Bioplastic production from cellulose of oil palm empty fruit bunch

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Abstract. Empty fruit bunch is available abundantly in Indonesia as side product of CPO production. EFB production in Indonesia reached 28.65 million tons in 2015. EFB consist of 36.67% cellulose, 13.50% hemicellulose and 31.16% lignin. By calculation, potential cellulose from EFB is 11.50 million tons. Cellulose could be utilized as source for bioplastic production. This research aims to develop bioplastic production based on cellulose from EFB and to increase added value of EFB. Cellulose fiber has no plastic properties. Molecular modification of cellulose, composite with plasticizer and compatibilizer is a key success for utilization of cellulose for bioplastic. Main steps of bioplastic production from EFB are: 1) isolation and purification of cellulose, 2) cellulose modification and 3) synthesis of bioplastic. Cellulose was isolated by sodium hydroxide methods and bleached using sodium hypochlorite. Purity of obtained cellulose was 97%. Cellulose yield could reach 30% depend on cellulose content of EFB. Cellulose side chain was oxidized to reduce hydroxyl group and increase the carboxyl group. Bioplastic synthesis used glycerol as plasticizer and cassava starch as matrix. This research was successfully producing bioplastic sheet by casting method. In future prospects, bioplastic from EFB cellulose can be developed as plastic bag and food packaging.

1. Introduction

Indonesia is the largest oil palm producers in the world, where its production predicted as about 31 million metric tons of oil palm in 2015 [1]. Crude oil palm (CPO) is extracted from the fruits and the lignocellulosic residual remains as oil palm empty fruit bunch (EFB). Accumulation of EFB in the mill is about 28.65 million metric tons per year. EFB has low commercial value and constitutes a disposal problem due to its large quantity. Conventionally, EFB is burned, disposed of in landfills, or composted to organic fertilizer. In order to prevent air pollution and other environmental problems, burning of EFB is forbidden. It is therefore of importance to optimally utilize EFB in order to solve these problems and at the same time utilize the resource for valuable products.

EFB is composed of 40.37% cellulose, 20.06% hemicellulose and 23.89% lignin [2]. Having high cellulose content, EFB has high potential as a source for cellulosic derived products, such as cellulose

fiber [3], nano cellulose [4], glucose [5], xylose (Zhang *et al.*, 2012) and ethanol [7]. Cellulose also has others potential uses as a source for bioplastic production. Cellulose has no plasticity feature. Uses of cellulose in bioplastic production need some modification. Derivate of the cellulose that has been used in bioplastic synthesis was cellulose nano crystals (CNC) [8], nano fiber cellulose (NFC) [9], cellulose acetate butyrate [10], cellulose acetate [11] and bio-PE [12]. Cellulose derivate was mixed composed with other biopolymers matrix in order to increase physical properties or as a filler, such as starch and polylactic acid (PLA).

The demand for bioplastic increasing along with the rising concern towards environmental problems caused by pretroleum-based plastic. Global production capacity of bioplastic increased by 38% per year during 2003-2007 and predicted will be reach 3.45 million tonnes in 2020. Cellulose and cellulose derivate are about 11% from the global capacity [12]. Cellulose from EFB could be used as source for bioplastic production. Potential cellulose from EFB are 11.5 million tonnes in Indonesia making EFB as good source for bioplastic. This research aims to develop bioplastic production technology from EFB. Cellulose are isolated using sodium hydroxide and sodium hypochlorite. Cellulose obtained from EFB are modified in order to increase physical properties of the bioplastic.

2.   Material and Methods

2.1.   Oil Palm Empty Fruit Bunches
OPEFB was collected from an oil palm mill in Bangka Island, Indonesia. Fresh EFB were chopped and sun dried until the moisture content was less than 10%. Dried EFB chopped into small pieces about 5 cm long and stored in a container at room temperature prior to the experiment. It was analyzed for its lignin, cellulose, and hemicelluloses contents.

2.2.   Cellulose isolation and purification
Dried EFB was delignified by sodium hydroxide in the dosage of 1 g NaOH/100 g EFB with consistency 10%. The digester heated until pressure inside the digester was 6 bar for 5 h. Pulp than washed with water to remove NaOH residue and black liquor. The pulp was beaten in laboratory beater to get pulp with freeness level of 300. Sodium hypochlorite (5.25% in water w/w) were used for cellulose purification. 100 gr of pulp (o.d. basis) was treated in a flask containing 3000ml of deionized water with 33.5 g sodium hypochlorite at 70-75°C. The addition of sodium hypochlorite was continued at 2 h intervals until the cellulose become white. The cellulose was left in acidified condition for 12 h before washing. Cellulose was washed three times using deionized water.

