Effect of Microcrystalline Cellulose (MCC) from Sugar Palm Fibres and Glycerol Addition on Mechanical Properties of Bioplastic from Avocado Seed Starch (Persea Americana Mill)

Maulida Lubis 1*, Mari Bangun Harahap 2, Muhammad Hendra S. Ginting 3, Mora Sartika 4, Hidayatul Azmi 5
1, 3, 4, 5 Departement of Chemical Engineering, Faculty of Engineering, University of Sumatera Utara, Medan, Indonesia
2 Departement of Physics, Faculty of Mathematics and Natural Sciences, University of Sumatera Utara, Medan, Indonesia

Abstract

The effect of microcrystalline cellulose (MCC) from sugar palm fibers and glycerol addition on mechanical properties of bioplastic from avocado seed (Persea americana mill) were studied. Sugar palm fibers was undergoing alkali treatment, bleaching process, and hydrochloric acid hydrolysis before microcrystalline cellulose can be produced. Degree of crystalinity of MCC were determined by X-Ray Diffraction (XRD), functional group using FT-IR and morphological analysis using Scanning Electron Microscope. Mechanical properties of bioplastic were determined by tensile strength, elongation at break, and functional group using FT-IR. Bioplastic was successfully fabricated through solution casting technique. Bioplastics were prepared from avocado seed starch and reinforced with 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 (v/w of starch). MCC dissolved in a solution of NaOH 5% (w/v) before mixed into the plasticized starch. The isolated MCC from sugar palm fibers are rod-like shape with diameter of 5,55-9,44 m and crystallinity 97.5%. From the analysis, the best condition of bioplastics obtained at comparison of mass starch-MCC 7 : 3 and the addition of glycerol 0,2 (v/w) for tensile strength 2,74 MPa and elongation at break 3,16%. The analysis of FT-IR showed the functional groups of bioplastics, which the majority of O-H groups were found at the bioplastics due to addition of MCC that represented substantial hydrogen bonds.

Keywords: Avocado Seed, Bioplastic, Glycerol, Microcrystalline Cellulose, Sugar Palm Fibers

Introduction

Demand of plastic products at this time continues to increase. Due to the rising demand of plastic products, it has been necessary to develop an ecological solution that serves as an alternative. This is mainly because of the fact that plastics are derived from crude oil, which is a non-renewable fossil fuel that subsequently produces high levels of environmental pollution (Ulloa & Gabriela PunnBurneo, 2012). The ecological solution is the development of biodegradable plastic or commonly called bioplastics. Bio-plastics are environmentally friendly as compared to traditional plastics for their production results in the emission of less green house gases such as carbon dioxide, which is one of the prime sources of air pollution and leads to environmental issues such as global warming, climate change, etc. (Reddy, Reddy, & Gupta, 2013).

The main constituent component of bioplastics is starch as a matrix. Starch is widely used in the form of biodegradable films in varied applications because it is a renewable, abundant and inexpensive material (Alves, Reis, Menezes, Pereira, & Pereira, 2014). Starch can be easily found from various sources in Indonesia. Avocado seed, which is typically discarded as waste (Mahawan, Tenorio, & Gomez, 2015), have around 30% starch content, and hence it serves as a potential starch source (Woldu & Tsigie, 2015).

Shinoj et al. (2011) reported that a better interaction between fibre particles and polymer matrix could improve mechanical properties of the biocomposites (Shinoj, Visvanathan, Panigrahi, & Kochubabu, 2011). Therefore, adding filler is necessary.

