Extraction of cellulose from oil palm empty fruit bunch using eco-friendly solvents for preparation of transparent cellulose thin film

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Abstract. The purpose of this research is to extract the cellulose using eco-friendly reagents of hydrogen peroxide and formic acid and determine the optimum reaction time for delignification process. The extracted cellulose and characterised using FTIR, TGA and PSA. The percentage yield of extracted cellulose were calculated. The highest yield was found to be 65.78 % at reaction time 120 min. The FTIR spectral studies confirm the removal of lignin from the delignified cellulose at peak 1613 cm⁻¹ and the TGA result shows the thermal degradation of extracted cellulose at 329.04, 329.92 and 330.99 °C at reaction time 60, 90 and 120 min. The PSA studies provided the evidence of extracted particle size of the cellulose become finer as the reaction time increase. The particle size observed for delignified cellulose at 60, 90 and 120 min are 68.4, 64.6 and 57.3 µm. The extraction of cellulose and characterization to determine the optimum reaction time was able to obtain. From the result obtained, it can be concluded that the longer the reaction time, the higher the percentage yield of cellulose extracted. Film formation was later carried out using the extracted cellulose from different reaction time.

Keywords: Transparent thin film; Extraction; Eco-friendly reagent

1. Introduction

Cellulose (C₆H₁₀O₅)ₙ is a natural linear polysaccharide. It is one of the abundant biomaterials on earth produced by plants or some bacteria. Plant cell walls are mainly composed by cellulose which help the plant to remain strong and rigid whereas the other component composed together with the cellulose [1]. Cellulose in plant fiber are in amorphous phase that linked with crystalline phase through the intermolecular and intramolecular of hydrogen bonding. The unique properties of the cellulose are low density, good mechanical properties and biodegradable [2].
Cellulose can be extracted by chemical, mechanical or enzymatic technique [3]. The chemical method can be conducted by using both alkali and acidic chemicals whereas the enzymatic technique involves specific enzyme such as cellulase and cultural medium with the presence of glucose and ethanol for cellulase consumptions in extraction process [4]. The mechanical method usually involves grinding and milling of the fiber with addition of small amount of chemicals as well as thermomechanical process such as steam fiber explosion [5].

The cellulose-based film has several characteristics such as light in weight, renewable, recyclable and compatible to the health and the environment. The casting technique are widely used as the thickness of the film produced will be distributed uniformly, maximum optical purity and low haze. Nowadays, the solvent cast technology are used widely in productions of film as it gives Extremely high quality [6].

Currently, the natural fibers such as lignocellulosic biomass from oil palm waste such as cellulose is one of the major applications in food packaging and film industry. The cellulose obtains from OPEFB via extraction method using eco-friendly reagent is widely explored and well documented in the literature. However, the optimization of reaction time in the extraction process has not been determined. Throughout this study, the optimum parameter specifically the delignification reaction time will be determine to achieve the most optimize and effective extraction process.

Besides, the preparation of transparent cellulose thin film are also widely explored and documented but the production of transparent cellulose thin film from cellulose extracted from OPEFB is limited [7]. The cellulose extracted were used to prepare the film.

The analytical, thermal and mechanical tests were conducted to determine the characterization of each sample. The test were performed by using Fourier-Transform Infrared (FTIR) Spectroscopy, Particle Size Analyzer (PSA), Thermogravimetric Analysis (TGA) and Tensile testing to determine the functional group, particle size, thermal stability and mechanical properties of the sample respectively. By conducting this study, the optimum reaction time of the extraction process were finalised.

2. Experimental section

2.1. Materials
Oil Palm Empty Fruit Bunch (OPEFB) of size 500 µm was purchased from MPOB, Selangor. Ethanol and Hydrogen Peroxide was purchased from Sigma Aldrich. Sodium Hydroxide, Dimethylacetamide (DMAc) and Lithium Chloride was purchased from R&M Chemicals Sdn Bhd. chemicals reagents purchased are of analytical grade and acquired from commercial sources in Malaysia.

2.2. Sample preparation
1000 g of 500 µm OPEFB were soaked with distilled water for 30 min and washed several times until the water observed become clear. The purpose of washing is to remove the dirt and other impurities from raw materials. The fiber was further dried at 50 °C until constant weight was obtained after 3 days.