2.3.   Oxidation of Cellulose
5 gr EFB cellulose (o.d. basis) was added into 1000ml Erlenmeyer glass. The cellulose than was impregnated by 500 ml of hydrogen peroxide with various concentrations (0%, 3%, 6% and 9%). The pH of the solution maintained at 11 using 0.1M NaOH or 0.1M HCl solution, as depending on the condition. The cellulose suspension was continuously shaken with electric shaker for 24 h. In the of reaction, the pulp filtered, washed for at least four time and then dried prior to subsequent treatment and analysis.

2.4.   Cellulose-starch bioplastic preparation
Bioplastic composite of cellulose-starch composite was prepared by solution casting and evaporation process using cassava starch as the polymers matrix and glycerol as plasticizer. 30 gr of cassava starch was suspended in 1000 ml distilled water and heated at 60°C for 15 minutes for gelatinization. Cellulose solution was added slowly to the gelatinized starch and stir until all cellulose mixed well in the gelatinized starch. The amount of cellulose was 0% (C0), 12.5% (C1), 25% (C2), 37.5% (C3), 50% (C4) and 75% (C5). Glycerol addition was 0%, 12.5%, 25%, 37.5% and 50%. The mixture was cooled and cast on acrylic plates and air dried. The film produced was peeled of and kept in zipper bag and stored in desiccator.

2.5. Analytical methods

The cellulose, hemicellulose, and lignin of the OPEFB were determined according to the Chesson-Datta Method [13] and TAPPI Standard. A Fourier transform infrared (FTIR) spectrometer (Impact 410 iS10, Nicolet Instrument Corp.) was used for determining changes in the structure of the EFB, pulp, cellulose and bioplastic film according to the method described in reference [7]. Each spectrum was obtained with an average of 32 scans and resolution of 4 cm−1 from 600–4,000 cm−1. The spectrum data was controlled by Nicolet OMNIC 4.1 (Nicolet Instrument Corp.) software and analyzed by eFTIR® (EssentialFTIR, Operant LLC). Bioplastic film micromorphology was visualized using light microscope with 100x – 400x magnification.

The carboxylic acid content of all pulp and cellulose samples was determined by a titration technique described elsewhere [14]. An air-dry cellulose sample equivalent to 0.5-1.0 g was weighted into a 200ml glass- stopper flask. 100 ml of calcium acetate solution were added. The flasks were shaken overnight, and then the suspension of fibers was filtrated. The color indicator murexide was used as as a metalchromic indicator. The pH value of the filtrate was adjusted to 12 by the addition of 0.1 M sodium hydroxide solution. The decrease in concentration of calcium acetate solution after contact with the fibers was determined by titration technique. Solution of 0.1 M EDTA was used as titrant.
Tensile properties which include the tensile strength and Modulus were determined using the ASTM D882-02 method. Films were cut manually into 1.5x10 cm and then stretched using at a crosshead speed of 12.5 mm/min. Testing conditions include relative humidity of 50±5 and temperature of 23±2°C. At least 7 samples per treatment were tested and values were averaged.

3.   Result and Discussion

3.1. Characteristic of empty fruit bunch

The initial content of EFB, pulp and cellulose presented in Table 1. EFB used in this research has high lignin content and higher than reported in other references [15]. These differences could arise depending on the source of the EFB, the historical treatments of the material prior to the analysis and the analytical method. Cellulose is the highest constituent of the EFB, then followed by lignin and hemicellulose. EFB will ready to degrade by microbes when exposes to the air on disposal field and lignocellulosic component will be decreased. EFB samples that have already decayed has low hemicellulose and cellulose content.

EFB strand has unique structure when examined under the microscope as shown in Figure 1. EFB strand and smaller fiber covered by a ball-like structure. These round-shape spiky is called silica bodies [15]. The silica bodies attached to circular craters which are spread relatively uniform over the strand. Extensive treatment of the EFB; such as washing, hammering and crushing could dislodge the silica bodies.

