

Extraction and Characterization of Cellulose from Empty Fruit Bunch (EFB) Fiber

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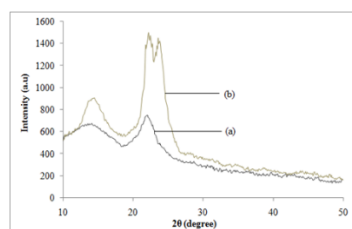
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Graphical abstract



Abstract

In recent years, the use of cellulose fibers in many fields has attracted significant scientific attention due to consumer and environmentally benign, especially in plastic industry, which has been used as cost-cutting fillers and hence provides the possibility of reinforcing polymers. Cellulose can be extracted from natural fibers by chemical and mechanical methods. However, the existing procedures either produce low yields and not environment friendly or energy efficient. The objective of this study was to develop a novel process that uses ionic liquid followed by alkaline method to extract cellulose from empty fruit bunch (EFB) fiber. Subsequently, the properties of original fiber and cellulose were determined by Fourier Transform Infrared (FTIR) Spectroscopy, X-Ray Diffraction (XRD) and thermogravimetric (TG) analysis. The results of the chemical compositions revealed that the modified alkaline treatment was able to remove a large fraction of lignin and hemicelluloses compared to unmodified alkaline treatment. Thus, this process represents an efficient treatment in extracting cellulose of highest yield.

Keywords: Empty fruit bunch fiber; cellulose; polymer; ionic liquid; alkaline treatment

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1.0 INTRODUCTION

Empty fruit bunch (EFB) is one of the lignocellulosic materials, which has great relevance to Malaysia, as a large quantity of the biomass is generated by oil palm industries. More than 11.9 million tons of oils and 100 million tons of biomass are produced in the oil palm industry in Malaysia. The biomass from oil palm residue include the oil palm trunks (OPT) and fronds (OPF), kernel shell, EFB, presses fruit fiber (PFF) and palm oil mill effluent (POME). In addition, the total crop of fresh fruit bunch is more than 30 million tons per year, which generate more than 10 million tons of EFB. Only 10% of the EFB is used and the rest are abundant [1].

It is well known that the natural fibers are mainly composed of cellulose, hemicelluloses and lignin. Pectin, pigments and extractives can be found in lower quantities. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix mainly composed of lignin and hemicelluloses [2]. Most of natural fibers primarily consist of cellulose, about 65–70% of plant. Cellulose, with the formula $C_6H_{10}O_5$ is an organic compound, which are crystalline [3]. The presences of non-cellulosic substances such as lignin and hemicelluloses that cover the cellulose inside have important effects on the final properties of the fibers.

Cellulose is a natural polysaccharide, where D-glucopyranose rings are connected to each other with β -(1→4)-glycosidic linkages. According to Kadla and Gilbert [4], the crystal packing

direction and the physical properties of cellulose are influenced by the presence of three hydroxyl groups, which are secondary OH at carbon 2 and carbon 3, and primary OH at carbon 6 positions. These hydroxyl groups display different reactivities from each other and are able to form hydrogen bonds. Cellulose is the main component of all plant materials and synthesized through photosynthesis process.

The aims of this study were to extract cellulose from EFB fiber through ionic liquid and alkaline treatment and the properties of untreated and cellulose fiber were investigated using FTIR, XRD and TG analysis.

2.0 EXPERIMENTAL

2.1 Materials

Empty fruit bunch fibers were collected from Kulai, Johor and were used as raw material in this study. The various chemicals used for extraction of cellulose are sodium chlorite, acetic acid, sodium sulfite, sodium hydroxide, ethyl acetate, acetone, 1-methylimidazole and 1-cholorobutane. All the chemicals are reagent grade and were used as received.

2.2 Extraction of Cellulose

A 0.7% (w/v) sodium chlorite (NaClO₂) solution was prepared and then acetic acid was added to acidify the NaClO₂ solution until the pH reaches 4. The fibers were boiling in NaClO₂ solution for 2 hours at 70–80°C whereby the ratio of fiber to NaClO₂ solution was set to 1:50 (g/mL). The bleaching process was repeated for four or five times until fiber become white and then filtered. After being filtered, the residue was washed for several times with distilled water and dried in air. The bleached cellulose obtained was heated to about 70 to 80°C in 5% (w/v) sodium sulfite solution for 2 hours. The fibers were filtered, washed and dried in air. After being dried, the fibers were treated in 17.5% (w/v) for 2 hours. The residue was washed for several times with distilled water and dried in air.

