All-cellulose composite isolated from oil palm empty fruit bunch

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Abstract. In this study, all-cellulose composite film which was fabricated by utilizing the cellulose extracted from empty bunch of palm oil has been successfully conducted. The film was initially prepared by performing chemical technique treatments involving alkaline treatments to remove the ligno-cellulosic contents. To obtain the nano-scale materials, the mechanical experiments were performed by using the homogenizer instruments, so the nanofiber cellulose could be obtained in addition to fabricate the film. Next, the cellulose fiber was partially dissolved by 8% LiCl/DMAC and it was used to fabricated composite film of all fiber cellulose. Functional groups of the cellulose fiber were characterized using FT-IR spectroscopy. The highest tensile strength was held by all fiber cellulose treated 2% NaOH, i.e 109.37 MPa, Young’s Modulus 3.56 GPa, and elongation at break 3.07%. The morphology was also determined using scanning electron microscopy (SEM) and showed the most regular surface structure owned by all fiber cellulose treated 2% NaOH as well.

1. Introduction

Cellulose, an abundant organic material, provides many advantageous in certain utilization or application. This biomaterial is contained within plant packed with other compounds which are lignin and hemicellulose. As biomaterial, cellulose is considered as promising material in the future based on its chemical properties, for instance, the biocompatibility. It is classified as biopolymer contains (1-4)-linked with β-glucopyranosyl residues providing stable condition both in intermolecular and intramolecular hydrogen bonding [1]. Due to its chemical structure, the crystalline and amorphous part could be determined within its fibrils by acid hydrolysis; however, the crystalline size may vary depending on its source [2]. Technically speaking, the mechanical strength of the cellulose is based on its crystalline properties and systems.

Indonesia is worldwide-recognized countries which has palm oil plantation. The plantation has been supporting the economical aspect of Indonesia since the colonialization era. The area that has the biggest palm oil plantation are both in Sumatra and Borneo Island with hundreds of thousands of acre of palm oil plantation, generating tones of organic waste every year.

To produce the cellulose, there are several methods which have been considered successful. In recent years, the extractions of cellulose based on many techniques have been manufactured by several research groups including by performing bacteria [3], electro spun [4], or homogenizer [5]. The differences of obtaining cellulose produce different result, but it is important to understand that the pretreatment of cellulose will provide easier process [6]. Additionally, either chemical or physical pretreatments provide significant impact to the obtained cellulose.
In this study we performed the combination of production of all-cellulose composite film. Firstly, the raw material, which is oil palm empty fruit bunch, contains high composition of lignin and hemicellulose compounds implying the resistance of extracting cellulose from the tissue. Hence, it can be obtained by reacting in the alkaline condition prepared with sodium hydroxide in specific concentration; however, the result is on form of aqueous suspensions [7]. Afterward, it is heated with high temperature (around 170°C) to produce steam explosion in alkaline condition as well. This treatment mainly aims to remove significant amounts of hemicellulose and depolymerization of lignin to elementary sugars and water-soluble oligomers respectively [8]. And finally, the mechanical disintegration is performed to break the fibrils into fiber, and the result therefore is partially dissolved in LiCl/DMAc solution to produce the all-cellulose composite film which is suitable to be utilized as a bio-based and biodegradable material, for instance food packaging material [9]. Hence, this study performs characteristics including FTIR, tensile strength test, and SEM.

2. Materials and method

2.1 Pre-treatment of oil palm empty fruit bunch

The raw material was collected from the dumping site nearby the crude palm oil plantation. After being heated to obtain the fruit, the bunch was in oiled condition. Therefore, to remove the impurities, the bunch was cut into certain length (around 3 to 5 cm). Then, it was washed in flowing water and dried in oven at 80°C for 5 hours. Finally, it was soaked in solution of sodium hydroxide 2% for 24 hours (solid and liquid ratio were 1:10).

2.2 Preparation of cellulose fiber using steam explosion method

Several variations of sodium hydroxide (NaOH) solution were performed during the steam explosion in order to obtain related association between the presences of NaOH. The pre-treatment brunches then are soaked and divided into three variations in bottles of solution of sodium hydroxide which are 2%, 4%, and 6% (solid and liquid ratio were 1:10), before being heated inside the autoclave for temperature reaching to 140° Celsius and pressure 170 Kpa. The pressurized treatment conducted for two hours. After being heated, the lignin and hemicellulose were removed, and the fibrils were soaked in aqueous solution to reach neutral pH.