Tabel 1. Lignocellulose content of the native EFB, pulp and cellulose

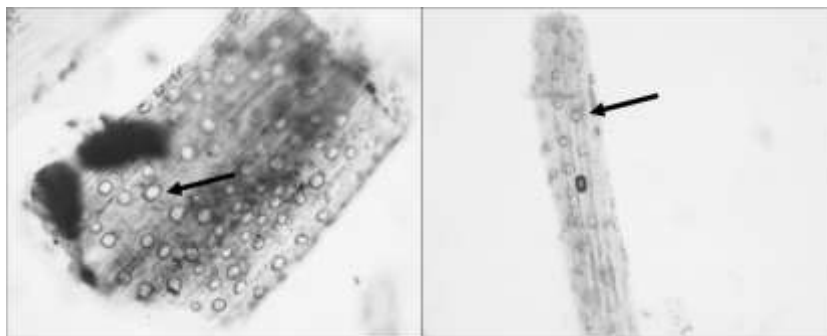| Parameter	EFB	Pulp	Cellulose
Ekstraktif/ How Water Soluble (HWS) (%)	17.79	-	-
Cellulose (%)	36.67	65.43	70.17
Hemicelulosa (%)	13.50	16.68	27.12
Lignin (%)	31.16	17.70	03.38
Ash (%)	0.89	0.18	0.16

Figure 1. Surface of the EFB strand covered by silica bodies (arrow).

Lignin are more soluble in alkaline condition, but cellulose not soluble in alkaline. EFB treatment by NaOH in high pressure and temperature will decrease the lignin content. Lignin content of the EFB pulp was 56.8% lower than to the initial content. Consequently, cellulose content of the EFB increased almost two times than the initial content. Hemicellulose content relatively stable after NaOH digesting. Sodium hypochlorite common used for pulp bleaching. Sodium hypochlorite oxidized lignin in the pulp. Lignin content after bleaching the EFB pulp reduced significantly.

Structural changes of the EFB, pulp and EFB cellulose were analyzed using FTIR, which reflect the changes in the functional group (Figure 2). Two spectra band has been decreased after cellulose isolation form EFB. O-H valence vibration at wavenumber 3338 cm^{-1} and symmetric CH_2 vibration were decrease. Spectra band in the range of 1750 to 1200 cm-1 also decreased. Decreasing of the several FTIR band correlated with the decreasing of the lignocellulosic component. Assignment of FTIR band published in other reference [7].
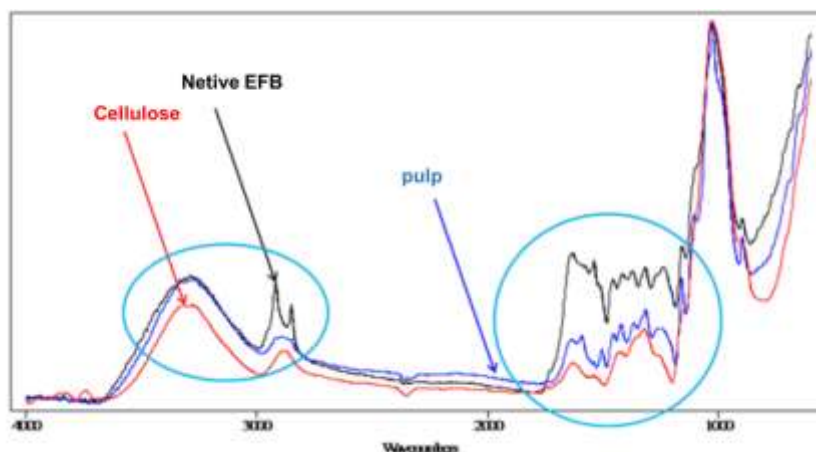

Figure 2. FTIR spectra of the native EFB, pulp and cellulose (bleached pulp).

Crystallinity of the lignocellulose could be predicted using a ratio from the specific FTIR band [16, 17]. The total crystallinity (TCI) and lateral order (LOI) indices, obtained from the 1420/893 and 1375/2900 cm^{-1} absorbance ratios respectively, were used to study the crystallinity changes. LOI and TCI values of the EFB, pulp and EFB cellulose shown in Figure 3. The LOI values was decrease after delignification and pulp bleaching, otherwise the TCI values was relatively constant. Delignification and bleaching of lignocellulose tend to decrease the crystallinity [18]. In this case, LOI was more sensitive to predict the crystallinity of the EFB and its derivate.
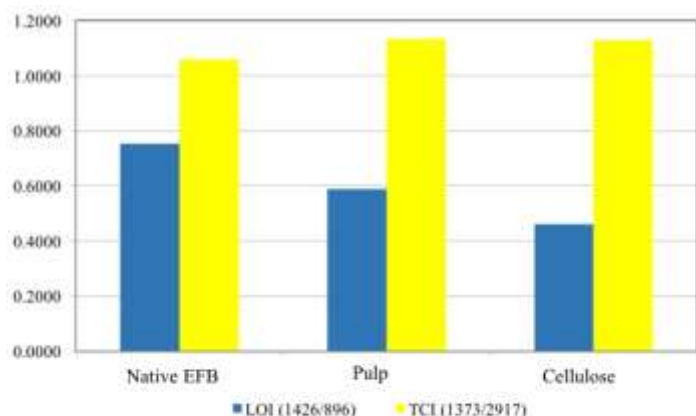
Figure 3. Determined lateral order (LOI) and total crystallinity (TCI) infrared crystallinity indices of native EFB, pulp and cellulose.