For modified version of the widely used alkaline method, the EFB fiber was firstly dissolved in 1-butyl-3-methylimidazolium chloride [(Bmim)Cl], followed by consecutively bleaching and alkaline treatment. The (Bmim)Cl was prepared by heating equimolar amounts of 1-methylimidazole and 1-chlorobutane under reflux at 110°C. After 24 hours, the solution was allowed to cool to room temperature and the resulting viscous solution was washed with ethyl acetate. The fiber was heated in (Bmim)Cl solution for 5 minutes at 110°C whereby the ratio of fiber to (Bmim)Cl solution was set to 1:20 (g/mL). Then, 1:1 water-acetone mixture was added to obtain precipitate. The treated material was washed with distilled water sufficiently and dried in air. Subsequently, the bleaching and alkaline treatment was conducted according to the above procedures.

2.3 Chemical Composition Measurement

Holocellulose content was determined by a modified sodium chlorite method according to Browning. On the other hand, the content of α-cellulose and lignin were determined according to the ASTM standards. The α-cellulose content was determined by further treatment of holocellulose with 17.5wt% sodium hydroxide solution in order to remove hemicelluloses, as specified in ASTM Standard Test D1103-55T. Hemicellulose content was calculated as the difference between the value of holocellulose and α-cellulose. Lignin content was determined according to the ASTM Standard Test D1106-56, which is insoluble in sulfuric acid.

2.4 Fourier Transform Infrared Spectroscopy

FTIR spectra of raw EFB and cellulose fibers were obtained by using Spectrum One-Perkin Elmer with software spectrum v5.02. The fibers were crushed into small particles and then blended with potassium bromide (KBr) followed by pressing the mixture into

ultra-thin pellets. In this analysis, ratio of fiber to KBr was approximately 1:99. A total of 100 scans were recorded in the range 370–4000 cm⁻¹ with a resolution of 2 cm⁻¹ for each sample.

2.5 X-ray Diffraction

The XRD patterns for untreated and cellulose fibers were measured using Ni-filter Cu Kα radiation, with a wavelength of 0.1541 nm at 40 kV and 40 mA. Powder samples were scanned in 2θ range varying from 10° to 50°. Equation (1) was used to calculate the crystallinity index of the fibers.

$$\text{Crystallinity index} = \frac{I_{200} - I_{\text{am}}}{I_{200}} \quad (1)$$

where I_{200} is the height of the 200 peak, which represents both crystalline and amorphous material while I_{am} is the lowest height between the 200 and 110 peaks, which represents amorphous material.

2.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out from 50 to 900°C at a heating rate of 10°C/min. Approximately 10 to 20 mg of each sample was heated under a nitrogen atmosphere with a gas flow of 20 mL/min in order to prevent any thermoxidative degradation

3.0 RESULTS AND DISCUSSION

3.1 Chemical Composition

The content of the three major components, which is α-cellulose, hemicelluloses and lignin, of the EFB fiber with and without using ionic liquid is summarized in Table 1.

From the data taken, it was found that the yield of extracted α-cellulose obtained from raw EFB fiber with ionic liquid was higher than those obtained without using ionic liquid. Moreover, it can be seen that the percentage of hemicelluloses after unmodified alkaline treatment was recorded to be around 5.23%. When the fibers were subjected first to ionic liquid followed by alkaline treatment, the hemicelluloses percentage of fibers decreased to 5%. The same trend can be observed for the percentage of lignin, whereby the lignin content decreases from 2.15% to 1.84% for unmodified and modified alkaline treatment, respectively.

Table 1 Chemical composition of the EFB fiber with and without using ionic liquid

Materials	α-Cellulose (%)	Hemicellulose (%)	Lignin (%)
Without ionic liquid	92.30	5.23	2.15
With ionic liquid	93.01	5.00	1.84

The decrease in the percentage of lignin and hemicellulose was a result of the swelling of the cell wall during alkaline treatment which causes the cementing materials gets dissolved. Another possible explanation for this decrease in lignin and hemicellulose percentage is the disruption of the hydrogen bonding in the network structure by sodium hydroxide solution. Meanwhile,

the dissolution of fibers in (Bmim)Cl led to a destruction of complex network of lignin and the following alkaline treatment had a contribution to the swelling of cellulose and thus, enhance the removal of lignin and expose more hemicelluloses to solvent.

