Modification and Characterization Starch Nanoparticles of Mangrove Fruit using Chemical-mechanical Method and Application as Basic Materials Making Hydrogel

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Abstract: Mangroves are plants that function as protectors of the land from ocean waves. Mangroves are a source of starch that has not been explored. To expand the application, the starch needs to be modified. Natural starch is made using wet extraction. Natural starch is synthesized into nanoparticle starch by chemical-mechanical methods. Modified Mangrove Fruit Starch can be used as a base for making hydrogels. Characterization of starch and starch nanoparticles includes proxy analysis, functional groups using the Fourier Transform Infrared Spectroscopy (FTIR). Test the PSA (Partiicle size analyzer) to find out the particle size. Crystallinity test of starch nanoparticles using X-Ray Diffraction (XRD). The morphological analysis of nanoparticles was carried out using the Scanning Electron Microscopy (SEM) instrument. Thermal test using Differential scanning calorimeter (DSC). The results showed that mangrove starch had a yield of 29.60% and particle size of mangrove nanoparticles of 38.79 nm.

1 INTRODUCTION

Starch is a natural biopolymer used in the food, chemical, pharmaceutical / biomedical, paper, textile and so on industries. Starch is renewable, non-toxic, edible and inexpensive and easy to obtain. Natural starch has several disadvantages that need to be modified so that it has the appropriate characteristics as industrial ingredients.

Desirable important properties of modified starch include higher brightness, lower viscosity, clearer gel formed, easier starch granules to rupture, higher gelatinization time and temperature (Koswara, 2009). Modification of several types of starch namely tapioca, sago can produce nanoparticle starch which serves as a matrix binding to herbal active ingredients and lactic acid bacteria (Sunarti, et al, 2015).

There are still many sources of starch that have not been developed, among others, mangrove fruit starch besides functioning as a protector of land from large ocean waves (Irwanto, 2006), rhizophora mucronata plants. also is one type of mangrove that can be used as a new food source. This is because this species contains high carbohydrates.

Nanotechnology has great potential to produce new composites. One application is nanocomposite in biomedicine. Nanocomposite can be done by inserting nanoparticles into the matrix. The nanoparticles commonly used for nanocomposites include carbon nanotubes, cellulose, silica, and chitin. Nanocomposite is generally used to improve mechanical properties and packaging properties (barrier properties) (Azeredo, 2009). Starch in the form of nanoparticles has several advantages including low suspension viscosity even though the concentration is relatively high, and has a high binding strength (Gularte and Rosell, 2011).

There are several previous studies that have been carried out to isolate starch and synthesis of starch nanoparticles. Among them are chemical methods of hydrolysis with strong acids H_2SO_4 (Wei, et al, 2014), dissolution methods and non-solvent precipitation (Saari, et al, 2017), ionic gelation methods (Yang, et al, 2015). Enzymatic method of enzyme hydrolysis using alpha amylase enzyme (Rahmawati and

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Yunianta, 2014). Combined method of enzyme hydrolysis and acid (LeCorre, et al, 2012). The mechanical method uses ultrasonication (Haaj, et al, 2013). From several studies on starch making it is known that chemical-mechanical methods have proven effective for isolating starch and reducing its size to starch nanoparticles (Kim, et al, 2013).

Based on this background, the authors are interested in conducting research on the modification and characterization of starch from mangrove nanoparticles with chemical-mechanical methods and their application as a basis for making hydrogels

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study are Mangrove Fruit, Aquadest, 2% Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4) 98% (E.Merck), Na-metabisulfite (E.Merck), Sodium Chloride (NaCl), Ethanol (E. Merck).

2.2 Extraction of Mangrove Starch

Extraction of mangrove starch was carried out by referring to the method developed by Wijayanti et al. (Wijayanti, et al, 2010). Mangrove fruit obtained from the coast in Aceh Tamiang Regency, mangrove fruit weighed 1 kg and then peeled and then washed into a 4% NaCl solution in 3 liters of water (comparison 1: 3). To find out the net weight, the peeled skin is weighed so that it gets clean weight. Then soaked with 0.075% Na-metabisulfite with a ratio of 1: 3. Then the tubers are washed with tap water, shredded and filtered while being given water. Then leave it to settle for 1 night, the filtrate is removed and the sediment is taken. The precipitate is dried at 40^{o}C, then milled and sifted with a 100 mesh sieve.

2.3 Characterization of Mangrove Fruit Starch

2.3.1 Proximate Analysis

Mangrove starch obtained by proximate analysis of the AOAC Method, 2006 (AOAC, 2006).

