INTRODUCTION

Plastic have become an integral part of our lives. The problems of conventional plastics are taking decades to degrade in nature and are produced by non-renewable sources like petroleum, coal and natural gas [1]. Conventional plastic not only take many decades for decompositions, but also produce toxins while degradation. Hence, there is need to produce plastics from materials that can be readily eliminated from our biosphere in an “ecofriendly” fashion [2]. It called bioplastics. Bioplastics are similar to conventional plastics in all aspects with the additional quality being able to naturally decompose and break into natural and safe byproducts. It is made partly or wholly polymers derived from biological source such as sugar cane, starch or cellulose from trees, straws and cotton [3].

Starch is one of the most important but flexible food ingredients possessing value added attributes for innumerable industrial applications. The most common sources of food starch are corn, potato, wheat, cassava/ tapioca, rice, etc. Starch is widely used in the form of biodegradable films in varied applications because it is a renewable, abundant and inexpensive material [4,5]. Starch can be easily found from various sources in Indonesia. Avocado seed, which is typically discarded as waste [6], have around 30 % starch content and hence it serves as a potential starch source [7,8].

All natural fibers are a renewable resources of raw material through their biodegradability. They have excellent specific strength and high modulus. Reduced density and lower cost of these fibers compared to synthetic fibers make their use advantageous. They also have a safer manufacturing process and exhibit good thermal properties and ease of separation in manufacturing with enhanced energy recovery, plus reduced tool wear [9]. Other advantages are: natural fibers offer good acoustic and thermal insulation properties combined with ease of processing [10]. Reinforcing fillers such as cellulose has proven to be the most promising material [11]. One of the most potential sources of cellulose is sugar palm fibers or called ijuk in Indonesia with cellulose content of 52.3 % [12]. Ijuk as one of the environmental-friendly materials obtained from Arenga pinnata plant (Arenga pinnata) [13]. Starch-based bioplastic have poor dimensional stability and mechanical properties. Its shortcoming can be resolved by the addition of plasticizers to improve its work-ability and suppress film brittleness [14].

The surface of the natural fibers can be modified and this can be achieved by physical, mechanical and/or chemical means [10]. De Mesquita et al. [15] reported that the fabrication of cellulose materials into micro as well as nano dimensions

Production of Bioplastic from Avocado Seed Starch as Matrix and Microcrystalline Cellulose from Sugar Palm Fibers with Schweizer’s Reagent as Solvent

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The mechanical properties of bioplastic prepared from avocado seed starch and microcrystalline cellulose from sugar palm fibers as filler using Schweizer’s reagent as solvent was studied. Bioplastics were prepared from avocado seed starch and reinforced with microcrystalline cellulose (MCC) from sugar palm fibers with composition ratio were 7:3, 8:2 and 9:1 (w/w) and using glycerol as plasticizer with variation of 0.1; 0.2; 0.3 and 0.4 (v/w of starch). Microcrystalline cellulose dissolved in the copper solution (Schweizer reagent) with ratio of MCC:copper solution is 1:10. Degree of crystallinity of microcrystalline cellulose was 97.5 %. Morphological analysis showed that the isolated microcrystalline cellulose from sugar palm fibers are rod-like shape with diameter of 5.55-9.44 µm and crystallite size of 25.08 nm. Mechanical properties of bioplastic showed that the best condition of bioplastics obtained at comparison of mass starch-microcrystalline cellulose 7:3 and the addition of glycerol 0.1 (v/w) for tensile strength 20.874 MPa and elongation at break of 6.22 %.

Keywords: Avocado seeds, Bioplastic, Microcrystalline cellulose, Starch, Sugar palm fibers.
enhances favourable characteristics such as excellent mechanical properties, high crystallinity and low molecular weight [15]. Microcrystalline cellulose (MCC) is a purified partially depolymerized non-fibrous form of cellulose that occurs as a white, odourless, tasteless, crystalline powder composed of porous particles [16]. A very important and major requirement for all the methods described is the dissolution of the polymer in given solvent. The first solvent for cellulose was discovered by the Swiss chemist Schweizer, whose applied copper hydroxide-ammonia (cuoxam, called Schweizer’s reagent). It can directly dissolve cellulose in a relatively short time, but their drawback is the instability of cellulose in these solvents when the cellulose is oxidized, which leads to degradation by a β-elimination mechanism [17]. Lubis et al. [8] reported that bioplastic reinforced with microcrystalline cellulose from sugar palm fibers and using sodium hydroxide as a solvent had a low mechanical properties. So that in this study, we use a different solvent to compare it. The strong interactions between microcrystalline cellulose and starch film matrix played a key role in reinforcing the formation of rice starch film composites [18].