2.3. Pre-treatment of oil palm empty fruit bunch (OPEFB)
The 30 g of OPEFB were dewaxed with 300 ml of 70 % ethanol using Soxhlet extractor for 3 hours and dried for overnight. 50 g of the dewaxed fibers were suspended in 10 % NaOH and autoclaved for one hour at 121 °C and 1.5 atm. The mixture of supernatant and fibers were separated and washed until clear water was observed. 10 g of treated fiber were suspended in 10 % H2O2 and placed into incubator shaker for 1 hour at room temperature for bleaching treatment. The bleached fibers were washed with distilled water and dried overnight.

2.4. OPEFB-cellulose extraction process
15 g of pre-treated fibers were soaked with the mixture of 20 % formic acid and 10 % H2O2 at ratio 1:1 (v/v). The soaked fibers were placed in water bath at 85 °C at different reaction times, which is 60 min, 90 min and 120 min each for delignification process. The delignified cellulose were washed with 10 % concentration of formic acid before further rinse with distilled water until pH 7 were obtained. The
yellowish extracted cellulose were then re-suspended in 10 % H₂O₂ each for 90 min at 60 °C for further bleaching. The process was repeated until the fiber turned whitish. The insoluble fraction of cellulose was collected and the percentage of yield (% wt) was calculated. The α-cellulose content was determined using Mohtar et al. [8].

Percentage of yield equation:

\[ Y_i \text{ (\% wt)} = \frac{A}{B} \times 100 \]  

Where,

i = Cellulose fraction
A = Weight of extracted cellulose from OPEFB, g
B = Weight of respective OPEFB used the extraction process, g

2.5. Transparent cellulose thin film preparation

2.5.1. Transparent cellulose thin film preparation method 1. According to Acharya et al. [9], 3 g of extracted cellulose at reaction time 60, 90 and 120 min were suspended in DMAc with concentrations of 5 % w/v. The suspension were heated for 30 min at 80 °C under continuous stirring condition and 8 g of LiCl were added after 30 min. The mixture continue heated at 80 °C under stirring condition for another 3 hours. The temperature were decreased to 50 °C at the end of heating and the temperature were maintained for overnight.

2.5.2. Transparent cellulose thin film preparation method 2. According to Zailuddin & Husseinsyah [10], 10 g of extracted cellulose from different reaction time were activated in distilled water for 5 hours at room temperature. The activation process was to swell the cellulose fiber before dehydrated in DMAc for 4 hours at room temperature. The prepared cellulose were filtered and dissolved in DMAc for another 20 min. 8 % of lithium chloride were added and the solution were stirred for 40 min continuously until the lithium chloride was completely dissolve in the solution.

2.5.3. Casting method to prepare transparent cellulose thin film. The cellulose solution prepared were casted on casting glass slide and were gently distributed to spread the solution uniformly on the glass slides for film preparation. The glass slides that were spread with the solution were left for gelation at ambient temperature for overnight. The gelation film were immersed in distilled water for generation. The water were exchanged every 5 hours for 3 days to regenerate the film and to remove the solvent. The wet film obtained were dried in freeze-dryer for 4 days. The freeze-dried film then undergo further characterization.

2.6. Characterization

2.6.1. Fourier-transform infra-red spectroscopy (FTIR). FTIR Spectrophotometer model Perkin Elmer Spectrum 400 FT-IR/FT-NIR was used to identify the functional group of the raw OPEFB, treated OPEFB, cellulose extracted and the transparent thin film prepared. The sample and KBr were mixed at ratio 100:1 until it is fully homogenised. FTIR spectra were analysed within wavelength of ranged between 400 and 4000 cm⁻¹ at a rate of 0.02 cm⁻¹.

2.6.2. Thermogravimetric analysis (TGA). The thermal stability of raw OPEFB, treated OPEFB and cellulose extracted as well as the transparent thin film prepared were determined using Mettler Toledo TGA machine according to ASTM E1131 method. Nitrogen gas were flowed at 20 ml min⁻¹ and heated from room temperature, which is 30 °C to 700 °C with heating rate of 10 °C min⁻¹.
2.6.3. Particle size analyzer (PSA). Particle size analysis were done using Mastersizer, Malvern 3000 model according to ASTM C209-20. The temperature set was at room temperature and the refractive index used was 1.746 with 1.000 absorption index. Water was used as the dispersant medium with the dispersant refractive index of 1.330.