*All correspondence related to this article should be directed to Mora Sartika, University of Sumatera Utara, Medan, Indonesia
Email: maulida@usu.ac.id
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to improve the mechanical properties of bioplastics produced. Reinforcing fillers such as cellulose has proven to be the most promising material (Maulida, Siagian, & Tarigan, 2016). Cellulose, the main component of all biomass, is the most abundant bio-macromolecule found in nature. It has been estimated that more than 7.5 × 10^10 tons of cellulose is produced annually (Habibi, Lucia, & Rojas, 2010). One of the most potential sources of cellulose is sugar palm fibers or called ijk in Indonesia with cellulose content of 52.3% (Sahari, Sapuan, Ismarrubie, & Rahman, 2012). Ijk is one of the most important parts of a plant sugar palm (Arenga pinnata). For a long time, sugar palm fibers has been used to prepare brooms, brush and water filler, but its use for preparing costly cellulose products would be of great advantage (Bhimte & Tayade, 2007).

De Mesquita et al (2010) reported that in addition to biodegradability and renewability, the fabrication of cellulosic materials into micro as well as nano dimensions enhances favorable characteristics such as excellent mechanical properties, high crystallinity, and low molecular weight (de Mesquita, Donnici, & Pereira, 2010). Microcrystalline cellulose (MCC) used as reinforcement filler for starch based edible films was analyzed by Wittaya et al. (2009). MCC is a purified partially depolymerised non-fibrous form of cellulose that occurs as a white, odourless, tasteless, crystalline powder composed of porous particles (Suvachittanont & Ratanapan, 2013). The strong interactions between MCC and starch film matrix played a key role in reinforcing the resulting rice starch film composites (Wittaya, 2009). MCC from sugar palm fibers is used as reinforcing filler because it could improve mechanical properties of bioplastic.

Starch-based bioplastic have poor dimensional stability and mechanical properties. Its shortcoming can be resolved by the addition of plasticizers to improve its workability and suppress film brittleness (Sanyang, Sapuan, Jawaid, Ishak, & Sahari, 2015). Utilization of avocado seed waste and sugar palm fibers in bioplastic manufacturing can reduce environmental damage caused by the use of conventional plastic. Therefore, the aim of this research to obtain the effect of MCC from sugar palm fibers and glycerol addition on mechanical properties of bioplastic.

**Literature Review**

**Starch-based Bioplastic**

The use of starch in the manufacturing of bioplastics began in the 70s (Curvelo, de Carvalho, & Agnelli, 2001). Starch is one of the most studied and promising raw materials for the production of biodegradable plastics, because starch is quite cheap, abundant, biodegradable and edible (Wittaya, 2012). The scientific and business community finds in starch a good alternative for biodegradable packaging applications, as it is a renewable resource widely available that can be obtained from different agricultural surplus and industrial leftovers from raw materials processing (Garc, Fam, Accorso, & Goyanes, 2015).

Starch granules contain two principal types of polysaccharides, namely amyllose and amylopectin. Both are polymer of solely D-glucose connected by (1-4)-linkages into shorter or longer chains. Amylopectin, the major component of most starches, consists of a large number of shorter chains that are bound together at their reducing and side by a (1-6) linkage, which makes this very large polysaccharide extensively branched. Amylose consists only of either a single or a few long chains, thus making the molecule linier or slightly branched (Elliasson, 2004).

Starch is one of the most studied and promising raw materials for the production of biodegradable plastics, because starch is quite cheap, abundant, biodegradable and edible (Wittaya, 2012). Thus, starch has attracted a great deal of interest as a potential alternative to conventional plastics for packaging applications (Sanyang et al., 2015).

**Microcrystalline Cellulose**

Cellulose from different sources differs in properties such as crystallinity, moisture content, surface area and porous structure, and molecular weight. MCC can be made from any materials other than wood and cotton that is high in cellulose ranging from pure cellulose. MCC is a purified partially depolymerised non-fibrous form of cellulose that occurs as a white, odourless, tasteless, crystalline powder composed of porous particles (Suvachittanont & Ratanapan, 2013). Crystalline cellulose is much stronger and stiffer, and considered to be a better reinforcing agent than amorphous cellulose or the native cellulose itself (W. Bai, 2009).
Glycerol

Glycerol is a simple polyol compound. It is a colorless, odorless, viscous liquid and has a high boiling point and freezes to form a paste. It is the plasticizer used in the film production. A plasticizer is an additive that softens the material it is added to (Ezeoha & Ezenwanne, 2013). Starch-based bioplastic have poor dimensional stability and mechanical properties. Its shortcoming can be resolved by the addition of plasticizers to improve its workability and suppress film brittleness (Sanyang et al., 2015). The ultimate role of plasticizers is to enhance the flexibility and processibility of starch by reducing the strong intermolecular interactions between starch molecules (Gutierrez, Morales, Prez, Tapia, & Fam, 2015).