**EXPERIMENTAL**

Avocado seed was obtained from avocado merchants located at H.M. Joni Rd. Medan, Indonesia and sugar palm fiber (ijuk) was collected from Binjai, Indonesia [8].

**Starch isolation:** Avocado seeds (100 g) were peeled and washed with clean water before shredded to small pieces. Then the shredded avocado seeds were blended with 100 mL water. Furthermore, starch slurry was filtered and later placed in tank for settling that took 1 h. Starch sediment was separated from the slurry and then washed again with distilled water. After the third settling, starch sediment was dried using oven on temperature 60 °C. Then starch was sieved with strainer 100 mesh for better homogeneous size [8].

**Extraction of α-cellulose from sugar palm fibers:** Sugar palm fibers were cleaned from impurity and cut into small pieces. Sugar palm fibers (50 g) were mixed with 700 mL nitric acid 3.5 % that contained 8 mg of sodium nitrite in a beaker glass. Then it was heated using hot plate on temperature 90 °C for 2 h. Furthermore, sugar palm fibers was washed with clean water till its filtrate neutral and filtered with filter paper. Then the fibers were added with the mixture of sodium hydroxide and sodium sulfite (2 %) solution and then heated at 50 °C for 1 h. Filtrate was cleaned with water till its neutral and filtered with filter paper. Then the fibers were heated with sodium hypochlorite (3.5 % 340 mL) till boiled for 10 min then cleaned again with water and filter with filter paper.

The α-cellulose was purified with 340 mL NaOH (17.5 %) solution at 80 °C for 30 min. Sample was washed by water until neutral and filtered with water then bleached by using H₂O₂ 10 % on temperature 60 °C for 30 min. Sample was washed again by water until neutral and filtered with filter paper [8].

**Isolation of microcrystalline cellulose (MCC) from α-cellulose:** α-Cellulose (5 g) was dissolved in 120 mL HCl (2.5 N) on boiling temperature for 15 min. Then it was poured to cold water and stirred rapidly with spatula and placed at free air for over night till the suspension was formed. The suspension was washed with distilled water until neutral. Then dried in the oven at 60 °C for 1 h. Then MCC was placed in desiccator [8].

**Preparation of a solution copper tetraamine ammonical/Schweizer’s reagent:** 34.5 g of copper(II) sulphate dissolved into 100 mL of water while stirring, ammonia was added drop-wise (13.5 M) until the precipitate dissolved perfectly, maintained at a temperature below 20 °C. Then added drop-wise a solution of sodium hydroxide (10 M), whipped continuously, the precipitate is filtered through a sintered glass filter (porosity number 3). The precipitate was washed with water until the filtrate was clear and sediment stirred with 200 mL of ammonia 13.5 M. Then filtered through a sintered glass filter and repeat filtering to produce residue as small as possible it will then produce filtrate blue.

**Film preparation:** Starch and MCC mass number was weighed with various ratios, which is 7:3, 8:2 and 9:1 in the amount of 10 g of total dry weight starch-MCC. Firstly, the MCC was dissolved in the copper solution (Schweizer reagent) with ratio of MCC:solution (copper) is 1:10. Starch solution was made by dissolving starch with distilled water in the beaker with ratio of starch:distilled water is 1:10 (w/v). Then the solution was heated while stirring using hot plate. After 10 min glycerol was added as plasticizer with variation 0.1; 0.2; 0.3 and 0.4 (mL/g from starch mass). The solution was heated while stirred until 70 °C of temperature achieved. Furthermore, MCC solution was added and kept heated until temperature 85 °C achieved. After mixing, the solution was cooled and then it poured onto flat mold and dried at 60 °C for 24 h. After the bioplastic is dried, it was removed from the mold and placed in the desiccator. Bioplastic was ready to be analyzed [8].

**Characterization of products**

**Characterization of starch:** Characteristics of starch that had been analyzed were starch, amylose and amylopectin protein, ash and moisture content. Analyzing of starch, amylose and amylopectin content was observed at Laboratorium Rekayasa, Institut Pertanian Bogor. Analyzing of protein, ash and moisture content was observed at Balai Ristek dan Standardisasi Industri (Baristand), Medan [8].

