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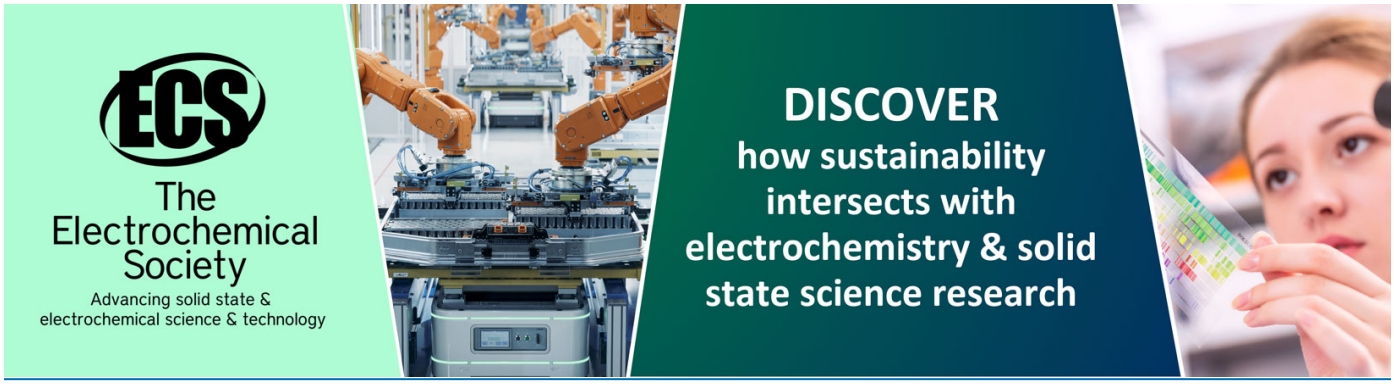

Production of bioplastic from jackfruit seed starch (*Artocarpus heterophyllus*) reinforced with microcrystalline cellulose from cocoa pod husk (*Theobroma cacao L.)* using glycerol as plasticizer

M Lubis[1*], A Gana[1], S Maysarah[1], M H S Ginting[1], and M B Harahap[2]

[1]Department of Chemical Engineering, Faculty of Engineering, University of Sumatera Utara, Medan, 20155, Indonesia
[2] Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Medan, Medan, 20221, Indonesia

*Email: maulida@usu.ac.id

Abstract. The production of bioplastic from jackfruit seed starch reinforced with microcrystalline cellulose (MCC) cocoa pod husk using glycerol as plasticizer was investigated to determine the most optimum mass and volume of MCC and glycerol in producing bioplastics. To produce MCC, Cocoa pod husk was subjected to alkali treatment, bleaching, and hydrochloric acid hydrolysis. The degree of crystallinity of MCC, were determined by XRD, functional group by FT-IR and morphologycal analysis by SEM. Analysis of bioplastic mechanical properties includes tensile strength and elongation at break based on ASTM D882 standard. Bioplastics were produced by casting method from jackfruit seed starch and reinforced with MCC from cocoa pod husk at starch mass to MCC ratio of 6:4, 7:3, 8:2, and 9:1, using glycerol as plasticizer at 20%, 25%, 30% (wt/v of glycerol to starch). From the result, the isolated MCC from cocoa pod husk were in a form of rod-like shape of length 5-10 µm with diameter 11.635 nm and 74% crystallinity. The highest tensile strength of bioplastics was obtained at starch to MCC mass ratio of 8:2, addition of 20% glycerol with measured tensile strength of 0.637 MPa and elongation at break of 7.04%. Transform infrared spectroscopy showed the functional groups of bioplastics, which the majority of O-H groups were found at the bioplastics with reinforcing filler MCC that represented substantial hydrogen bonds.

