Isolation and characterization of starch from the hump of kepok banana (Musa balbisiana. L) as a precursor of biodegradable polyurethane synthesis

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Abstract. Starch from hump (Musa balbisiana L.) was isolated by the maceration method. Bond characterization and determination of gelatinization temperature, morphology, and particle size were conducted using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Colorimetry (DSC), respectively. This isolation produced starch with a yield of 17.2%, amorphous phase portion 78.8%, particle size of 70 nm, and the starch gelatinization process occurred at 67.5°C. Based on these data, the obtained starch has high potential to be applied as a precursor to synthesize polyurethane biopolymers.

1. Introduction
Kepok banana peel is a raw material that is abundant, renewable, and biodegradable [1]. To obtain high-quality starch from the peel can be done easily and simply, namely, the maceration method [1,2]. About sixty million tons of starch is extracted annually from various sources throughout the world. About 60% of the starch produced is processed into food products (bread products, sauces, soups, sweets, syrups, ice creams, chips, sausages, baby food, fat substitutes, specialty coffee, beer, and other drinks; about 40% is used for pharmaceuticals and non-edible products, such as fertilizers, seed coatings, paperboard, packaging materials, adhesives, textiles, diapers, bioplastics, building materials, oil drilling, and composites in polyurethanes [1,3].

Polyurethanes are versatile polymers, have a strong structure, excellent mechanical and optical properties, and have good solvent resistance [4]. Polyurethane is usually used as a thermoset polymer, which is the highest demand in the pharmaceutical industry [5]. Therefore, producers strive to meet these needs by synthesizing from chemicals hexane diisocyanate (HDI) and poly trimethylene carbonate (PTMC) [6].

Polyurethanes found on the market are generally in the form of films. The polyurethane film was synthesized from 4,4-methylene-bis (cyclohexyl isocyanate), poly(ε-caprolactone)diol or poly (oxetetramethylene)glycol and 1,4-butanediol [7-9]. Large-scale production of these polymers poses a significant threat to the environment because it is difficult to degrade or takes a long time to degrade in the environment [10]. This case has encouraged researchers to develop biodegradable polymers [4,11].

The method that can be done to make a polymer becomes biodegradable is through the addition of starch in its synthesis process [10]. This synthesis needs starch which meets specific requirements, i.e., about surface morphology, particles size, and gelatinization temperature. In this research, we have been isolated starch from kepok banana hump (KBH) and determined its surface morphology by SEM, bonding characteristics by FTIR, and temperature of gelatinization and melting point by using DSC.
All analysis result data indicated that the obtained starch eligible to be used as a precursor to synthesize polymer biodegradable.

2. Experimental

2.1 Material
Banana humps were obtained from Sengkang, South Sulawesi, Indonesia; methanol, sodium metabisulfite, concentrated sulfuric acid, reagents Molisch, potassium hydroxide, sodium sulfate, sodium hydroxide, and phenolphthalein indicators were purchased from Merck.

![Diagram of starch fabrication processes](image)

Figure 1. The illustration fabrication processes of starch from KBH

2.2. Preparation of KBH Starch
About 2 Kg of the banana hump was blended in sodium metabisulfite solution with a ratio of 1:2 w/v to a pulp, and then filtered. The filtrate was added with 200 ml of aquadest, shaken, and then allow at room temperature for 24 hours. The precipitate formed was separated by decantation ways. This maceration process was repeated once more. The collected of brown-colored deposits obtained then washed with 50 ml of methanol. The precipitate is dried in an oven at 65 °C for 24 hours, cooled to room temperature, crushed, and sieved with a 100 mesh sieve [12]. The fabrication processes of the starch in this study can be seen in Figure 1.

2.3. Determination of moisture content
The weighing bottle is dried at 105°C for 30 minutes, cooled in the desiccator for 15 minutes, then weighed (c gram). One gram of starch is put into the weighing bottle and then weighed (d). The bottles containing starch are heated in an oven at 105 °C for 5 hours, cooled in a desiccator for 15 minutes then weigh again. Heating is continued and weighed at every 1-hour distance until the weight difference between 2 consecutive weights is not more than 0.25% (e) [12]

Water content = \( \frac{d-e}{d-c} \times 100\% \) (1)
Porcelain dish was dried in the oven for 2 hours then put in a desiccator for 1.5 hours and weighed (x grams). Two grams of sample was placed in a porcelain container and weighed (y grams), flattened in a furnace at 500˚C for 4-5 hours to form white ash. Porcelain and ash were cooled in a desiccator and weighed (z grams). Ash content was calculated using the formula [12]:

\[
\text{Ash content (\%)} = \frac{z-x}{y-x} \times 100\% 
\]

The illustration of the bonding mechanism between starch with ethanol and sodium metabisulphite is shown in Figure 2.