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Analysis of mangrove starch functional groups using the Fourier Transform Infrared Spectroscopy (FTIR) tool. The FTIR spectrum of the sample was recorded using the Bruker OPUS 7.5.18 infrared spectrometer (Bruker, Germany) at wavelengths from 400 to 4000 cm^{-1} at a speed of 20 cm^{-1}.

2.4 Isolation of Nanoparticles of Mangrove Starch

Starch nanoparticles are prepared using a modification of the procedure described by Angellier, et al (2004). Briefly, mangrove fruit starch (44.07 g, dry solid) was dispersed in an acidic solution of H_2SO_4 (3.16 M, 300 ml), and the dispersion was stirred with a magnetic stirrer (200 rpm) at 40 ° C. After various periods of hydrolysis, the sample taken and neutralized with NaOH (1 M) to neutral pH and centrifuged at 3500 rpm for 10 minutes. Added deionized water (300 ml) into the precipitate, and the mixture stirred for 30 minutes at room temperature. This washing process is repeated twice to remove the remaining salt. Next, the starch was deposited, and the suspension was centrifuged at 500 rpm for 10 minutes to separate the solids in the supernatant. Then it was ultrasonified at the highest amplitude (90%) for 15-30 minutes. Then freeze drying was used to obtain starch nanoparticle powder.

2.5 Characterization of Mangrove Starch Nanoparticles

2.5.1 Proximate Analysis

Particle size was characterized using Particle Size Analyzer (PSA) nanoq cordouan v2.0.0.1

2.5.2 X-Ray Diffraction (XRD) Analysis

Analysis of crystallinity of mangrove starch using X-Ray Diffraction (XRD) was operated at 40 kV and current of 30 mA of electricity using Cu Kα radiation at 1.5418 A wavelength and scanned from 0.0050 (2 Θ / s).

2.5.3 Scanning Electron Microscopy (SEM) Analysis

The surface morphology of mangrove starch nanoparticles was characterized using SEM (DX EVO MA 10 Carl Zeiss, Germany).

2.5.4 Differential Scanning Calorimeter (DSC) Analysis

Thermal properties of nanoparticle starch using Differential scanning calorimeter (Shimadzu). This analysis is carried out to measure the energy absorbed or emitted by a sample which gives measurements of calorimetry and transition energy at a certain temperature.

3 RESULTS AND DISCUSSION

3.1 Extraction of Mangrove Starch

Making mangrove starch is done by wet extraction. The yield of mangrove fruit starch was 29.60%. The high rendeman of large-potential mangrove fruit starch is developed into a starch source and alternatively becomes a new food source (Kardiman, et al, 2017). The resulting mangrove fruit is brownish white. The results of extracting mangrove fruit can be seen in Figure 1.

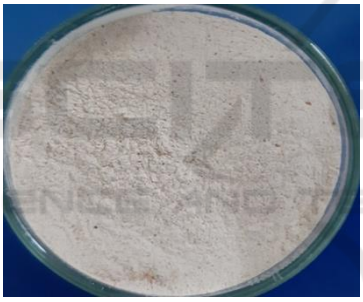

Figure 1: Mangrove Fruit Starch.

3.2 Characterization of Mangrove Starch

3.2.1 Analysis Proximate

For the results of a preliminary analysis of mangrove starch following the procedure of the Association of Official Analytical Chemist (AOAC), 2006, it can be seen in Table 1 below. Proximate analysis result showed that starch mangrove fruit is a surce of high carbohydrate.

Table 1: Test Results Mangrove Fruit Starch Proximate.

Proximate Components	Content (%)
Protein	4.26
Crude fiber	36.98
Starch	56.61
Crude fat	0.76

3.2.2 Analysis Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrum from mangrove starch nanoparticles can be seen in Figure 2.

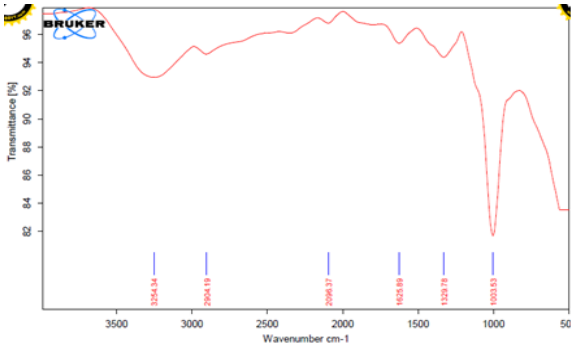

Figure 2: FTIR spectrum of mangrove starch.

