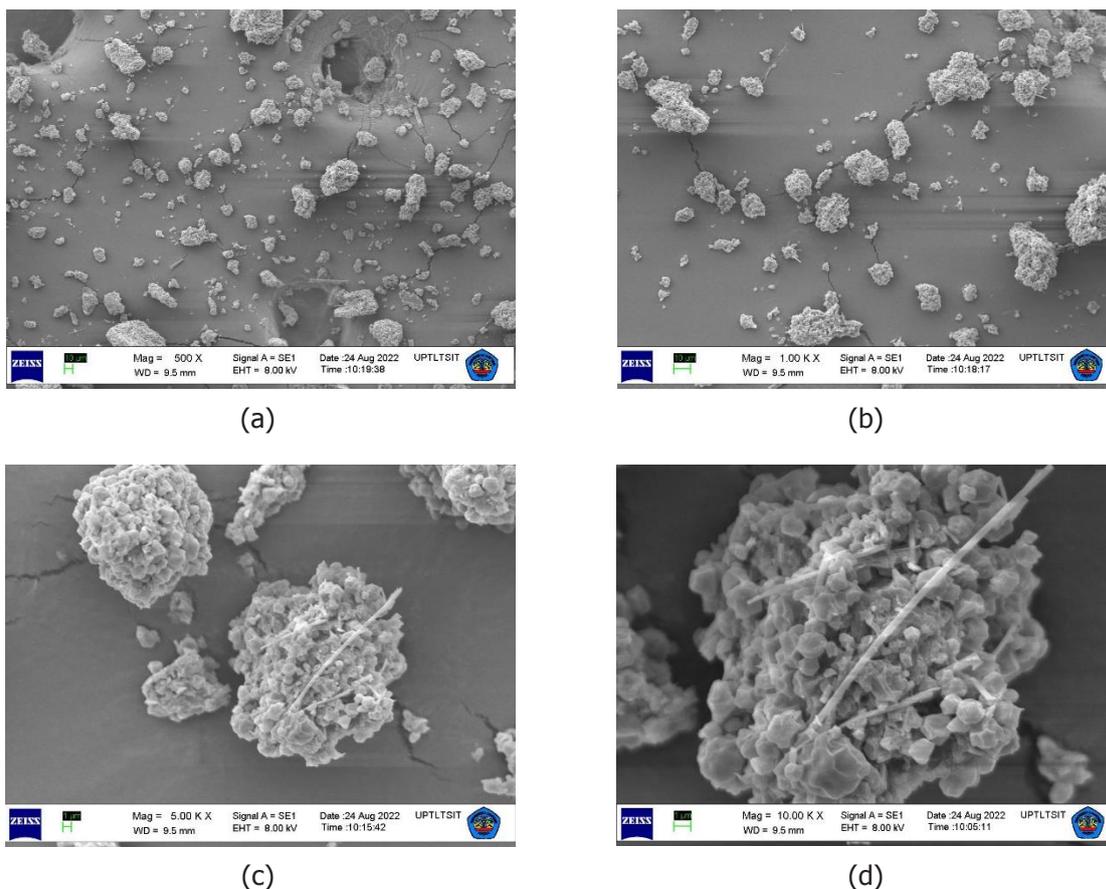


Figure 2. Microstructure observation of porang nanomaterial with different magnifications (a) 500x (b) 1000x (c) 5000x (d) 10,000x

(nm). Yokoyama et al. (2018) affirmed that particles falling within the nanometer scale ranging from 1 nm to 1 μ m are commonly referred to as nanoparticles.

Campelo et al. (2020) expounded on how ultrasonic waves induced during the sonication process give rise to cavitation bubbles within the solution medium. These