![Chemical Bond](image1)

**Figure 2.** Illustration of the bonding mechanism between starch with ethanol and sodium metabisulphite.

2.4 *Molisch Test.*

Starch solution (1%) of 2.5 mL is put in a tube, then added with 2 drops of Molisch reagent and 1.5 mL of concentrated H2SO4, then shaken then let stand. Positive tests are marked with purple rings [13].

![Carbohydrate test](image2)

**Figure 3.** Carbohydrate test by using Molish reagents

Isolation of starch from KBH obtained a yield of 17.2%. Result of carbohydrate test in this study using Molish reagents is shown in Figure 3. Further starch testing in this study encompasses of microscopic
testing: pH test, water content, ash content, viscosity, gelatinization temperature, melting point, and free fatty acid levels. The results are shown in Table 1.

**Table 1.** Characteristics of Starch in this study extracted from KBH.

| No | Form of Testing                             | Results          |
|----|--------------------------------------------|------------------|
| 1  | Recovery                                   | 17.2 %           |
| 2  | pH                                         | 6.12- 6.33       |
| 3  | Water content                              | 13.8%            |
| 4  | Ash content                                | 0.49%            |
| 5  | Viscosity (1% gel)                         | 834 cps          |
| 6  | The peak temperature starts the gelatinization process | 67.5°C          |
| 7  | Melting point                              | 184 °C           |
| 8  | Free fatty acid levels                     | 9.34%            |
| 9  | Drying shrinkage                           | 14.3%            |

**3. RESULTS AND DISCUSSION**

The pH value of KBH starch solution at various concentrations of 1%, 2%, 3%, and 4% was 6.33; 6.23; 6.15; and 6.12, respectively. The data shows an increase in pH with a decrease in concentration. This case occurs because an increase in concentration results in an increase in the number of hydrogen ions in solution [12]. Nevertheless, the starch value of the solution is still in the pH range 4-7 as a requirement to be used as a precursor in the synthesis of biodegradable polyurethanes [12,14].

Beside pH value, water content of starch is an important factor to be considered due to the MDI which used in the synthesis of polyurethanes is very reactive to water. Thus, the starch that is used wherever possible does not contain water. Water content in starch to be applied as precursors in synthesized polyurethane biopolymers is must not more than 15% [12,18]. Besides being related to the reaction with MDI, the starch's water content also affects the resistance in storage. Moisture content can trigger mold growth in starch. The starch moisture content in which mushrooms grow well is in the range of 14-15% [15]. In this study, water content of KBH was 13.81%, so the starch obtained in this study fulfilled the requirement to be used as precursor in synthesis and storage of a polyurethan.

Starch generally consists of 96% organic matter and trace mineral elements too [16]. Based on the result using equation 2, ash content in KBH starch which obtained through burning starch at 500°C is 0.49%. The ash content obtained has fulfilled the requirement to be the precursor of polyurethane biopolymer synthesis due to is still below of 0.6% [12,17].
Viscosity is also an essential parameter for starch, mainly if it will be used as a precursor in a reaction that produces heat. When the starch suspension is heated, the starch swells and causes the starch granules to swell due to water absorption and eventually gelatinization [17]. The value of KBH starch viscosity measurement with a concentration of 1% was 834 cps, and it turns out that this value is still in the range of starch viscosity values obtained from bananas in general, namely 280.23 - 3703 cps [12].

Another property of starch that also needs to be considered if it is to be used as a precursor is the temperature at which it has gelatinized. The temperature of starch gelatinization can be determined by the DSC method [12,19]. Figure 4 shows that the initial gelatinization of KBH starch occurred at 50°C, the peak of gelatinized starch occurred at 67.5°C, and melting occurred at 84.0°C.