3. Result and discussion

3.1. OPEFB pre-treatment

The primary steps before extracting cellulose from the fiber is pre-treatment. The main purpose of pre-treatment process is to destroy the lignin structure, decrease the cellulose crystallinity and increase the lignocellulosic materials porosity prior to further treatment [11]. The transmittance peak located at 3400 cm⁻¹ in both raw and pretreated OPEFB is attributed to the –OH stretching vibration of cellulose [12]. The peak was slightly decreasing in the intensity after pre-treatment due to heating process introduced at high temperature to the fiber during autoclaved. As the lignin was removed along during the pre-treatment, the intensity of -CO stretching band of lignin at peak 1613 cm⁻¹ were decreased [13]. The removal of lignin was proven in figure 1. Delignification was done prior to further removal of lignin. The peaks at 1170 cm⁻¹ were shown in all sample as it attributes to the deformation of C-H rocking vibration and C-O-C pyranose [14]. To conclude, lignin functional groups presented in untreated OPEFB were diminished along the process.

Figure 1. FTIR spectrum of (a) untreated; (b) dewaxed; (c) autoclaved and (d) bleached OPEFB.

3.2. Extraction of cellulose from pre-treated OPEFB

Further delignification of cellulose fiber has effectively removed the lignin fraction and produced chlorine-free cellulose with percentage yield as reported in previous research of Ranganagowda et al. [15] and Nazir et al. [12] that reported the extracted cellulose from OPEFB at reaction time 120 min is at 64 % and 65 % respectively. The synergistic effect of formic acid will remove lignin by partial oxidation. The lignin were converted into carboxylic acids and removed in the form of water-soluble fraction and leave insoluble cellulose suspended in aqueous medium [16]. The percentage yield of extracted cellulose calculated is computed in the table 1. The highest percentage yield of delignified cellulose is at 120 min reaction time followed by at 90 and 60 min. The content of cellulose are 65.78 %, 64.13 % and 61.65 % respectively. Thus, the optimum reaction time for delignification of cellulose is at 120 min.
Table 1. Percentage yield of extracted cellulose from OPEFB.

| Reaction time, min | Initial weight, g | Final weight, g | Yield, % (w/w) |
|-------------------|-------------------|----------------|--------------|
| 60                | 15.02             | 9.26           | 61.65        |
| 90                | 15.00             | 9.62           | 64.13        |
| 120               | 14.99             | 9.86           | 65.78        |

The transmittance peak at 1613 cm\(^{-1}\) in figure 2 were assigned to -CO stretching of lignin. At reaction time 120 min, the transmittance peak of lignin functional group shows the least intense. Thus, the presence of lignin was removed form delignification process. The intensity peak of C-O-C of aryl-alkyl ether in lignin (figure 2) decreases as the reaction time increases. The delignified cellulose at 120 min reaction time has the lowest lignin intensity compared to delignification of cellulose at 60 min reaction time. Figure 2 shows the FTIR Spectra of delignified cellulose at reaction time 60, 90 and 120 min shows the transmittance peak at 2907 cm\(^{-1}\). The peak were attributed to -CH of cellulose groups stretching vibrations was presence after delignification process but become less intense due to damage of cellulose structure during the process. To conclude, the lignin component was successfully removed from the untreated fiber.

Figure 2. FTIR spectrum for delignified cellulose at reaction time (a) 60 min; (b) 90 min; (c) 120 min.

3.3. Thermogravimetric analysis (TGA)

From the result obtained, the initial weight loss for first decomposition is attributed to loss of water content and volatile substance at temperature for the first 300 °C [17]. The second composition shows the thermal degradation of the cellulose. Dewaxed fiber has the highest inflection point, which is at 345.35 °C. The bleached fiber has the second highest inflection point at 339.50 °C, which then followed by autoclaved at 345.35 °C and untreated fiber at 317.03 °C. The delawaxed fiber shows the highest inflection point compared to other pre-treated and untreated fiber due to the presence of –OH group of cellulose during dewaxed process, which was absence in untreated and other pre-treated fiber. Inflection point for untreated fiber was the least since the fiber consists of wax, pectin, and other lignocellulosic component that has low thermal degradation. Figure 3 shows the overlay thermal degradation curve for untreated OPEFB and pre-treated fiber.
Figure 3. Overlay thermal degradation curve for untreated OPEFB and pre-treated fiber.

The delignified cellulose at 120 min reaction time has the highest inflection point for the second decomposition which is 330.99 °C and followed by delignified cellulose at 90 min and the least is delignified cellulose at 60 min with inflection point of 329.92 °C and 329.04 °C, respectively. The highest cellulose yield was at 120 min delignified cellulose and it has the highest concentration of cellulose as it was delignified at optimum reaction time compared to other delignified cellulose. Thus, more heat is needed to degrade the more concentrated cellulose which makes the inflection point obtained is high. The thermal stability of the samples shows increment along with the process due to the increased in crystallinity and intermolecular hydrogen-bonded after the removal of amorphous content. Figure 4 shows the overlay thermal degradation curve for delignified cellulose at different reaction time.