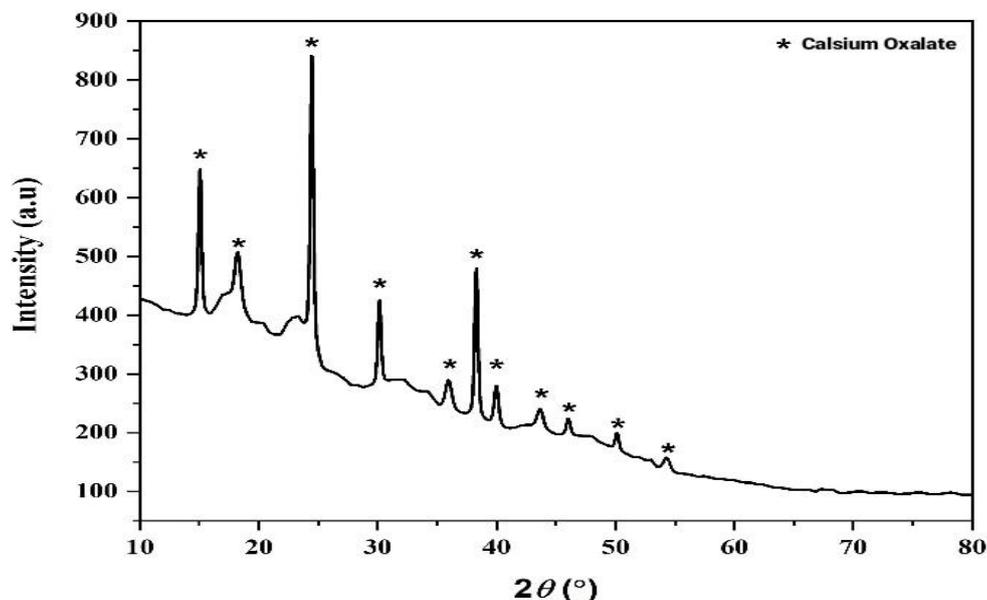


Figure 3. Diffractogram of porang nano material

cavitation bubbles break apart the particles into smaller sizes during processing. Bel-Haaj et al. (2013) reported that the use of high-power ultrasonication (180 W) can reduce the particle size of maize starch from 950 to around 650 nm for 20 minutes, and achieve the lowest (300 nm) after 60 minutes. Based on this comparison, particle size reduction depends on the sonication power and duration.

The microstructure of porang nanomaterial has been observed (Figure 2). The sonication process generated the cavitation bubble that has an impact on the granules producing smaller particles (Figure 2.a.). The rounded granule structure was identified as starch, and after sonication, it lead to disruption and changes in the shape of the granule. The porang starch was severely deformed and formed a crystal-like shape after sonication treatments (Figure 2.d.). The ultrasonic energy was trapped by the dispersed granules, which produced high-frequency vibrations and destroyed starch granules (Monroy et al., 2018). The needle-like form indicates the presence of calcium oxalate which interacted with porang starch. The presence of calcium oxalate resulted in lower solubility of starch in water value since the mineral was insoluble in water. This statement was supported by Haara et al. (201), where oxalate had two forms based on its solubility in water, namely soluble oxalic acid and non-soluble form calcium oxalate.

The XRD spectrum of porang nano material detected three highest diffraction peaks at $2\theta = 15.0398^\circ$, 38.2610° , and 24.4375° with intensity values of 49.02%, 54.05%, and 100%, respectively (Fig. 3). Phases formed were

observed with a PCPDFWIN, and the main phases were calcium oxalate hydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) with a monoclinic crystal structure with a P21/n space group (JCPDS No. 20-0231). The analysis result showed that the porang nanomaterial extracted contains calcium oxalate crystals. Chairiyah et al. (2016) reported that there were four variations of the crystals in porang, namely raphide, druse, prism, and styloid. Prychid et al. (2008) stated that druse and raphide crystals were most commonly found in porang tubers with needle-like morphology. This finding supported the result of the microstructure observation of porang nanomaterial (Figure 2).

Bioplastic Characteristics

Bioplastic from a mixture of corn starch, porang nanomaterial, and glycerol has a brownish transparent color and formed a thin plastic (Figure 3). The development of a brownish hue in the bioplastic is attributed to the heating process, which induces a non-enzymatic browning phenomenon influenced by the inherent color of the constituent material. Since porang nanomaterial possesses a brownish tint, this characteristic extends to the resulting bioplastic. The thickness was quantified using a digital micrometer, revealing a range spanning from 0.23 mm to 0.39 mm, with an average measurement of 0.26 mm. In addition, this thickness moderately surpasses the maximum value of 0.25 mm stipulated by the JIS (2019) standard for bioplastic thickness.

The result of this study is the same value as another. Aryanti & Abidin (2015) reported that corn



Figure 3. Application of porang nanomaterial to bioplastic (left: casted solution, right: bioplastic after drying)

starch bioplastics' thickness increased in the higher concentration of plasticizers. The corn starch bioplastic thickness increased from 0.188 to 0.266 mm, 0.234 to 0.266 mm, and 0.206 to 0.246 mm with different plasticizers. Furthermore, the thickness of bioplastics can be affected by the starch concentration.

CONCLUSION

In conclusion, the physical and chemical properties of porang nanomaterial were investigated. The chemical properties included starch, amylose, ash, and calcium oxalate contents of 41.41%, 13.49%, 7.87%, and 2.52%, respectively. The particle size of porang nanomaterial ranged from 603.7-952.1 nm with an average of 722,6 nm. The bioplastic had the form of a thin brown layer with a thickness value ranging from 0.23-0.39 mm with an average of 0.26 mm. This study applied porang nanomaterials to develop bioplastic and achieved a near-complete adherence to the established standards for bioplastic used in food packaging, as measured by thickness criteria. Further investigations were conducted to explore the mechanical properties of bioplastic derived from porang nanomaterials. Additionally, it was deemed important to evaluate strategies for reducing the presence of calcium oxalate within the porang nanomaterials. This assessment held significance due to the imperative of eliminating calcium oxalate to ensure the suitability of these materials for applications within the realm of food.

ACKNOWLEDGEMENT

The authors are grateful to the Research and Community Service Institute, Universitas Lampung (LPPM Unila) for funding this study.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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