3.2 Oxidation of EFB cellulose

Hydrogen peroxide is a strong oxidant and common used in paper industry. Oxidation of the lignocellulose are applied in order to change the reactivity due to an alteration in the number and allocation of functional groups. Changes of the functional group of the cellulose evaluated using FTIR analysis as shown in Figure 4. Some peak increased and the other was constant. Peak at wavenumber 1722 cm^{-1} and 1633 cm^{-1} increased. These peaks assigned as CO stretch unconjugated from carboxyl groups and CO conjugated, respectively. Oxidation of the cellulose could increase the carboxyl group of the cellulose [14,17]. Oxidation may be break the covalent carbon to carbon bond and made new carboxyl group [19].
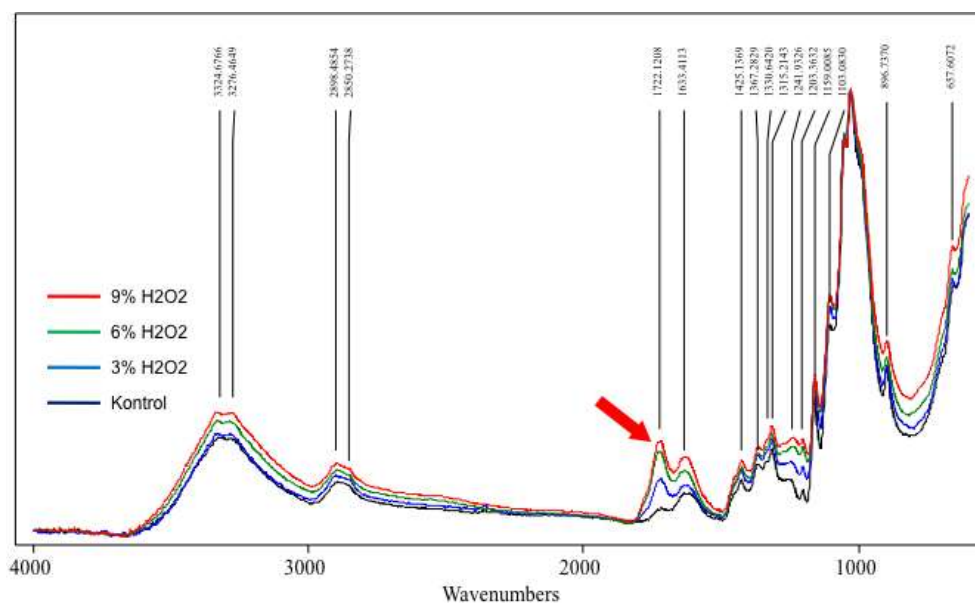

Figure 4. FTIR spectra of the oxidized EFB cellulose with different H_2O concentration.

Oxidation of the cellulose also will reduce the crystallinity as indicate in LOI value. LOI value decreased with the increasing of the percentage of hydrogen peroxide (Figure 5). Damage of the cellulose strand increased by increasing the percentage of the hydrogen peroxide and some strand could be broken. Amorphous region of the cellulose strand is more sensitive to attack. Breaking of the cellulose may be occur in the amorphous region. Damage in crystalline region suspected to be the cause of reducing the crystallinity of the cellulose.
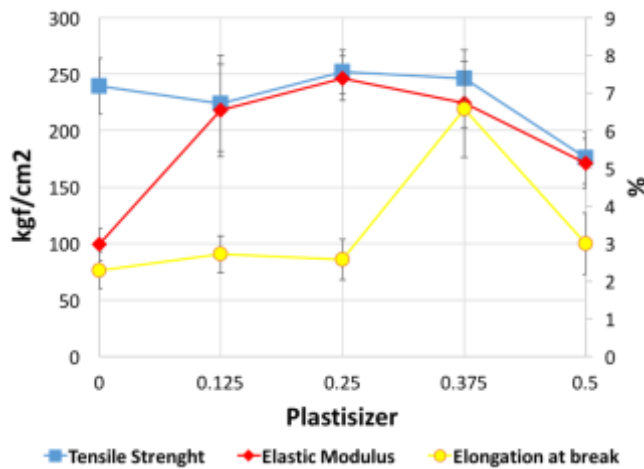
Figure 5. Lateral order index (LOI) of the EFB cellulose oxidized in different H_2O_2 concentration: O% (Control), 3%, 6% and 9%.