The shape of the widening peak is seen in the absorption area of 3000 - 3600 cm^{-1}. This vibration shows the vibration of the stretching region of hydrogen with O-H bonds (carboxylic acids). The vibrational peak in the area of 2850 - 2960 cm^{-1} and vibration in the area of 1340 - 1470 cm^{-1}, this stretch shows the vibration of the aliphatic C-H bond. In the absorption area with wave number 1636 cm^{-1}, this vibration shows the vibration of the C = C bond. This peak shows the vibration of the area which is cyclic or aromatic ring and in the absorption area of 1050 - 1300 cm^{-1} This vibration shows the vibration of the stretching region of hydrogen with the C-O bond). The results of FTIR spectroscopic analysis showed that the mangrove starch provides a spectrum that describes the structure of starch.

3.3 Synthetic Mangroveti Fruit Starch Nanoparticles

The making of mangrove starch nanoparticles consists of several stages, namely: the acid hydrolysis stage, the neutralization stage of the mechanical stage and the phase of separation or often called the chemical-mechanical method.

In this study, the hydrolysis of mangrove starch was dispersed in an acid solution of 3.16 M H_2SO_4, the use of sulfuric acid was too concentrated to convert starch to glucose and the dispersion was stirred with a magnetic stirrer (200 rpm) at 40 ° C. After various periods of hydrolysis, samples were taken and neutralized with NaOH (1 M) to neutral pH and centrifuged at 3500 rpm for 10 minutes. Added deionized water (300 ml) into the precipitate, and the mixture stirred for 30 minutes at room temperature. This washing process is repeated twice to remove the remaining salt. Next, the starch was deposited, and the suspension was centrifuged at 500 rpm for 10

minutes to separate the solids in the supernatant. Then it was ultrasonified at the highest amplitude (90%) for 15-30 minutes. Then freeze drying was used to obtain starch nanoparticle powder.

The point of Hee-Young Kim et al., (2013) the chemical treatment aims to degrade amorphous regions in starch granules. Mechanical treatment is carried out such as homogenization by ultrasonication in starch that has undergone chemical treatment before. During the hydrolysis process, starch nanoparticles continue to be produced because starch granules are fragmented by acid but producing starch nanoparticles may tend to form aggregates that are easily deposited as microparticles. To inhibit aggregation or to separate nanoparticles, ultrasonic treatment is applied to starch dispersion, and changes in the size distribution of starch particles are examined by dynamic light scattering. Mild acid hydrolysis combined with ultrasonication can effectively produce starch nanoparticles. Ultrasonication plays an important role in separating the aggregates of nanoparticles that can form during hydrolysis, thus effectively increasing the yield of starch nanoparticles. However, starch nanoparticles which are processed by ultrasonication can reduce the crystallinity of starch.

3.4 Characterization of Starch Nanoparticles

3.4.1 Results of Particle Size Analyzer (PSA) Analysis

Particle Size Analyzer (PSA) is a characterization that can be used to determine particle size and distribution in a solution.

This method uses the principle of light scattering. In this study wet method was used for the particle size testing process. In the wet method using dispersion media to disperse the test material. So that the starch nanoparticles to be tested are dissolved in distilled water for 4 hours at room temperature while the stirring process is carried out so that the particles do not agglomerate (clump) each other. Thus the measured particle size is the size of a single particle. Besides the measurement results in the form of distribution, the measurement results can be assumed to have described the overall condition of the sample.

Based on Figure 3, there is a symmetrical peak which indicates the particle size distribution is evenly distributed in all parts. The peak appears in an area with an average particle size of 38.79 nm. The size and distribution of the particles produced reflects or represents the size of the particle diameter in its bulk state.

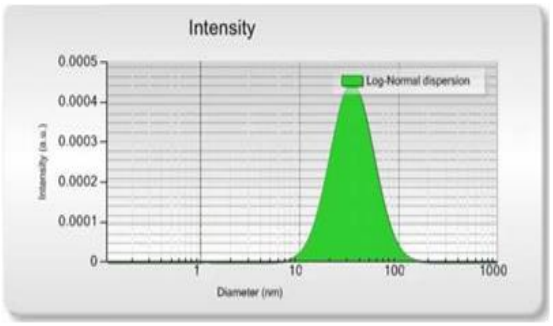

Figure 3: Distribution curve for the size of the Mangrove Starch Nanoparticles.