3.2 Fourier Transform Infrared Spectroscopy

The FTIR spectra spectroscopy is an indispensable technique for tracking changes in the chemical structures of the fibers after the

various treatments which they received. The FTIR spectra of the untreated and cellulose fibers are shown in Figure 1.

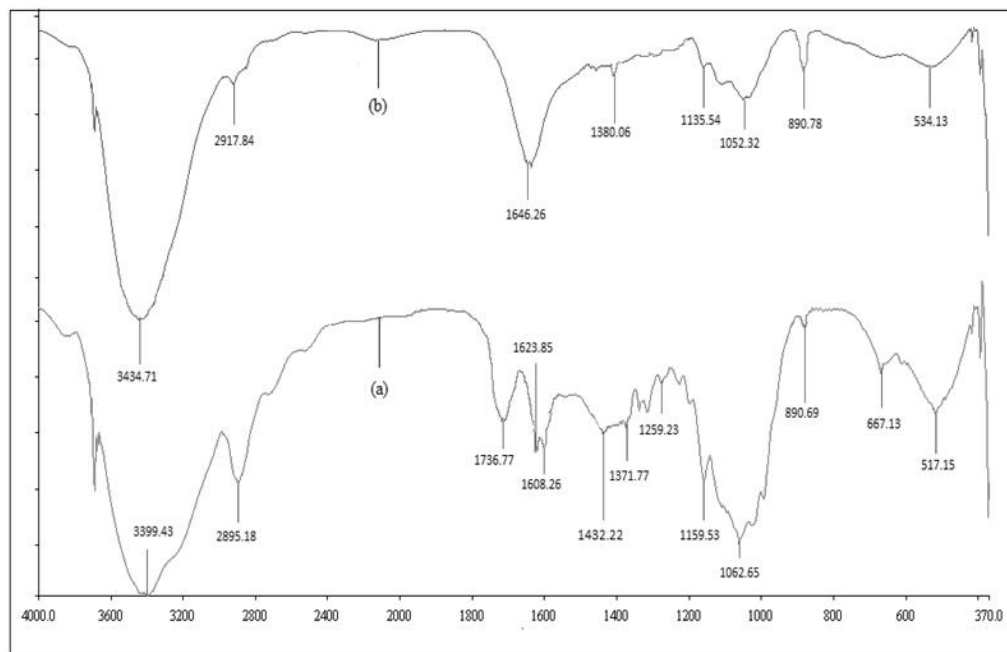


Figure 1 FTIR spectra of (a) untreated fiber, and (b) cellulose

As shown in Figure 1, all samples presented two main regions of absorbance. The first one at low wavelengths corresponding to the range 500–1750 cm^{-1} , and the second one at higher wavelengths in the range 2800–3500 cm^{-1} , in agreement with the report by Moran⁵. The absorption peak located in the range 3300–3450 cm^{-1} and 2890–2900 cm^{-1} in all samples are attributed to the hydroxyl group and aliphatic saturated C–H stretching vibration, respectively [5–7]. The peaks appearing from 1330 to 1360 cm^{-1} is due to the bending vibration of the C–H and C–O groups in the polysaccharide aromatic rings in cellulose, hemicelluloses and lignin [8]. Meanwhile, stretching of C–O and O–H was reflected by peaks appearing in the region 1050–1070 cm^{-1} and the peak at 1055 cm^{-1} arises could be due to the C–O–C pyranose ring stretching vibration in all samples [9–10].

Stretching vibrations of C=C bonds in the lignin are found in the 1608–1623 cm^{-1} , whereby the peak at 1623 cm^{-1} is caused by vibrations of C=C bonds in the benzene stretching ring. Meanwhile, the vibration of the aromatic rings can be seen at 1608 cm^{-1} in the spectra of the untreated fiber, which is attributed to the C=C stretching of the carboxyl groups [9]. In addition, lignin presented characteristic peak at 1432 cm^{-1} due to the presence of methoxy–O–CH₃ while the vibration peak at 1259 cm^{-1} has been related to the C–O–C stretching of the aryl-alkyl ether [11]. Disappearance of all these peaks from the spectra of the treated fibers can be ascribed to treatment of the EFB fibers with sodium chlorite followed by sodium hydroxide as these treatments are known to remove most of the lignin from the EFB fibers.