In starch solution, viscosity and gelatinization have a close relationship. Starch does not dissolve in cold water, but when heated, gelatinization will occur because heating will increase viscosity resulting in starch swelling [17]. Swelling of the starch causes the starch granules to rupture and cannot return to its original position called gelatinization. Gelatinization temperature is influenced by the size of starch granules, the greater the size of the starch, the lower the gelatinization temperature. This case happens because large starches have the ability to absorb more water [17]. The XRD analysis results (Figure 5) showed that KBH starch formed two fractions, namely semi-crystalline and amorphous. The calculation of the crystallinity fraction of KBH starch in this study uses Equation 3 [20]. Based on KBH starch XRD spectra data, it gives a crystalline value of 78.8%. This value indicates that the KBH starch in the form of an amorphous fraction, and this form is a common form of starch.

\[
\text{Crystallinity} = \frac{\text{crystal fractional}}{\text{crystal fractional} + \text{amorphous fractional}} \times 100 \tag{3}
\]
Figure 5. XRD spectra of KBH starch

The XRD spectrum of KBH starch has also been compared with the starch spectrum from banana peels obtained from previous studies [2]. As shown in Figure 5, KBH starch that has been freed from fatty acid has a spectrum similar to the spectrum of banana peel starch where the peaks at $2\theta = \pm 23^\circ$ were sharper than the similar peak in the KBH starch without the releasing process from fatty acid. It is meant that the starch contained free fatty acid was more in amorphous form than the starch fatty acid freed.

Morphology of KBH starch has been analysis by SEM method and gave pictures as in Figure 6. Both at 10,000x (a) and 25,000 (b) magnifications appear round and slightly oval in starch in one stack. At 10,000x magnification, the diameter of the dominant particle is measured between 66-69 nm; whereas at a magnification of 25,000x, the measured diameter of the dominant particle is at around 27 nm. Figure 6 (b) also shows that KBH starch particles are dominant in the amorphous form.
Identification of functional groups contained in KBH starch was carried out by FTIR spectroscopy method. The FTIR spectrum in Figure 7 shows the absorption band of O-H vibrations at wavenumbers 3415.0 cm⁻¹, saturated C-H at 2927.0 cm⁻¹, and C-O groups at 1157 cm⁻¹. These three bands are in accordance with the presence of alcohol groups in the structure of starch. The presence of the peak vibration absorption of C=O at 1735.0 cm⁻¹ indicates the presence of carbonyl compounds derived from other compounds in starch, possibly fatty acid esters or alginates. The presence of these peaks indicates that even though it has been purified, KBH starch still contains a number of impurities. The absorption band at 1641 cm⁻¹ correlates with the C=C group and shows that the esters are derived from unsaturated fatty acids. The absorbance at 1456.0 cm⁻¹ corresponds to the methylene framework (-CH₂-) in starch molecules. The spectrum of KBH starch is consistent with the potato starch spectrum, which had been isolated by previous researchers [21].
Compounds accompanying KBH starch have been traced using GCMS. The GCMS spectra showed the presence of several types of compounds, both in the form of saturated fatty acids and unsaturated fatty acids, ethyl esters of fatty acids, and others. These compounds are presented in Table 2.

Table 2 shows that the compounds that accompany KBK starch are dominated by fatty acid compounds with a total of 78.66%, the remaining 21.34% are ethyl ester and ether compounds. This is what causes KBH starch in amorphous form. If the fatty acids are dominant in a starch, the starch tends to form an amorphous structure [22], whereas if the ethyl ester and ether compounds are dominant, the starch tends to form a crystal structure [21].

In addition to FTIR data, starch which was successfully isolated from KBH has also been proven by analysis using Molisch reagents. Adding Molisch reagents to the starch solution results in a purple ring. The formation of the purple ring corresponds to the structure of the starch, which is composed of polyhydroxy aldehyde monomers. This result is the basis used to show that starch is a potential material used as a precursor for the synthesis of polyurethane biopolymers, where the hydroxyl groups are expected to react with MDI to form urethane groups.
Tabel 2. Impurities Compounds in KBH starch

