Preliminary study on the fabrication of cellulose nanocomposite film from oil palm empty fruit bunches partially solved into licl/dmac with the variation of dissolution time

S Gea¹, D Andita¹, S Rahayu¹, D Y Nasution¹, S U Rahayu², A F Piliang²

¹Department of Chemistry, University of Sumatera Utara, Medan, Indonesia
²Department of Physics, University of Sumatera Utara, Medan, Indonesia

*E-mail: s.gea@usu.ac.id

Abstract. This study aims to fabricate cellulose nanocomposite film from oil palm empty fruit bunches (OPEFB) and to compare the difference in resulted films, which were treated with various dissolution time. The method applied to generate cellulose fiber was steam explosion method; also, the alkali treatment was employed. In order to form cellulose nanocomposite film from cellulose nanofibers, LiCl/DMAc was used as the solvent with the dissolution time varied, namely 30 minutes and 60 minutes. The chemical structure was investigated using Fourier transform infrared (FT-IR) spectroscopy, whereas the surface morphology was done using scanning electron microscope (SEM). The FT-IR results show all appropriate vibration peaks to confirm that the cellulose nanofibers and nanocomposite film were successfully produced. From the photographs of the cellulose nanocomposite film as well as SEM photographs, it can be concluded that 60 minutes dissolution time gives smoother surface and more transparent film than those of 30 minutes.

1. Introduction
Oil palm is one of a promising commodity in Indonesia due to its use as crude palm oil (CPO). Thus, Indonesian Government extends their oil palm plantations to 10,955.231 hectares in 2014 with the total production of CPO of 29,344,479 tons (Direktorat Jenderal Perkebunan, 2014). Regarding the production of CPO, the residues are conducted, namely 23% of oil palm empty fruit bunches (OPEFB), 8% of the shell, 12% of fiber, 66% of liquid waste [1].

OPEFB itself has attracted researchers’ attention nowadays because of its abundance, having a large cellulose content (45,9%), dan having a small lignin content (16,5%). Besides, it also has a considerable hemicellulose content (22,8%) [2]. Such compositions make OPEFB become a potential raw material that can be used as chemical feedstock, glucose, and even bioethanol. However, the use of OPEFB is still limited to fertilizer, alternative material for filling car seat cavity, mattress, briquettes, and raw material for paper production [3]. Therefore, the expansion to apply OPEFB is still needed. One of it is the utilization of OPEFB as a basic material for nanocomposite film.

In order to fabricate the nanocomposite film from OPEFB, some methods are applied. To date, steam explosion method is a proper method to be used. This method was found by Mason et al (1926) as the initial process of biomass processing. The processes employed are opening the fiber and making the
Several researches have been done to isolate cellulose nanofibers from raw material using steam explosion method. Chaerin et al. (2010) isolated cellulose nanofibers from pineapple leaves fiber using steam explosion method [5]. The size of cellulose nanofibers obtained was 5-60 nm. Besides, Ghaderi et al. (2014) also conducted a research about the fabrication of all-cellulose nanocomposite from bagasse to be applied as food packaging. Their research was done by employing LiCl/N,N-dimethylacetamide (LiCl/DMAc) as the solvent and steam explosion as the method. The nanocomposite produced had the maximum tensile strength of 140 MPa [6]. Similarly, Sinaga et al. (2018) also found that cellulose nanocomposite film from corn cobs can be generated using the same method and solvent as Ghaderi et al. (2014) conducted [7].

Related to the dissolution process using LiCl/DMAc, some researches also investigated the effect of various dissolution time. Sinaga et al. (2018) varied the dissolution time between LiCl/DMAc and cellulose nanofibers and found that longer dissolution time resulted in smoother film surface, they concluded that dissolution time affected the results of the film [7]. Similarly, Soykaebkaew et al. (2009) who fabricated bacterial cellulose nanocomposite using surface selective dissolution method stated that the increase of dissolution time of BC in the solvent resulted in smaller ribbons of bacterial cellulose, thus the surface become smoother [8].

To our best knowledge, there are only a few researches conducted the experiment about the fabrication of nanocomposite film from OPEFB, particularly about the effects of the difference in solvent contact time. Therefore, this study aims to examine the effect of different dissolution time in yielding cellulose nanocomposite film from OPEFB. The dissolution time used is limited to 30 minutes and 60 minutes only. The results were then characterized using Fourier Transform Infrared (FT-IR) to confirm the fruitfulness of the cellulose nanocomposite film synthesis. Also, scanning electron microscope (SEM) was employed to discover the difference in the morphology of the results.

2. Materials and Methods

2.1. Materials

Oil palm empty fruit bunches (OPEFB) were collected from the residue of oil palm plantation industry in Sei Buluh, North Sumatera (Indonesia). Those OPEFB were then washed by using water, dried, chopped and stored at room temperature. The samples obtained were the primary sources in this study. The chemicals used, which are namely sodium hydroxide, acetic acid, sodium chlorite and oxalic acid, were purchased from Merck & Co. Several equipments were employed to conduct steam explotion: a homogenizer (DAIHAN HG-15D) and a laboratory autoclave (with 26 psi of pressure).