1. Introduction

In daily life, plastics are used almost everywhere in the world for various purposes because plastics are inexpensive, readily available, durable and versatile [1]. However, the main raw material in producing plastics derived from petroleum is declining and non-renewable. In addition, the plastics can not be destroyed quickly and naturally by destructive microbes in the soil. This causes the accumulation of waste, pollution and environmental damage [2]. The environmental, economic and safety challenges have prompted many scientists to replace part of a petrochemical-based polymer with another biodegradable type, called bioplastics [3]. Bioplastics are a renewable type of plastics because its constituents come from plants such as starch, cellulose, lignin, and animals such as casein, protein and lipids [4]. But there is still lack in the development of bioplastics as its high cost of production leads to

certain limitations. An alternative for a low cost and a renewable substrate has been proposed by using agriculture waste (AW) [5].

One of the major components of bioplastics is starch. Starch is often used in the form of biodegradable films in a variety of applications as they are renewable, abundant and inexpensive materials [6]. In jackfruit contains about 100-500 jackfruit seeds or about 8-15% by weight of the jackfruit itself with a high starch content [7]. In producing of bioplastics, the addition of fillers is essential to increase the strength and toughness of the bioplastic products. The addition of fillers such as cellulose has been shown to be a very promising material [8]. One of the materials that have cellulose potential is cocoa pod husk which is an agro-industrial waste produced from the cocoa plant (*Theobroma cacao L.*). Cocoa pod contains 74% fruit peel, 2% placenta and 24% seeds [9]. Cocoa pod husk contains 11% hemicelluloses, 35% cellulose, 15% lignin, 6% pectin, and other mineral elements such as K (3.18%), Ca (0.32%) and P (0.15%) [10]. Also, the addition of plasticizer serves to increase the flexibility of bioplastic. Glycerol is a good plasticizer to reduce the internal hydrogen bonds that will improve the intermolecular distance [11].

2. Materials and Methods

2.1. Materials

Starch from jackfruit seeds obtained from jackfruit merchant in Langsa, Aceh, Indonesia. Cocoa pod husk as raw material for microcrystalline cellulose production is taken from Kampung Padang area, Sei Rampah, North Sumatera, Indonesia. Aquadest (H_2O), Sodium Hydroxide (NaOH), Sodium Hypochlorite (NaOCl), from Rudang Jaya Chemicals Store. Acid Chloride (HCl) from Laboratory of Microbiology Engineering, Chemical Engineering, University of Sumatera Utara, Indonesia.

2.2. Producing of Microcrystalline Cellulose from Cocoa Pod Husk

Cocoa pod husk powder of 100 g was inserted into beaker glass then added 1.5 L NaOH 4% and heated for 2 hours at 100ºC. The residue is filtered and washed with aquadest to neutral pH. The residue is bleached with 2.5% sodium hypochlorite soaked 1 L for 24 hours at room temperature then filtered, and the residue washed with aquadest to neutral pH. The obtained residue added 17.5% NaOH as much as 650 ml then heated at 80 ºC for 1 hour. The residue is filtered and washed with aqua dest to neutral pH. Bleaching with 500 ml of 2.5% sodium hypochlorite and heated at 100 ºC for 5 minutes. The residue is filtered and washed with aqua dest until the pH is neutral. Dried in an oven at 60 ºC for 12 hours. The obtained powder of microcrystalline cellulose was hydrolyzed using 2.5 N HCl by boiling for 10-15 minutes and filtered. The obtained residue is washed to neutral with aqua dest then dried and mashed.

2.3. Producing of Jackfruit Seed Starch

Jackfruit seeds as much as 100 g peeled parts of the outer shell, and its skin then cleaned with clean water. Seeds cut to the size of approximately one cm^2 then crushed using a blender with added water. The mixture is filtered until the resulting dregs and liquid filtrate (starch suspension). The obtained suspension is then deposited for 24-48 hours. The starch-rich liquid then filtered using Whatman filter paper no.1 to obtain wet starch. The precipitate obtained was dried in an oven at 70 °C for 30 minutes. Dried starch powder then sieved with a 100 mesh sieve.