2.3 Bleaching treatment of steam exploded fiber

To remove the excess of lignin and hemicellulose residues, the fibers were soaked in 10% H₂O₂ at 70°C for 3 hours and stirred on a hotplate stirrer. After that, they were washed by distilled water.

2.4 Chemical disintegration of acid hydrolysis

To obtain the fibers, the chemical disintegration using acid compounds was performed. The fibrils which had neutral pH then were soaked in 10% hydrochloric acid and the material was prepared for being sonicated for 2 hours. Afterwards, the material was washed with distilled water until the pH reaching 7.

2.5 Mechanical disintegration of homogenization

The next technique was the mechanical disintegration by performing the homogenizer. The fibers were soaked with distilled water and they were homogenized by homogenizer for 4 hours with 8000 rpm [10].

2.6 Preparation of all fiber cellulose

2.6.1 Cellulose Activation Process. All fiber cellulose was produced by firstly activated it in aquadest, acetone, and N,N-dimethyl acetamide respectively at room temperature for 1 hour while stirred. After that, it was pressed in hydraulic hot press equipment at 80°C for an hour [11].
2.6.2. Dissolution with LiCl/ DMAc. Activated all fiber cellulose was partially dissolved and stirred in 8% LiCl/DMAc (solid to liquor ratio of 1:10) for 120 minutes. This solution then poured into glass plate, kept for overnight, and washed with aquadest. The last, it was pressed with hydraulic hot press at 70°C for 1 hour using wire mesh which had 400 mesh pore size.

3. Results and discussion
3.1. Fourier Transform infrared (FT-IR) Spectroscopy
The cellulose fibers treated in various alkaline concentrations had been isolated from empty fruit bunch of palm oil and also analyzed by using FT-IR spectroscopy. A Shimadzu FT-IR-PRESTIGE 21 spectrophotometer was used to obtain the spectra. The cellulose fiber were ground and mixed with KBr (sample:KBr ratio, 1:99) to prepare pastilles. FT-IR spectra were recorded in a spectral range of 4000–450 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\), taking four scans for each sample. Figure 1 shows the FT-IR spectra of chemically treated empty fruit bunch fibers.

Based on the spectra, it can be seen that the broad absorption band in 3700-3100 cm\(^{-1}\) region are existed, which correspond to the O-H groups as the main constituent of the fibers. Moreover, the peaks in area 3425 cm\(^{-1}\) are also related to the O-H stretching band, which is, caused by vibrations of the hydrogen bonded to the hydroxyl groups. The aliphatic C-H stretching vibrations are exhibited by the peaks in 2908 cm\(^{-1}\) area while another O-H groups, which are attributed to the bending of absorbed water and carboxylate groups, are presented in 1635 cm\(^{-1}\) area [10].

The peaks in area 1427, 1373, and 1319 cm\(^{-1}\) are respectively due to the bending vibration of H-C-H and O-C-H, bending of C-H, and rocking vibration of \(-\text{CH}_2\) at C\(_6\) of glucose ring. Another lower intensity peaks among them are seen in region 1111 and 1056 cm\(^{-1}\), those present C-O-C stretch and vibrations of C-C, C-OH, C-H ring and side groups [12]. Deformation and stretching of C-O-C, C-C-O, and C-C-H in \(\beta\)-glycosidic linkage of glucose ring, that shows the characteristic structure of cellulose, are revealed in wavenumber 894 cm\(^{-1}\) [10].

3.2. Mechanical properties characterization
Tensile strength testing, as one of the mechanical properties determinations of material, of the all fiber cellulose film has been conducted. The mechanical properties of all-cellulose composite film were
measured by Instron 5567 tester at test speed at 5 mm/min at room temperature. The specimen gauge length was 50 mm and the width was 15 mm. From the test, the mechanical properties of the samples could be identified and the results are given in Table 1.