| No | Group                        | Name of Compound                          | Percentage |
|----|-----------------------------|-------------------------------------------|------------|
| 1  | Saturated fatty acids.      | eicosanoic acid                           | 1.26%      |
|    |                             | hexadecanoic acid                         | 21.96%     |
|    |                             | heptadecanoic acid                        | 1.39%      |
|    |                             | tetradecanoic acid                        | 1.14%      |
|    |                             | pentadecanoic acid                        | 1.22%      |
|    |                             | palmitic acid                             | 22.52%     |
| 2  | Unsaturated fatty acids     | Cis-13 – octadecanoic acid                | 5.59%      |
|    |                             | acid 11,13-dimethyl-12-tetradesene        | 4.78%      |
|    |                             | -1-of-acetate                             | 11.24%     |
|    |                             | acid 9,12-octadecadienoic                 | 5.59%      |
|    |                             | octadecanoic acid                         | 1.97%      |
|    |                             | acid (E8) -8-octadecanoic                 |            |
| 3  | Fatty acid ethyl ester      | ethyl hexadecanoic                        | 21.96%     |
| 4  | Ether                       | methyl alpha-D-xilofuranoside (ether)     | 2.97%      |

4. Conclusion
The isolation of starch from KBH gave amorphous solid with a 17.2% yields. The starch contains amorphous phase portion 78.8%, the particle size in 10,000x magnification is 66-69 nm, and the starch gelatinization process occurred at 67.5°C. Based on these data, the obtained starch has high potential to be applied as a precursor to synthesize a biodegradable polyurethane.

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References
[1] Mesquita CB, Leonel M, Franco CML, Leonel S, Garcia EL, Santos TPR 2016. J. Biomac 89 632-639
[2] Hadisoeawignyo L, Foe K, Tjandrawinata RR 2017. IFRJ 24 1324-30
[3] Tai L, Adhikari R, Shanks R, Adhikar B 2017. J. Carbopol 163 236-46
[4] Sulaiman S, Khan SM, Jamil T, Aileen W, Shafiq M 2014. AJAS 701-10
[5] Mansur S, Othman MHD, Ismail AF, Kadir SHSA, Lusiana RA 2019. J. Materials Science and Engineering 99 491-504
[6] Trinca RB, Abraham, Felisberti MI 2015. J. Materials Science and Engineering 56 511-51
[7] Krol P, Uram L, Krol B, Piechowska K, Walczak M 2018. J. Materials Science and Engineering 93 483-94
[8] ChoiDS, Moon SG, Ryu B, Lee K, Lee J 2018. J. Polymer 138 146-55
[9] Babae A, Rezaei M, Lotfi R, Sofia M 2019. J. Polymer 138 53-68
[10] Nakkabi A, Itohane N, Dary M, Duran EM, Fahmi M 2015. IOSRJEN 6 82-86
[11] Amaral JS, Sepulveda M, Cateto CA, Fernandes IP, Rodrigues AE, Belgacem MN, Barreiro MF 2017. J. Polymer Degradation and Stability 97 2069-2076
[12] Hang TV, Scarlett C, Vuong QV 2018. J. Functional Foods 40 238–48
[13] Mohammad 2018. World Journal of Chemical Education 682-86
[14] Perez A.B, Acevedo E.A, Garcia-Valle D.E, Ramirez J.A. 2019. J. of Biological Macromolecules. 122405-409
[15] Carocho M, Heleno S, Rodrigues P, Barreiro MF, Barros L, Isabel CFFR 2019 LW776-83
[16] Sundum T, Szécsény KM, Kaewtatip K 2018. J. Carbohydrate Polymer 191 198-204
[17] Han H, Hou J, Yang N, Zhang Y, Chen H, Zhang Z, Shen Y, Huang S, Guo S. Int. J. Biol. Macromol 2019 12637-43
[18] Fabian C, Ayucitra A, Ismadji S, Ju YH 2011. J. Taiwan Institute of Chemical Engineers 42 86-91
[19] Dankar I, Haddarah A, Omar FEL, Pujolà M, Sepulcher F 2018. J. Food Chemistry 2607-12
[20] Schirmer M, Höchtötter A, Jekle M, Arendt E, Becker T 2013. J. Food Hyd 3252-63
[21] Pelissari FM, Menegalli FC, Andrade MM, Mahecha PJD, Sobral A 2012. Starch article 64 82–391
[22] Chen B, Guo Z, Miao S, Zeng S, Jia X, Zhang Y, Zheng B 2018. J. Food Engineering 23752-59