Figure 4. Overlay thermal degradation curve for delignified cellulose at different reaction time.
3.4. Particle size analyzer (PSA)

The result were obtained in the point of distribution of untreated OPEFB at Dv (90) is 207 µm. The size of sample become finer for dewaxed and autoclaved fiber with Dv (90) which are 202 µm and 190 µm, respectively. The smallest particle size was obtained during bleaching process with Dv (90) of 50.8 µm. The particle size in pre-treatment was decreasing along the process. During bleaching process, the fiber were destructed or modified to remove the colour bodies by degrading it into smaller and soluble units [18].

For delignified cellulose, smallest size of particle is 57.3 µm at 120 min delignification reaction time. The delignified cellulose at 90 and 60 min reaction time has the derivative size of 64.6 µm and 68.4 µm. Theoretically, the longer the reaction time, the smaller the particle distribution size until it reach its optimum condition as the delignification process removed amorphous structure of the fiber and the microfibrils were obtained in the process. According to Mohtar et al. [8], it is reported that the smaller size of particle were obtained when longer hydrolysis time applied to isolate the nanocellulose from OPEFB. The particle size and distribution gives impact on the properties such as rheology, film gloss, surface area and packing density of film. Table 2 shows the particle size obtained for untreated OPEFB, pre-treated and delignified cellulose.

Table 2. The particle size distribution for untreated OPEFB, pre-treated and delignified cellulose.

| Sample                     | Size classes, µm |
|----------------------------|-------------------|
|                            | Dv (10) | Dv (50) | Dv (90) |
| Untreated OPEFB             | 18.90   | 83.70   | 207.00  |
| Dewaxed                    | 24.50   | 94.60   | 202.00  |
| Autoclaved                  | 34.80   | 78.00   | 190.00  |
| Bleached                   | 23.40   | 35.00   | 50.80   |
| Delignified cellulose at 60 min | 33.60 | 48.60   | 68.40   |
| Delignified cellulose at 90 min | 31.50 | 45.70   | 64.60   |
| Delignified cellulose at 120 min | 30.26 | 46.40   | 57.30   |

3.5. Transparent cellulose thin film

The cellulose-based transparent thin films were prepared using 2 different methods. The weight of cellulose used is according to method 1 and 2 of Acharya et al. [9] and Zailuddin & Husseinsyah [10], respectively. The cellulose film was unable to be prepared using method 1 as the film did not solidified. According to Acharya et al. [9], hydrolysed cellulose fiber with size 30 µm [9] were used, meanwhile the extracted cellulose size is 57.3 µm fiber. The cellulose fiber was only dissolved partially in the solvent during cellulose solution preparation which cause less interaction between cellulose and the solvent. This is because the surface area exposed of the fiber to solvent is limited compared to the approached method [19]. Figure 5 indicates the outcome for the film prepared for method 1.
Figure 5. Casted cellulose solution from delignified cellulose (a) 60 min; (b) 90 min using method 1 and delignified cellulose (c) 120 min and (d) MCC using method 1.

The approached method used cellulose fiber with size 50 µm [10]. The film also unable to be prepared but after several repeated preparation the film was successfully formed according to method 2, but no tests has been done to date.

4. Conclusions

To conclude, from this study the cellulose were successfully extracted using eco-friendly reagents which are formic acids and hydrogen peroxide which make the cellulose pulp obtained was chlorine-free. The optimum reaction time of cellulose were also determined by calculating the percentage yield of cellulose at 120 min with the yield of 65.78 %. The result extracted cellulose were characterized using FTIR, TGA and PSA. The FTIR result shows the lowest lignin intensity at 120 min compared to the other with the thermal degradation obtained at 330.99 °C, which is the highest, compared to other reaction time and the finest particle size were obtained at 120 min reaction time which is 57.3 µm. However, the transparent cellulose thin film was not able to be prepared according to method 1, as the extracted cellulose used was larger than the required size according to the respective method meanwhile the film was successfully prepared using method 2. Therefore, the objective to extract cellulose and preparation of transparent cellulose thin film proposed were able to be achieved, but the characterization of the film were unable to be achieved. The cellulose were recommended to undergo acid hydrolysis treatment to produce nanocellulose before film preparation as the size of the cellulose might affect the film produced.

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