Methodology

Starch Extraction of Avocado Seed Starch

Starch used in this research of bioplastic was starch which extracted from avocado seeds. Avocado seeds was obtained from avocado merchants located at H.M. Joni Rd, Medan, Indonesia. Avocado seeds (100 gram) 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 hour. 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 oC. Then starch was sieved with strainer 100 mesh for better homogeneous size.

Preparation of MCC

Extraction of α-Cellulose from Sugar Palm Fibers

Sugar palm fibers were cleaned from impurity and cut into small pieces. Sugar palm fibers (50 gram) were mixed with 700 ml nitric acid 3.5 % that contained 8 mg of sodium nitric in a beaker glass. Then it was heated using hotplate on temperature 90 oC for 2 hours. 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 on temperature 50 oC for 1 hour. 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 minutes then cleaned again with water and filter with filter paper.

The α-cellulose was purified with 340 ml NaOH 17.5 % solution on temperature 80 oC for 30 minutes. Sample was washed by water till neutral and filtered with paper filter then bleached by using H2O2 10% on temperature 60 oC for 30 minutes. Sample was washed again by water until neutral and filtered with filter paper.

Isolation of Microcrystalline Cellulose (MCC) from α-Cellulose

Then it was poured to cold water and stirred strongly with spatula and placed at free air for one night till the suspension was formed. The suspension was washed with distilled water until neutral. Then dried in the oven at temperature 60 oC for 1 hour. Then MCC was saved in desicator. Characterization of MCC were crystallinity analyzed using X-ray diffraction (XRD), functional group analyzed using Fourier Transform Infra-Red (FTIR) and morphology analyzed using Scanning Electron Microscope (MCC).

Film Preparation

Number of starch and MCC mass wanted was weighed with various ratios 7 : 3, 8 : 2, and 9 : 1 in the amount of 10 gram of total dry weight starch-MCC. MCC was dissolved first in the NaOH 5% (w/v) solution. Starch solution was made by dissolving starch with distilled water in the beaker glass with ratio starch : distilled water 1 : 10 (w/v). Then the solution was heated while stirred using hotplate. After 10 minutes glycerol was added as plasticizer with variation 0.1; 0.2; 0.3 (ml/g from starch mass). The solution was heated while stirred till temperature 70 oC achieved. Furthermore, MCC solution was added and keep heated till temperature 85 oC achieved. After mixing, the solution was cooled down and then it cast onto flat and dried with temperature 60 oC for 24 hours. After bioplastic dried, it was removed from the flat and saved in the desicator. Bioplastic was ready to be analyzed.

Mechanical properties of bioplastic that had been analyzed were tensile strength based on standard procedure ASTM D638-02a

Results and Discussion

Characterization of Avocado Seeds Starch

The yield of starch extracted from the avocado seeds is 16%, in which from 100 grams of avocado seed could produce avocado seed starch as much as 16 grams. Figure shows that avocado seed starch produced was brown with the particle size of 100 mesh. Chandra et al. (2013) reported that brown starch due to the phenolic compounds namely dopamine (3,4-dihydroxy phenilalanin) that contained in avocado seed that can cause enzymatic browning reactions due to oxygen (Chandra, Inggrid, & Verawati, 2013)

![Starch Isolated from Avocado Seeds](image)

Fig. 1. Starch Isolated from Avocado Seeds

Characterization of Microcrystalline Cellulose

MCC have been prepared from -cellulose (fig. 2a) of sugar palm fibers as shown in Fig. 2b. The yield of MCC from sugar palm fibers was 60%. MCC (fig.2b) that was produced on this research were good as the material was odorless with white granular powder.