2.2. Isolation of α-Cellulose from OPEFB

Raw fiber of OPEFB were chopped into short fibers (length: ±3-5 cm) and reacted with 2% w/v NaOH and left for 12 hours in a beker glass. Then, the sampel was put into an autoclave and kept under 26 psi of pressure and at a temperature of 130°C for 2 h. The pressure was released immediately after that process and the fibers were washed in water in order to gain neutral pH. Next, the bleaching process was applied by using H2O2 10% at 70°C for 2 hours. The obtained cellulose fiber from OPEFB was then washed with distilled water. The α-cellulose was filtered dried at 60°C in an oven, and used for FT-IR investigation.

2.3. Isolation of Cellulose Nanofibers

The amount of α-cellulose, which was treated with HCl 10%, was somcated for 2 hours. Suspension was then diluted with distilled water and allowed to settle over night. Next, the washing and filtration were
employed in order to obtain neutral pH. Then, the fibers were suspended in water and homogenized under continuous stirring with a homogenizer at 8,000 rpm for 4 hours. Suspension was then filtered and dried at 45°C in an oven, and used for FT-IR and SEM investigation.

2.4. Preparation and Characterization of Nanocomposite Film
The dried cellulose nanofibers was reacted with DI-water, acetone dan N,N dimethylacetamide (DMAc) for 1 hours at room temperature, followed by dissolution process with LiCl/DMAc 8% for 30 and 60 minutes (the time applied was called as dissolution time). Next, the samples was poured into the mold and dried with hydraulic press equipment for 1 hour at 70°C. Then, the cellulose nanocomposite was yielded and used for FT-IR and SEM investigation.

2.5. Characterization
The dried nanofibers of OPEFB were mixed with KBr powder and examined using FTIR (Shimazu-IR Prestige 21) unit with scanning region of 4000-500 cm⁻¹ at 16 cm⁻¹ resolution and averaging of 45 scans. The same terms were applied to cellulose nanofibers and cellulose nanocomposite film. The morphology of the surface of cellulose nanocomposite film was discovered by using scanning electron microscope (SEM) (Bruker) with the magnification 500 times under 10.00 kV of voltage. The photograph of each sample stage was taken using 8 megapixels camera.

3. Results and Discussion
3.1. Chemical composition of fibers
The chemical composition of OPEFB is summarized from all stages of treatment. In the raw form of OPEFB (fiber), there are other components besides cellulose, hemicellulose and lignin, namely pectin, wax, moisture content, etc (Figure 1(a) and 1(b)). When the fibers are exposure to alkali treatment, the hemicelluloses were removed. Besides, the steam explosion treatment also decreased the proportion of the hemicellulose and lignin (Figure 1(c)). However, the remainder of hemicellulose and lignin still existed. It can be erased by bleaching treatment, obtaining almost pure cellulose, so the samples are more suitable for extracting whiskers (Figure 1(d)), which is called as α-cellulose. Homogenizing was performed to obtained smaller size of fiber, called cellulose nanofibers (Figure 1(e)). After the cellulose nanocomposite film obtained from different dissolution time (30 minutes and 60 minutes), there is a brightness difference in their appearances that can be seen from Figure 1(f) and 1(g), as later confirmed by SEM analysis. It suggests that 60 minutes of dissolution time gives better appearance of the film. Thus, the dissolution time play a substantial rule in forming the nanocomposite film besides the solvent used.
Related to the forming of cellulose fiber from OPEFB using steam explosion method, some explanation are revealed. According to Fernandez et al. (1999) in alkali treatment followed by steam explosion, the hemicelluloses are partially hydrolyzed; also, the lignin is depolymerized. Thus, sugars and phenolic resin compounds, which are partly soluble in water, increase [9]. In addition, Xiao et al. (2001) mentioned that during that process, there are a damaged in alkali-labile linkages between lignin monomers, or between lignin and polysaccharides. Carboxylic or phenolic groups as acidic molecules are ionized in alkaline solution, so they might boost the solubilization of the lignin [10]. It occurred because of hydrolysis treatment using hot alkali [11].

3.2. Fourier Transform Infrared (FT-IR) Spectroscopy Analysis
The FT-IR spectra spectroscopy is carried out to discover the alteration of the chemical structures of the fibers from OPEFB after the treatments using steam explosion method as well as the difference in the structure for various dissolution time. Those spectras are shown in Figure 2.
As shown in Figure 2, cellulose, cellulose nanofibers, cellulose nanocomposite film (30 and 60 minutes) signified two main regions of absorbance; at low wavelengths (500–1750 cm\(^{-1}\)) and at higher wavelengths (2800–3500 cm\(^{-1}\)). This result is in accordance with the study done by Abderrahim et al. (2015) who measured the commercial cellulose and Lani et al. (2014) who obtained the cellulose from OPEFB [12]. As can be seen that there is no vibration peak observed at around 1700 cm\(^{-1}\) from all spectras due to the removed of hemicelluloses, which is showed by C=O stretching, or the disappeared ester carbonyl groups in the p-coumaric units of the lignin. This is believed to be caused by the alkali treatment [13]. Besides, Figure 2 also depicted the movement of wavenumber from cellulose nanofibers to cellulose nanocomposite film, which indicated the effect of dissolution using LiCl/DMAc, The similar situation was also found by Sinaga et al. (2018). To be concluded, these results show that the isolation of cellulose as well as the cellulose nanocomposite film from OPEFB have been done successfully.