2.4. Producing of Bioplastic

The amount of starch and microcrystalline cellulose mass is weighed by the variation of the 6: 4, 7: 3, 8: 2 and 9:1 ratio of 10 g of the total dry weight of starch to microcrystalline cellulose. Then the starch solution made with a ratio of starch: aqua dest 1:20 and microcrystalline cellulose solution with 5% NaOH solution by 40 ml. The starch solution was heated while stirrer was mixing for 10 minutes and then added glycerol with 20%, 25%, 30% variation of the total dry weight of starch to microcrystalline cellulose. Microcrystalline cellulose solution was then added to the mixture after 20 minutes. The

mixture was then heated while stirred to a temperature 88,15 ºC. The mixture is cooled and printed on a 25 x 25 x 3 mm acrylic mold. Bioplastic is dried in an oven at 60 ºC for 24 hours. Bioplastic is removed from the oven and cooled to be removed from the mold.

2.5. Microcrystalline Cellulose Characterization

2.5.1. X-Ray Diffraction (XRD).
This analysis is performed to measure the crystallinity and the resulting microcrystalline cellulose diameter. This analysis was conducted at Physical Chemistry Laboratory, State University of Medan.

2.5.2. Scanning Electron Microscope (SEM).
This analysis aims to observe the morphology of microcrystalline cellulose from cocoa pod husk. This analysis was conducted at Integrated Laboratory, Diponegoro University, Semarang.

2.6. Bioplastic Mechanical Test

2.6.1. Tensile Strength.
Tensile strength was measured with GoTech Universal Testing Machine (UTM) using the standard of ASTM D882. Tensile strength was calculated as follow :

$$\text{Tensile Strength} = \text{Max Load} \times \text{Gravity} \quad (1)$$

2.6.2. Elongation at Break.
Elongation at break is an indication of bioplastics flexibility, and it's expressed as a percentage. Elongation at break was calculated as follows:

$$\text{Percent elongation (\%)} = \frac{\text{(Elongation at rupture)}}{\text{(Initial gage length)}} \times 100\% \quad (2)$$

2.6.3. Fourier Transform Infrared Spectroscopy (FT-IR)
Functional groups of bioplastics were analyzed by using IR Prestige-21 Shimadzu. This analysis was conducted at the Pharmaceutical Research Laboratory, University of Sumatera Utara.

3. Results and Discussions

3.1. Microcrystalline Cellulose Characterization

3.1.1. X-Ray Diffraction (XRD)

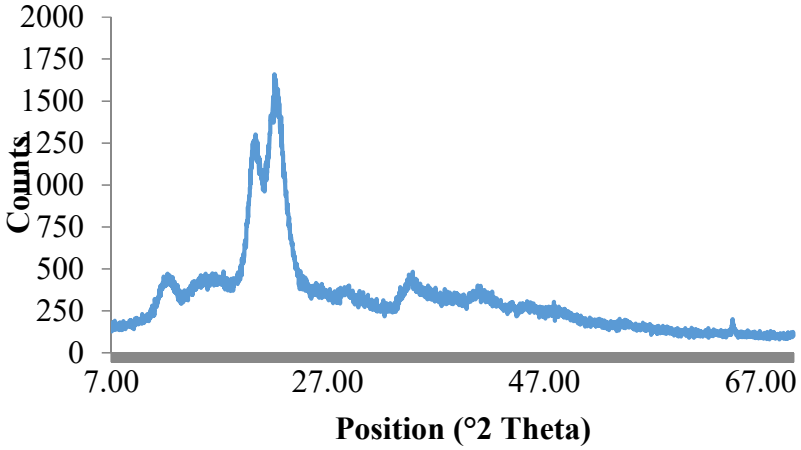

Figure 1. X-Ray Diffraction Graph of Microcrystalline Cellulose from Cocoa Pod Husk

From figure 1. It shows that the absorption peaks of the spectra generated by microcrystalline cellulose are at 2θ = 12.14°; 20.20° and 22.08°. The value of crystallinity was obtained by calculating the intensity of the XRD analysis using Segal method with the equation below [12] :

$$CrI = \frac{I_{002} - I_{AM}}{I_{002}} \times 100\% \quad (3)$$

The percentage crystallinity of microcrystalline cellulose from cocoa pod husk obtained is 74%, this value is much higher when compared with other non-wood materials (52-53%) [13]. The diameter of the crystal can also be calculated on the results of crystallinity analysis by X-Ray Diffraction using Scherrer's equation with the equation below [14] :

$$B(2\theta) = \frac{K\lambda}{L.Cos\ \theta} \quad (4)$$

The absorption peak of the spectra generated by microcrystalline cellulose is at 2θ = 12.14°; 20.20° dan 22.08°. By calculating the crystal diameter of microcrystalline cellulose at the apex of 2θ=22.08° using the Scherrer's equation, the diameter of the crystal was 11.635 nm.