![microcrystalline cellulose](image)  ![Sugar Palm Fibers](image)

Fig. 2 α-cellulose (a) and microcrystalline cellulose (b) of sugar palm fibers

Crystalinity

Crystalinity of MCC was determined by X-ray Diffraction (XRD) at Badan Tenaga Nuklir Nasional (BATAN), Serpong-Tangerang, Indonesia. The XRD pattern of MCC sample prepared from sugar palm fibers were shown in Fig. 3.
The absorption peak that occurred at 2-theta (2θ) were 12.01°; 20.06° dan 21.91°. The sharper peak for MCC, indicative of a high crystallinity degree in the structure of MCC (Jahan, Brunswick, & Brunswick, 2011). Crystallinity Index of MCC were calculated from the X-ray diffraction patterns based on the following equation (Q. Wang, Chen, Niida, Mitsumura, & Endo, 2014):

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\text{Index of crystallinity of the sample MCC obtained is high at 97.5%}. \\
\text{The percentage of crystallinity MCC from sugar palm fibers (97.5%) was considerably high than other non-woods (52-53%) (Jahan et al., 2011). High crystallinity related to acid hydrolysis process for preparing MCC. During the acid hydrolysis of cellulosic materials, amorphous regions are disintegrated, resulting in a highly crystalline substrate with different degrees of the crystallinity index (Costa, Moris, & Rocha, 2011). Karim et al. (2014) 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 (Karim, Chowdhury, Bee, Hamid, & Ali, 2014).}
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**Analysis Morphology**

Morphological analysis of MCC was resulted using SEM at Laboratorium Penelitian dan Pengujian Terpadu, Gadjah Mada University, Yogyakarta. Morphology of MCC sample prepared from sugar palm fibers were shown in Fig. 3.

**Mechanical Properties of Bioplastic**

MCC of sugar palm fiber forms obtained were rod shaped with average diameter of 5.55-9.44 μm. It was same with the MCC obtained from sisal that had needle or rod shape (Habibi et al., 2010; Wirjosentono, 2014). Particle shape should have been a critical determinant in the density determination. Particle shape were also reflected in the porosity, particles with larger size have a lower porosity (Bhimte & Tayade, 2007).
Tensile Strength

The effect of microcrystalline cellulose from sugar palm fiber and glycerol addition on the tensile strength of bioplastics are shown in fig. 5.

From fig. 5 could be seen that with increasing mass of MCC cause the value of tensile strength of bioplastic also increasing. Bioplastic with MCC content 7 g and 0.2 v/w glycerol provided the maximum tensile strength for 2.74 MPa. The addition of MCC on gelatinized starch films resulted in grouping of intermolecular hydrogen bonding that cause a molecular bond of amylose more compact (Damar & Krisna, 2011).

A drop in tensile strength value is shown for bioplastic with MCC content 2 g and glycerol content 0.3 v/w. According to Wittaya (2009) this deviation is possibly due to higher content of MCC contributed to retarding the intermolecular interaction thus resulting in aggregates and heterogeneous film structure (Wittaya, 2009).

Figure 6 also shows with the increasing of glycerol addition, it can lower the tensile strength of bioplastics produced. The high tensile strength values can be attributed to the numerous hydrogen bonds between the starch chains. These bonds contribute to cohesiveness and low flexibility When glycerol was incorporated in the starch network, competition for hydrogen bonding occurred. As a result, direct interactions between the starch chains were partly reduced due to hydrogen bond formation with glycerol, allowing the polymer chains more freedom of motion (Bertuzzi, 2012). Abdorreza et al. (2011) 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 (Abdorreza, Cheng, & Karim, 2011).