3.3 Physical characteristic of bioplastic
Tensile strength, elastic modulus and elongation at break of the cellulose bioplastic composite was shown in Figure 6. Tensile strength was little reduced by 12.5% plasticizer addition and then little bit increase until 37.5%. Elastic modulus increase significantly when plasticizer added and remain constant until 0.5% addition. Elongation at break almost constant until 25% plasticizer addition and then increase significantly at 37.5%. Addition glycerol more than 60% will reduce the elongation at break. Reducing of these characteristic because composite become more loose between matrix and fiber. These evidence also reported in reference that higher glycerol addition will reduce the physical properties [20].
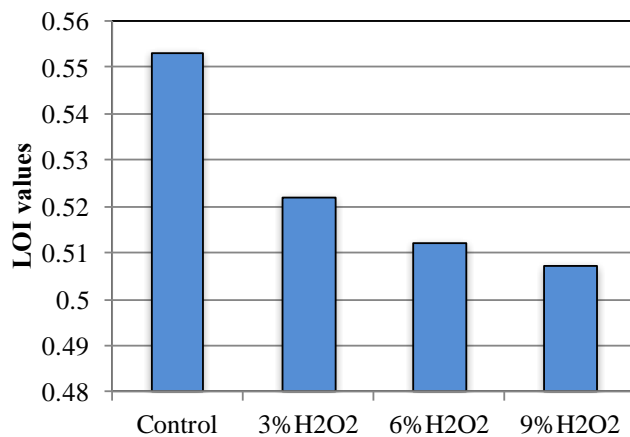

Figure 6. Tensile strength, elastic modulus and elongation at break of the bioplastic cellulose composite.

Cellulose arrangement in the bioplastic composite evaluated using light microscope and shown in Figure 7. Starch bioplastic is transparent and no fiber could be shown under the light microscope. Addition 12.5% cellulose in the bioplastic composite shown more gab between cellulose fiber. Addition more cellulose will increase the density of the fiber inside the bioplastic composite.
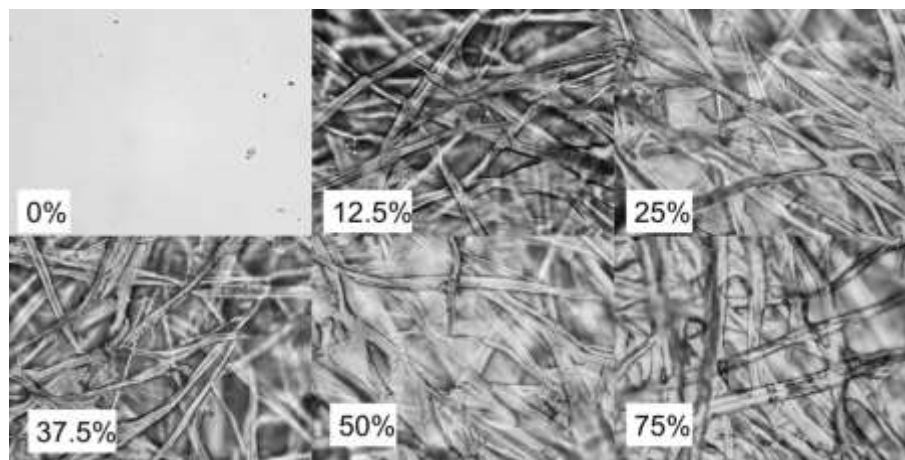
Figure 7. Cellulose arrangement in bioplastic with different percentage from: 0% until 75%.

Opacity of the bioplastic film shown in Figure 8 and Figure 9. Addition of the cellulose will reduce the opacity of the bioplastic film. Cellulose fiber is less transparent than starch. Higher density of the cellulose fiber as shown in Figure 7 will prevent the light and reduce the opacity of the bioplastic composite.

Figure 8. Transparency of the EFB bioplastic with different cellulose content: 0%, 12.5%, 25%, 37.5%, 50% and 75%.

Figure 9. Transparency of the EFB bioplastic with different glycerol content: 0%, 12.5%, 25%, 37.5% and 50%.

4.   Conclusion

Lignocellulosic content of EFB was 36.67% cellulose, 13.50% hemicellulose and 31.16% lignin. Delignification of EFB by sodium hydroxide and subsequence bleaching by sodium hypochlorite was remove lignin and increase percentage of holocellulose more than 97%. Oxidation of the EFB cellulose reduce the crystallinity and increase carboxyl content of the EFB cellulose. Bioplastic composite successfully made from EFB cellulose with cassava starch as a matric and glycerol as plastisizer.

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