**Characterization of microcrystalline cellulose:** Characterization of MCC for crystallinity, functional group and morphological analysis. Crystallinity of MCC was determined using X-ray diffraction (XRD) at Badan Tenaga Nuklir Nasional (BATAN), Serpong-Tangerang. The crystallographic height 002 (I₀₀₂) and amorphous height (Iₐₐₛ) were used to calculate the apparent crystalline index (apparent Cr.I.) and was calculated by eqn. 1 [18]:

\[
CrI = \left( \frac{I_{002} - I_{AM}}{I_{002}} \right) \times 100
\] (1)

The apparent crystallite size L was calculated from the Scherrer equation (eqn. 2) based on the width of the diffraction patterns with absorption peak 2θ = 20.06° [18]:

\[
L = \frac{K \lambda}{B(2\theta) \cos(\theta)}
\] (2)

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Functional group was analyzed using Fourier transform infrared (FTIR) at Laboratorium Penelitian, Faculty of Pharmacy, University of Sumatera Utara. Morphology was analyzed using Scanning Electron Microscope (SEM) at Laboratorium Penelitian dan Pengujian Terpadu, Universitas Gadjah Mada, Yogyakarta [8].

Mechanical properties of bioplastic: Test of mechanical properties involves tensile strength and elongation at break. Product of bioplastic was chosen and cut forming specimen for tensile strength test based on standard of ASTM D 638 at Laboratorium Penelitian, Faculty of Engineering, University of Sumatera Utara [8].

Characterization of bioplastic: Functional group was analyzed using Fourier transform infrared (FTIR) at Laboratorium Penelitian, Faculty of Pharmacy, University of Sumatera Utara and morphology was analyzed using scanning electron microscope (SEM) at Laboratorium Penelitian dan Pengujian Terpadu, Universitas Gadjah Mada, Yogyakarta [8].

RESULTS AND DISCUSSION

Characterization of avocado seed starch: The yield of starch extracted from 100 g avocado seed could produce avocado seed starch as much as 16 g or percentage of starch was 16 %. Avocado seed starch produced was brown in colour with the particle size of 100 mesh. Andy, dkk. (2013), the emergence of brown on avocado seed starch was caused avocado seed contained phenolic dopamine compound (3,4-dihydroxy phenilalanin). This phenolic compound caused reaction of browning enzymatically which was caused by reaction between oxygen and phenolic substance with catalyst polyphenol oxidase [19].

Characterization of avocado seed starch was aimed to know the percentage of each component contained in the starch produced, include starch, amylose, amylopectin, water, ash and protein content so that the quality of starch produced is known [8,20]. The result of avocado seed starch characteristic was given in Table-1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage (%)</th>
</tr>
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<tbody>
<tr>
<td>Water</td>
<td>16.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.23</td>
</tr>
<tr>
<td>Lipid</td>
<td>1.09</td>
</tr>
<tr>
<td>Protein</td>
<td>2.16</td>
</tr>
<tr>
<td>Amylose</td>
<td>0.07</td>
</tr>
<tr>
<td>Amylopectin</td>
<td>73.55</td>
</tr>
</tbody>
</table>

Characterization of avocado seed starch: The percentage yield of MCC from sugar palm fibers was 60 % [8]. Microcrystalline cellulose that was produced on this research was good as the material was odourless with white granular powder.

Crystallinity and crystallite size of microcrystalline cellulose: Crystallinity and crystallite size of MCC was determined by X-ray diffraction at Badan Tenaga Nuklir Nasional (BATAN), Serpong-Tangerang, Indonesia. The XRD pattern of MCC sample prepared from sugar palm fibers were shown in Fig. 1.

The absorption peaks occurred at 2-theta (2θ) were 12.01°, 20.06° and 21.91°[8]. The sharp peak for MCC, indicative of a high crystallinity degree in the structure of MCC [8,21].