Table 1. Mechanical properties of all-cellulose composite film prepared with various NaOH concentration.

| Time (Minutes) | Materials                  | Tensile Strength (MPa) | Young’s Modulus (GPa) | Elongation at Break (%) |
|---------------|----------------------------|------------------------|-----------------------|-------------------------|
| 120           | Treated AFC NaOH 2%        | 109.37                 | 3.56                  | 3.07                    |
| 120           | Treated AFC NaOH 4%        | 63.93                  | 2.51                  | 2.55                    |
| 120           | Treated AFC NaOH 6%        | 31.88                  | 1.38                  | 2.31                    |

Based on the data, it can be seen that giving the treatment of the fiber with different concentration of sodium hydroxide solution significantly drops the mechanical properties. Yet, the tensile test results exhibit the best mechanical properties are held by the all fiber cellulose composite film which treated by 2% NaOH (tensile strength of 109.37 MPa, Young’s modulus of 3.56 GPa, and elongation at break of 3.07%) and the lowest mechanical properties are identified on the all fiber cellulose composite film contacted 6% of NaOH (tensile strength of 31.88 MPa, Young’s modulus of 1.38 GPa, and elongation at break of 2.31%). This phenomenon agreed with the research which also had been successfully conducted by Rambabu et al. (2015) showing decline trend of the tensile strength test results of the cellulose fiber film treated by various concentration of alkali solution. From the results, it is obvious that the higher concentration of alkali influences the strength of the all fiber cellulose film. Higher concentration of NaOH disrupts the inter- and intra- hydrogen bonds between hemicellulose, lignin, and cellulose, the more hemicellulose and lignin could be removed and separated from cellulose [13].

The decrease of mechanical properties test results is also noted by the stress-strain curve in Figure 2. It is clear that the highest result is reached by all fiber cellulose film at 2% of NaOH which has stress of 109.37 MPa and strain of 0.03%. Lower numbers are also possessed by the film of 4% and 6% (respectively stress/strain: 63.93/0.02 and 31.88/0.02). These are showed that the more concentrated of NaOH solution contacted with all fiber film, the lower stress and strain would be obtained.

![Figure 2 Stress-strain curves of all-celulose composite film.](image-url)
3.3. Morphology Analysis Using SEM
The morphological structure of the all-cellulose composite film was analyzed using Bruker Energy Dispersive Analysis (EDS) Scanning Electron Microscope. With three different concentrations of sodium hydroxide treatment given to obtain cellulose fiber, three different surface structure of the all-cellulose composite film have been generated using SEM and their results are presented by Figure 3.

![SEM images of all-cellulose composite films treated by (a) NaOH 2%, (b) NaOH 4%, and (c) NaOH 6%.](image)

**Figure 3** SEM images of all-cellulose composite films treated by (a) NaOH 2%, (b) NaOH 4%, and (c) NaOH 6%.

Based on the SEM images, it can be seen that the most well-organized surface structure is performed by the all-cellulose composite film treated by 2% NaOH. As we have understood about the concept of the all-cellulose composite, which both the matrix and the filler are cellulose, the cellulose fibers are well-partially dissolved in 8% LiCl/DMAC solution and become the matrix while the other fibers are trapped being the filler. Compared with Figure 3(b), the least fiber as the filler is exhibited on Figure 3(c), where most of the fibers are dissolved.

4. Conclusion
The cellulose fiber had been characterized using FT-IR spectroscopy showing the appearance of broad absorption band in 3700-3100 cm\(^{-1}\) region which relates to the O-H groups, and the wavenumber of 894 cm\(^{-1}\) was also seen as deformation and stretching of C-O-C, C-C-O, and C-C-H in β-glycosidic linkage of glucose ring. The decrease of tensile strength, Young’s Modulus, and elongation at break were occurred on all-cellulose composite film treated from 2% until 6%. Yet, the best mechanical properties of the all-cellulose composite film was reached by AFC treated 2% NaOH whose tensile strength of 109.37 MPa, Young’s modulus of 3.56 GPa, and elongation at break of 3.07% and the least mechanical properties was belonged to AFC treated 6% NaOH with tensile strength of 31.88 MPa, Young’s modulus of 1.38 GPa, and elongation at break of 2.31%. SEM analyzer had been also used to characterize the morphology of the all-cellulose composite film and presented the most arranged structure was handled by the all-cellulose composite film treated by 2% NaOH.
Acknowledgment
The authors gratefully acknowledge Rector of University of Sumatera Utara for the financial support via Penelitian Unggulan Universitas Talenta Project 2017.

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