3.1.2. Scanning Electron Microscope (SEM)

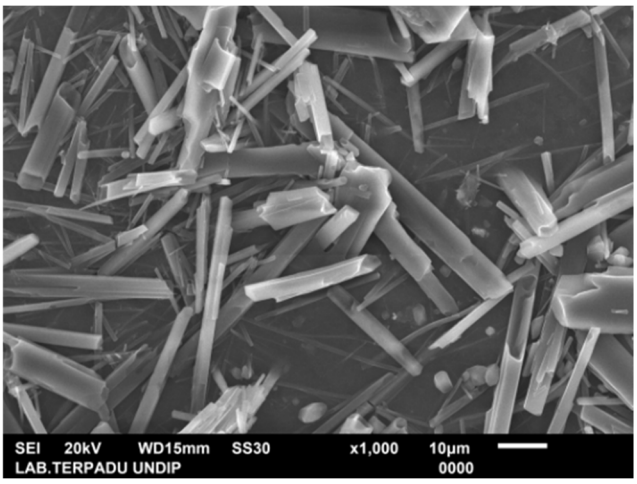

Figure 2. Microcrystalline cellulose with magnification 1000x

Figure 2. shows the SEM result of microcrystalline cellulose from cocoa pod husk with 1000x magnification. From the SEM analysis, it can be seen that most of the microcrystalline cellulose from cocoa pod husk morphology of rod-shaped is interconnected with a size of about 5-10 µm.

Microcrystalline cellulose morphology derived from sisal shows the same result, i.e., rod-shaped [15] [16]. Several pieces of micro fibers are found in the observed microcrystalline cellulose. Particle shape is an important determinant in determining the density of material. The particle shape of material also describes the porosity of the material. Particles of larger size have a lower porosity [17].

3.2. Bioplastic Mechanical Test Analysis

3.2.1. Tensile Strength

Figure 3. shows the highest tensile strength value is 0.637 MPa for composition ratio of starch: MCC 8:2 with the addition of glycerol 20 %. While the lowest tensile strength value is 0.147 MPa for composition ratio of starch: MCC 6:4 with the addition of glycerol 30%. The addition of microcrystalline cellulose of gelatinization starch film involved grouping of intermolecular hydrogen bonding that causes a molecular bond of amylose in starch more compact [18]. In this case homogeneity of bioplastic is the other important factor of bioplastic with a good characteristic. This homogeneity is related with the solubility of microcrystalline cellulose in NaOH as a solvent. Kontturi (2015) report that a part of cellulose crystalline could partially soluble in a solution of NaOH 5-20% after the accurate pretreatment than part of amorphous could soluble in NaOH 4% [19]. In this research, the solution of NaOH 5% (w/v) used as solvent.

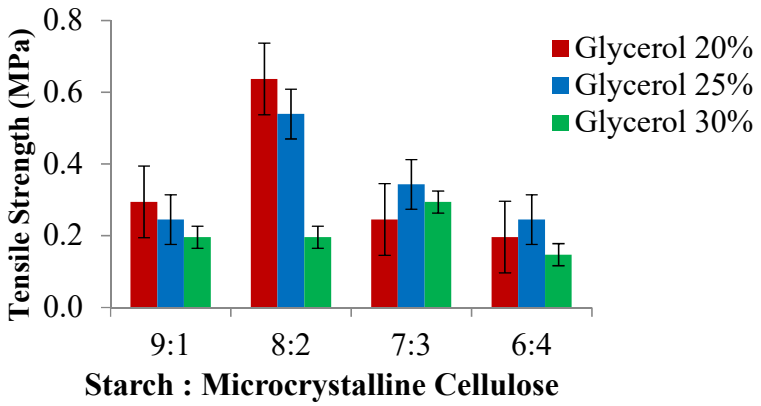

Figure 3. The effect of microcrystalline cellulose and glycerol addition on tensile strength of bioplastic from jackfruit seed starch