Elongation at Break

The effect of increasing MCC and glycerol content of bioplastic on the elongation at break of bioplastics are shown in Fig. 6.
Figure 6 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 chitosan 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 13.36%.

The observed increase in film elongation is because plasticizers decrease the intermolecular bonds between amylose, amylopectin and amyloseamylopectin of the starch matrix and thus, substitute them with hydrogen bonds formed between plasticizer and starch molecules. Such disruption and reconstruction of starch molecular chains reduce the rigidity and promotes flexibility of films by allowing more chain mobility (Sanyang et al., 2015). 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. MCC who tend to be more actively interact with hydrogen and other monomers on bioplastics (Setiani, Sudiarti, & Rahmidar, 2013).

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 MCC, sugar palm fibers, avocado seeds starch, bioplastic from avocado seeds starch without MCC and bioplastic from avocado seeds starch with MCC and glycerol were shown at fig. 7.

Fig. 7. The FTIR Analysis Results of Avocado Seeds Starch, MCC, Sugar Palm Fiber, Bioplastic From Avocado Seeds Starch without MCC, and Bioplastic From Avocado Seeds Starch with MCC and Glycerol

Figure 7 shows that the analyzing result of FTIR avocado seed starch which owns O-H group binded with hydrogen, C-H alkanes, C=O and C-O ethers. The existing of those groups had represented the content of avocado seed starch which is consisted of amylose and amylopectin and reducing glucose (C6H10O5)n (Irwan, Sunardi, & Syabatini, 2013). This result showed the same result with Ginting and Tarigan (2015) of functional group analysis of avocado seed starch (Ginting & Tarigan, 2015).

The FTIR analysis results between MCC and sugar palm fibers show the peak which is related with C-O stretch part of hemicellulosa, pektin 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 (Chalid & Prabowo, 2015). There is a absorption peak at wave number 1489 cm-1 on the sugar palm fibers that indicate the existence of a ring of lignin in the fibers. However, the FTIR analysis results of MCC didn’t show the peak with wave number that refers to the existence of lignin. According to Dufresne, et al (1997) in Lubis (2016) 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 (Dufresne, Caville, & Vignon, 1997; Lubis, 2016).

From figure 7 could be seen the characteristics of bioplastic without adding MCC and bioplastic with adding MCC and glycerol have the same functional groups and no new cluster formed. However, there is an increasing wave number of functional groups O-H
for starch and MCC which are from 3394.72 cm⁻¹ in starch, to be 3603.03 cm⁻¹ in bioplastics and from 3437.15 cm⁻¹ in MCC to be 3603.03 cm⁻¹ in bioplastics. Increasing 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 amylose-chitosan-amylopectin (Ginting, Kristiani, & Siagian, 2015).

**Scanning Electron Microscope (SEM)**

SEM micrographs of fractures bioplastics with filler MCC and plasticizer glycerol Using a magnification of 5000x were shown in Fig. 8.

![SEM Micrographs of Fractures Bioplastics with Filler MCC and Plasticizer Glycerol Using a Magnification of 5000x](image)

From figure 8 could be seen that bioplastic film has jagged surface and less compact structure because there were still found void presence in the film. It was caused by the microcrystalline cellulose did not dissolved completely in NaOH 5% solution. Wang et al (2008) reported that solubility of microcrystalline cellulose in NaOH was about only 25-30% (N. Wang, Ding, & Cheng, 2008). Less compact structure from these fibers caused more water absorption, those figure also shows less smooth and cavity surfaces. These less smooth surface indicate the film was not quite homogeneous (Setiani et al., 2013).

**Conclusions**

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 m crystallinity of 97.5% was obtained from sugar palm fiber. Starch-based bioplastic films can be prepared by solution casting with the isolated MCC as reinforcing filler. Addition of MCC content increased the value of tensile strength but decreased the value of elongation at break. Otherwise, adding glycerol content decreased the value of tensile strength and increased the elongation at break value.

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