Furthermore, from the analysis of those four FTIR spectras, the absorption peaks located in the ranges 3300–3500 cm\(^{-1}\) are assigned to the hydroxyl group (-OH), whereas those, which range from 2890 cm\(^{-1}\) to 2900 cm\(^{-1}\), are attributed to and aliphatic saturated C–H stretching vibration [14]. In addition, stretching of -C-O- group of secondary alcohols and ethers functions, which exist in the cellulose chain backbone, was reflected by vibration peaks in the region 1040–1070 cm\(^{-1}\) and the absorption band at 894.97 cm\(^{-1}\) is characteristic of β-glycosidic linkage between glucose units [12].

However, there is a peak appeared at 1635.64 cm\(^{-1}\) for all spectras. Related to that, Le Troedec et al. (2008) explained that the mentioned peak was carried out by the reaction between sodium hydroxide
and the hydroxyl groups of celluloses, subsequently the water molecules were formed [15]. As also described by Abraham et al.(2011), even though the drying process was applied, there was still the existence of water absorption in the cellulose molecules, which is difficult to be removed because of the cellulose-water interaction [16].

In addition, the cellulose nanocomposite film obtained using 30 minutes shows similar pattern to that of 60 minutes, even though the vibration peaks resulted are a bit different each other as can be seen from Figure 2(c) and 2(d), but those peaks are still in the same region and assigned to the same groups. However, from the percentage of transmission obtained show that the sample of 60 minutes gives higher transmission than that of 30 minutes, this confirmed that the nanocomposite film of 60 minutes dissolution time gives a more transparent film.

3.3. Scanning Electron Microscope (SEM) Analysis

SEM was performed to discover the surface morphology of the cellulose nanofibers and the cellulose nanocomposites film produced. As depicted in Figure 3(a), the surface of cellulose nanofibers is rough and having pores in some areas, whereas the surface of cellulose nanocomposites (Figure 3(b) and 3(c)) is smooth. This occurred due to the dissolution process using LiCl/DMAc (Sinaga et al.(2018)). In addition, the surface of nanocomposite film from 60 minutes dissolution time pointed a smoother surface than that of 30 minutes. It is in agreement with Sinaga et al.(2018), the longer dissolution time, the smoother surface yielded. This result confirms the photograph results in Figure 1(f) and 1(g).

![Figure 3](image)

**Figure 3** SEM photograph of (a) cellulose nanofibers, (b) cellulose nanocomposite film (30 minutes of dissolution time), (c) cellulose nanocomposite film (60 minutes of dissolution time)

4. Conclusion

From the results obtained, It can be concluded that the cellulose nanofibers and nanocomposites film can be successfully generated from oil palm empty fruit bunches (OPFEB) by using alkali treatment and steam explosion method. The FT-IR spectras show no vibration peaks of lignin and hemicellulose, as also confirmed by the finding of other studies. The LiCl/DMAc as a solvent to form the cellulose nanocomposites film was properly used with the variation of dissolution time, namely 30 minutes and 60 minutes. The cellulose nanocomposite film of 60 minutes gives smoother surface and more transparent film than those of 30 minutes. There is no difference in vibration peaks found between the two. Therefore, those results suggest that the research to compare longer dissolution time and their mechanical properties is needed to be done in the future.
Acknowledgement
The authors would like to thank to Rector of University of Sumatera Utara for the funding from the project of PUU-Talenta 2017.

References
[1] Barea et al 2005 Microorganisms in soils: roles in genesis and functions (Heidelberg: Springer Berlin) pp 195-212
[2] Darnoko 1992 Berita Pen.Perkeb. 2 85
[3] Wardani et al 2014 Craft 3 1
[4] Mason and William H 1926 Process and apparatus for disintegration of wood and the like. U.S. Patent No. 1,578,609
[5] Cherian et al 2010 Carbohydrate Polymers 81 720
[6] Ghaderi et al 2014 Carbohydrate Polymers 104 59
[7] Sinaga M E Z et al 2018 Oriental J. Chem. 34 562
[8] Soykeabkaew N et al 2009 Cellulose 16 435
[9] Fernandez-Bolanos J et al 1999 Bioresource Technol. 68 121
[10] Xiao B et al 2001 Polymer Degradation and Stability 74 307
[11] Bismarck A et al 2005 Natural fibers, Biopolymers and Biocomposites 10 9780203508206.
[12] Abderrahim B et al 2015 World J. Environ. Eng. 3 95
[13] Alemdar A and Sain M 2008 Bioresource Technol. 99 1664
[14] Lani N S et al 2014 J. Nanomater. 2014 13
[15] Le Troedec M et al 2008 Composites Part A: Appl. Sci. Manufact. 39 514
[16] Abraham E et al 2011 Carbohydrate Polymers 86 1468