The amount of cellulose which is dissolved in a solution of NaOH-water depends on polymerization degree and also its cellulose crystallinity [20]. Based on the graphic, tensile strength at high filler loading (7:3 and 6:4) has declined because the presence of high content of MCC fillers might contribute in retarding the intermolecular interaction of the starch films. This induces the development of a heterogeneous film structure, featuring discontinuities, resulting in the decrease in tensile strength of films [8]. From figure 3. could be seen that the tensile strength value tends to drop with increasing of glycerol volume addition. Because more variation of glycerol added then the tensile strength get lower. This case causes by molecules of plasticizer will disturb compact of the starch, decreasing interaction of hydrogen bonding and increasing the polymer mobility [21]. Molecules of glycerol will disturb compactness of constituents molecules. This condition effected the increasing of edible film flexibility. After that, the elongation and tensile strength of edible film become decrease [22]. But, there is tensile strength in a composition ratio of starch: MCC 8:2 and glycerol 20% increased than it dropped again. Abdorreza et al (2011) stated that its deviation caused by the ability of plasticizer sustain crystallinity of bioplastic film. The flexibility could increase by the addition of plasticizer, but it also formed plasticizer crystal in film [23].

3.2.2. Elongation at Break

Figure 4. shows that by the increasing of microcrystalline cellulose mass then elongation at break value of bioplastic will be decreased. While by the increasing of glycerol volume addition, elongation at break value of bioplastic will be increased. The highest of elongation at break value is 15.76% for bioplastic with MCC content 4 g with glycerol 30%. The lowest of elongation at break value is 1.82% for bioplastic with MCC content 3 g with glycerol 20%.

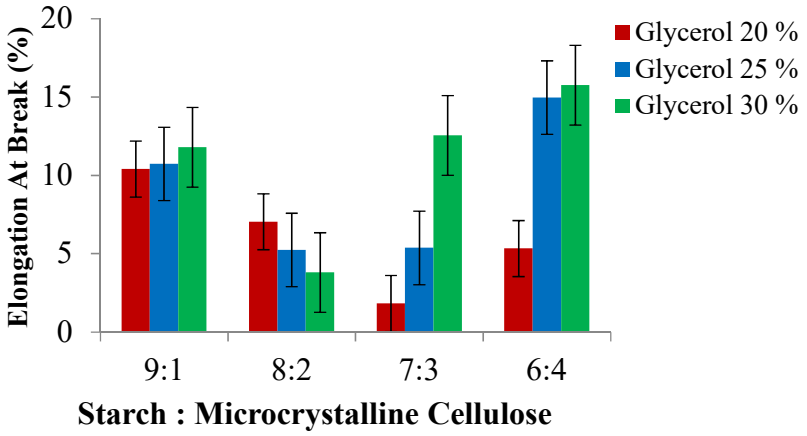

Figure 4. The effect of microcrystalline cellulose and glycerol addition on elongation at break of bioplastic from jackfruit seed starch

Based on the results, it shows that with increasing glycerol addition cause the percentage of elongation also increasing, because glycerol can increase the distance between molecules that make bioplastic become more elastic [24]. The percentage of elongation is inversely proportional to tensile strength. With more fillers added to the plastic film, then the elongation will be dropped, but the tensile strength is increased. A drop in elongation supposed happened because there is strong interaction between composition of bioplastic substance, that is starch molecules with fillers. This bonds happened between starch molecules with fillers is more tight and compact so that bioplastic is more strength that effected the film becomes difficult to stretchable and elongated, it will reduce the percentage of film elongation [25]. But, there is a deviation for composition ratio of starch: MCC 8:2 and the addition of glycerol 20 % and 30% where there is decreasing elongation at break value by glycerol addition. The addition of plasticizer in low concentration to medium concentration (1% - 25%) facilitated the formation of a crystal in a starch film, which is direct to antiplasticizer behavior. This is due to movement from polymer chain which is cause water molecules, and plasticizer disappear slowly, it impacted to the amylose and amylopectin form strong hydrogen bonding, so it happens recrystallization or retrogradation [26].