3.4.2 Results of Particle Size Analyzer (PSA) Analysis

Determination of the crystallinity of mangrove fruit nanoparticles was done by XRD, which is by placing samples of mangrove fruit nanoparticles in a place so that they can rotate on one axis. Then irradiate the sample with X-rays, so the field devices in the crystal reflect the X-ray beam. Then the beam is received by the detector, so that the diffractogram is obtained. The diffractogram of the polymer samples produced contained crystalline and amorphous regions which mixed randomly. The diffractogram of X-ray crystalline polymers has a sharp peak, while amorphous polymers have a wide peak. For the XRD analysis of mangrove fruit starch nanoparticles can be seen in Figure 4 below.

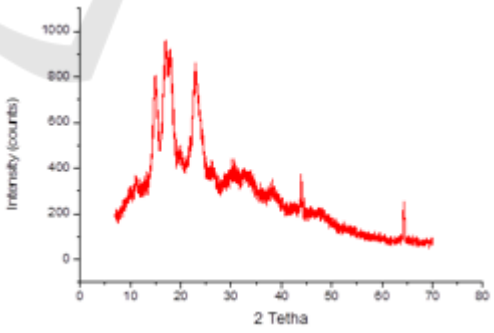

Figure 4: Distribution curve for the size of the Mangrove Starch Nanoparticles.

The highest mangrove starch nanoparticle peaks were formed at 150 and 230, indicating that mangrove fruit nanoparticles were successfully synthesized.

3.4.3 Results of Scanning Electron Microscopy (SEM) Analysis

Morphological analysis was carried out to see the pore size of the hydrogel with variations in the addition of mangrove starch nanoparticles in this case using the Scanning Electron Microscopy (SEM) tool. For SEM photos can be seen in Figure 5 below.

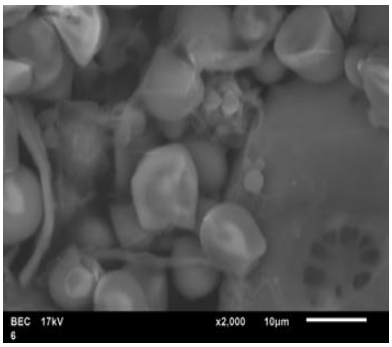

Figure 5: Results of SEM of Mangrove Fruit Starch Nanoparticles.

The treatment of acidic and mechanical hydrolysis during the precipitation process can cause the formation of smaller particles when starch is degraded. This mechanical treatment causes the cutting of bonds between amylose and amylopectin molecules when starch is degraded so that the shape and size of the particles of starch do not return to their original conditions, this indicates that the structure of starch has been modified. Based on morpholytic analysis of starch using SEM, it was seen that the starch particles after precipitation were still not completely separated and still combined to form pores. This porous structure can affect the functional characteristics of nanocrystalline starch.

3.4.4 Results of Analysis of Mangrove Starch DSC Analysis

Differential Scanning Calorimetry (DSC) is a thermal property analysis technique where the function is measured. DSC is used to study thermal properties and phase changes in calorimetry of a material. DSC analysis has been conducted on mangrove starch samples which can be seen in Figure 6.

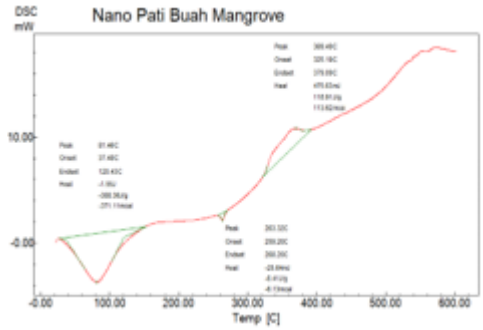

Figure 6: Graph of Analysis Results of DSC Nanoparticles of Mangrove Starch.

In Graph 5 shows changes in endothermic reactions and exothermic reactions of mangrove starch nanoparticles. At temperatures of 81.46^{o}C showed the temperature of the endothermic reaction (heat absorbing), at temperatures of 369.49^{o}C showed the exothermic reaction temperature, which stated that the material had been degraded (damaged), this meant that mangrove starch nanoparticles could be used below the degraded temperature which was below 369.49^{o}C.

4 CONCLUSIONS

Mangrove starch nanoparticles were successfully isolated by chemical-mechanical methods, through three stages of using acid hydrolysis stage, H2SO4 3.16 M, mechanical phase neutralizing with NaOH (1M) using centrifugation at 500 rpm for 10 minutes and ultrasonication at highest amplitude (90%) for 15-30 minutes. FTIR Characterization Results of mangrove starch nanoparticles provide a spectrum that describes the structure of starch, the highest peak of mangrove starch nanoparticles formed at 150 and 230, This shows that mangrove fruit nanoparticles were successfully synthesized and the size of starch nanoparticles obtained was 38.79 nm.

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