Index of crystallinity of the sample MCC obtained is high at 97.5 % [8]. The percentage of crystallinity MCC from sugar palm fibers (97.5 %) was considerably high than other non-woods (52-53 %) [21]. High crystallinity related to acid hydrolysis process for preparing MCC [22]. At the time of acid hydrolysis, cellulose chains apart rapidly at 1.4 glycosidic bond so produce short-chain cellulose. Amorphous part of the glycosidic bond partially degraded to form an acid insoluble nature of the final product, while the crystalline leaves a residue and only a change slightly due to acid hydrolysis. A slight change in the structure of the crystalline portion cellulose microcrystalline and amorphous parts will result in removal an increase in the degree of crystallinity of the microcrystalline cellulose [23]. Karim et al. [24] reported for the treated sample, the disordered amorphous region was decreased with the increase of the hydrogen bond crystalline region of the cellulosic matrix, which might be due to the partial breaking up of glycoside linkages inside the amorphous region, whereas the crystalline region was almost unaltered [8].

Crystallite size can also be calculated on the test results of crystallinity by XRD, the absorption peak of the spectra produced by the sample MCC was at 2θ = 12.01°; 20.06° and 21.91°. By calculating the crystallite size of MCC on the absorption peak 2θ = 20.06° obtained the diameter of crystals is equal to 25.08 nm. Crystallite size affects the compatibility or the compactness of a material. The smaller size of the crystal, improved the compatibility of a material [8,25].

Tensile strength of bioplastic: The effect of microcrystalline cellulose from sugar palm fiber and glycerol addition on the tensile strength of bioplastics are shown in Fig. 2.

Fig. 2 shows that with increasing mass of MCC cause the value of tensile strength of bioplastic also increasing. From figure above could be seen the highest tensile strength value of bioplastic with MCC content 3 g and 0.1 v/w glycerol earned the magnitude 20.874 MPa. This is due to good adhesion between starch and cellulose where about hydroxyl groups on the starch and cellulose to form hydrogen bonds in surface. Strong hydrogen bonding between the surface of cellulose and starch produce a powerful network that provides effective results in the matrix [26].

The lowest tensile strength value is shown for bioplastic with MCC content 2 g and 0.4 v/w glycerol earned the magni-
tude 3.234 MPa. According to Wittaya [18] this deviation is possibly due to higher content of MCC contributed to retarding the intermolecular interaction thus resulting in aggregates and heterogeneous film structure. Deviation occur because the mass of microcrystalline cellulose high filler contributing to a slowdown in the interaction between the molecules of starch bioplastics. This led to the development of bioplastics structure becomes heterogeneous and the result of discontinuities [18]. The same result was reported by Teixeira et al. [27] with reduced tensile strength in filler use cellulose nanofiber 10 % and increased again in the addition of fillers 20 %.

Fig. 2 also shows that the increasing of glycerol addition, cause the tensile strength of bioplastics produced decreased. The addition of glycerol reduced the dispersion of solids resulting physical properties of the weak against bioplastics. The addition of glycerol led to a decrease in attractive force between molecules, causing resistance to mechanical treatment of bioplastics decreased. Polar group (-OH) around the plasticizer chain led to the development of hydrogen bonding interactions plastic polymer that replaces polymers in biopolymer films. Increased concentration of glycerol will produce a reduction in the intermolecular interactions so that the movement of the molecular chains will drop [28]. Abdorreza et al. [29] reported that the flexibility of the film could be increased by increasing the plasticizer content, but this can lead to crystallization of plasticizer in the film [8].

Elongation at break of bioplastic: The effect of increasing MCC and glycerol content on the elongation at break of bioplastics are shown in Fig. 3.

Fig. 3 shows the results of elongation at break as the addition of MCC content decreased the value. Meanwhile, addition of plasticizers to bioplastics have the opposite effect on elongation at break. The addition of MCC resulted in a decreased value of elongation at break. Bioplastic with MCC content 1 g and 0.4 v/w glycerol provided the maximum elongation at break value for 6.22 %.

The addition of fillers can lower percent elongation at break of bioplastics. This is because the synthesis of biodegradable plastics that contain hydrogen bonding that occurs between starch and cellulose. The resulting bond strength of the material is increased so the percent of elongation at break decreases. The addition of plasticizers serves as a conduit on the elastic properties of bioplastics, so the more plasticizers are given will increase the value of the plastic extension. Plasticizer can reduce internal hydrogen bonding molecules and lead to weakening of the intermolecular attractive force adjacent polymer chains, thereby reducing the tensile breaking. Besides, the addition of plasticizers can reduce brittleness and increase the flexibility of the polymer film [17].