3.2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 5 represented the characteristic of absorption peak FT-IR analyze of microcrystalline cellulose of cocoa pod husk, bioplastic from jackfruit seeds starch and glycerol without MCC, bioplastic from jackfruit seed starch with MCC and glycerol, and also jackfruit seeds starch. The dark blue line presented FT-IR spectra of jackfruit seeds starch with spectrum peak that indicate O-H group, C-H alkanes, C=C alkenes, C=O aldehyde and C-O eter in jackfruit seeds starch. This FT-IR result are consistent with Maulida research (2016) which is reported same function group with jackfruit seeds starch [27].

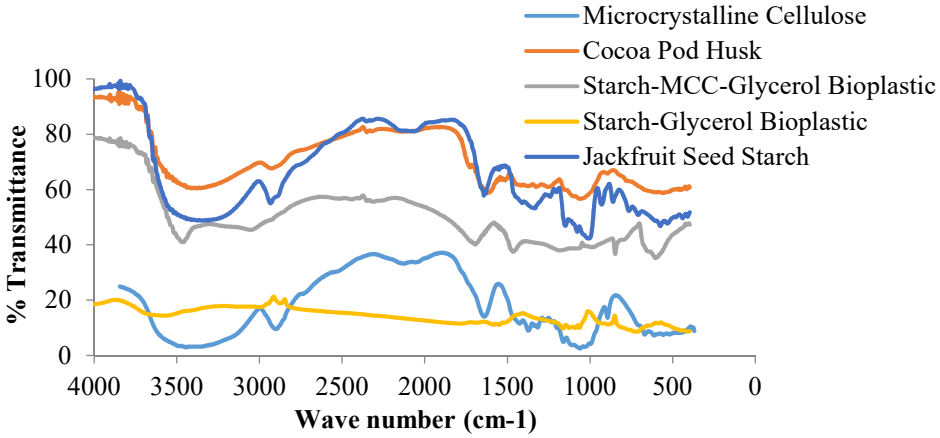

Figure 5. Characteristics of FT-IR spectra analysis

The presence of functional group has represented the contents of jackfruit seeds starch which is consisted of amylose and amylopectin and also reducing sugar $(C_6H_{10}O_5)n$. The blue line represented the characteristic of absorption peak of microcrystalline cellulose at wave number 3445 cm^{-1}, it indicates the existence of -OH groups and at absorption peak with wave number 2903 cm^{-1} indicate the existence of C-H groups which is proved there is C-H bonding at the end of cellulose structures and C-O carbonyl at wave number 1374.1 cm^{-1} is also typical cellulose. Orange line represents the characteristic of the absorption peak of cocoa pod husk which has many similarities with microcrystalline cellulose sample, because of microcrystalline cellulose result is chemical process from cocoa husk, so the groups indicated the existence of cellulose are in similar wave number. The appearance of absorption peak at cocoa husk is 3383 cm^{-1}, 2927 cm^{-1}, 1612 cm^{-1}, 1249 cm^{-1}, 1056 cm^{-1}, and 898 cm^{-1}. On starch-glycerol bioplastic with yellow line could be seen the absorption peak shows that OH groups, C-H alkanes, O-H carboxylates, C=O aldehyde, and C-O carboxylates, is same with bioplastic from jackfruit seed starch with MCC and glycerol with grey line, the appearance of absorption peak is not showing the existence of new groups formation. But, there is an enhancement of O-H bonds wave number of starch and microcrystalline cellulose 2931.6 cm^{-1} of starch, become 3001.04 cm^{-1} at bioplastic, and from 3445.71 cm^{-1} at microcrystalline cellulose become 3464.15 cm^{-1} at bioplastic.

4. Conclusion

The isolated MCC from cocoa pod husk is result in the form of rod-like shape 5-10 µm with diameter 11.635 nm and crystallinity 74%. The best condition of bioplastics obtained at the comparison of mass starch: MCC 8:2 and the addition of glycerol 20% for tensile strength 0.637 MPa and elongation at break 7.04%.

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