Reducing of elongation at break value as a result of the addition of MCC mass due to reduced the role of glycerol as a plasticizer. Microcrystalline cellulose who tend to be more actively interact with hydrogen and other monomers on bioplastics [8,30]. These results clearly suggest that the relatively poor ductility of bioplastic was improved after blending proper amounts of MCC with the starch solution [31].

**Functional group analysis:** Functional group analysis was resulted using FTIR at Laboratorium Penelitian, Faculty of Pharmacy, University of Sumatera Utara, Medan. The FTIR spectra of bioplastic from avocado seeds starch with MCC and glycerol were shown in Fig. 4.

Fig. 4 shows that the analyzing result of FTIR of avocado seed starch which owns O-H group binded with hydrogen, C-H alkanes, C=O and C-O ethers [8]. The existing of those bands indicate the bioplastic produced from avocado seeds starch with MCC and glycerol.

Fig. 4 shows the FTIR analysis result of bioplastic from avocado seed starch with MCC and glycerol.
The FTIR analysis results of MCC and sugar palm fibers show the peak which is related with C-O stretch part of hemicellulose, pectin and lignin compound in range 1300-1000 cm⁻¹ and some peaks related with C-C stretch part in ring of lignin in range 1500-1400 cm⁻¹ [13]. There is a absorption peak at wavenumber 1489 cm⁻¹ on the sugar palm fibers indicate the existence of a ring of lignin in the fibers. However, the FTIR analysis results of MCC didn’t show the peak with wavenumber that refers to the existence of lignin. According to Dufresne et al. [33] in Lubis [34] the loss of absorption peaks at wave number in the range of 1500-1400 cm⁻¹ on the FTIR results of MCC showed that the existence of lignin and hemicellulose in the MCC has been terminated properly by the delignification process with acid and bleaching treatment that serves to remove lignin and hemicellulose from material lignocellulosic.

Fig. 4 also showed the characteristics of bioplastic without adding MCC and bioplastic with adding MCC and glycerol have the same functional groups and no new cluster formed. Bioplastic with added MCC and glycerol have functional groups; C-H with wavenumber 729.09 cm⁻¹, C=O carboxylate with wavenumber 1701.02 cm⁻¹, C-O with wave number 1176.56 cm⁻¹ and O-H with wave number 2997.38 and 3618.46 cm⁻¹. The value of wavenumber O-H group is due to the interaction of hydrogen when the component of starch and MCC mixed on bioplastics manufacturing process, in which the hydrogen bonds consist of bonds between chains of amylose-amylose, amylose-amylopectin, MCC-MCC and amylo-amylopectin [8,35].

**Morphological analysis using scanning electron microscope (SEM):** SEM micrographs of fractures bioplastics with filler MCC and plasticizer glycerol and MCC from sugar palm fiber using a magnification of 700x and 5000x were shown in Fig. 5.

Fig. 5a showed that the bioplastic film has jagged surface but has a compact structure. A high mechanical properties of bioplastic showed that the filler and matrix have an unite and compact structure. It was caused by the microcrystalline cellulose dissolved completely in copper solution 10 mL [8]. Homogeneity of the structure of bioplastics is one of the indicators that can demonstrate improvements in the value of the mechanical strength of the bioplastics [36].

Fig. 5b shows that MCC of sugar palm fiber forms obtained were rod shaped with average diameter of 5.55-9.44 µm [8]. It was same with the MCC obtained from sisal that had needle or rod shape [37,38]. Microcrystalline cellulose basically formed from crystallites with size of colloidal. crystallites having a diameter of about 15-20 µm. The crystallite aggregates may form agglomerates during the drying of the cellulose slurry so as to form a particle diameter of 20 to 200 µm [39,40].

**Conclusion**

Microcrystalline cellulose can be isolated from sugar palm fiber through alkali treatment and acid hydrolysis. Rod-shaped microcrystalline cellulose with an average diameter of 5.55-9.44 µm, crystallinity of 97.5 % and crystallite size of 25.08 nm was obtained from sugar palm fiber. Starch-based bioplastic films can be prepared by solution casting with the isolated MCC as reinforcing filler. The best condition of bioplastics obtained at comparison of mass starch-MCC 7:3 and the addition of glycerol 0.1 (v/w) for tensile strength of 20.874 MPa and elongation at break of 6.22 %.

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