Furthermore, the most noticeable difference between spectra of the untreated fiber and those of the chemically treated ones is disappearance of the vibration peak observed at 1736 cm^{-1} from the spectra of the alkali treated fibers. This peak is also absent in the sulfuric acid hydrolyzed cellulose. The peak observed at 1736 cm^{-1} in the spectra of the untreated fibers is likely to be associated

to the C=O stretching in the acetyl and uronic ester groups of hemicelluloses or the ester carbonyl groups in the *p*-coumaric units of the lignin. Another possibility is that carboxyl or aldehyde absorption could be arising from the opened terminal glycopyranose rings or oxidation of the C–OH groups [12–13]. This peak has disappeared from the spectra of cellulose fibers and it is believed to be due to removal of hemicellulose by the bleaching and alkali treatment.

By comparing the spectra of the untreated and treated EFB fibers, the peak present at 1646 cm^{-1} corresponding to the treated fibers are related to the absorption of water by cellulose. Appearance of this peak in the spectra of the cellulose fibers are probably due to reaction of sodium hydroxide with the hydroxyl groups of celluloses and subsequent formation of water molecules [8]. As pointed out by Abraham [14], even though the treated fibers were subjected to the drying process, the water adsorbed in the cellulose molecules is very difficult to extract due to the cellulose–water interaction.

From the FTIR analysis, it has been concluded that almost all the lignin and hemicelluloses were removed after the process of bleaching and alkali treatment. This arises from the absence of the absorption bands in between 1500–1600 cm^{-1} and 1730–1740 cm^{-1} , which is related to the lignin and hemicelluloses components, respectively.

3.3 X-ray Diffraction

The X-ray diffraction patterns of the untreated EFB fiber and cellulose are shown in Figure 2.

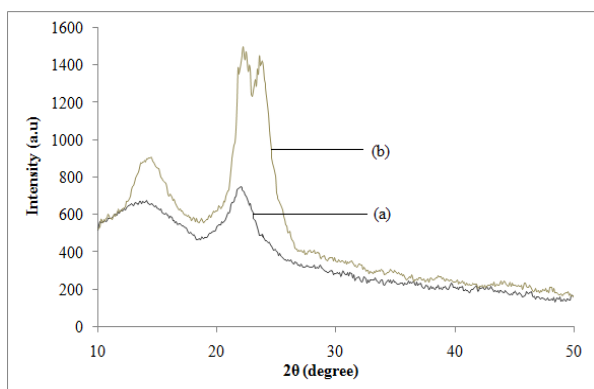


Figure 2 X-ray diffraction patterns for (a) untreated fiber; and (b) cellulose

It can be noted from Figure 2 that all samples had diffraction peaks at around $2\theta=22^\circ$ and $2\theta=18^\circ$, representing the presence of crystalline and amorphous cellulose structure, respectively. The crystallinity index of untreated EFB fiber (calculated by Segal formula) was approximately 38% while that of cellulose fiber was estimated 63%. For comparison, the crystallinity index of cellulose from EFB fiber in previously published studies was found to be around 61% [13] and 55% [15]. Therefore, it can be concluded that the bleaching process with sodium chlorite followed by treatment with sodium hydroxide, as employed in this study, is suitable in order to obtain cellulose fibers with high crystallinity. In addition, the crystallinity of cellulose obtained was higher than that of the untreated fiber can be explained due to the high removal efficiency of non-cellulosic components from the fibers, which are generally amorphous [13-14].

Generally, cellulose in natural fibers comes in four types of cellulose that are classified as type I, II, III and IV. It is interesting to note that the untreated EFB fiber shows typical cellulose I structure, based on the fact that there is no doublet in the main peak at $2\theta=22^\circ$ [16-17]. After treating the EFB fiber with sodium hydroxide, the crystalline peak appears as a doublet at $2\theta=22^\circ$ and $2\theta=23^\circ$, representing transformation of native cellulose from cellulose I to cellulose II. A significant variation in diffraction pattern of untreated and cellulose fibers can be explained by the replacement of OH groups by ONa groups during alkaline treatment. Subsequent rinsing with water will remove the linked Na-ions and thus causing the cellulose to be converted to a new crystalline structure, which is cellulose II [18].

3.4 Thermogravimetric Analysis

The decomposition of hemicelluloses, lignin and cellulose at different temperature are strongly influenced by the differences in their chemical structures. According to Lee [19], thermal degradation of lignocellulosic materials starts with an early decomposition of hemicelluloses, followed by the early pyrolysis of lignin, depolymerization of cellulose, active flaming combustion and char oxidation. The thermogravimetric (TG) curves of the EFB fibers before and after treatments are shown in Figure 3.

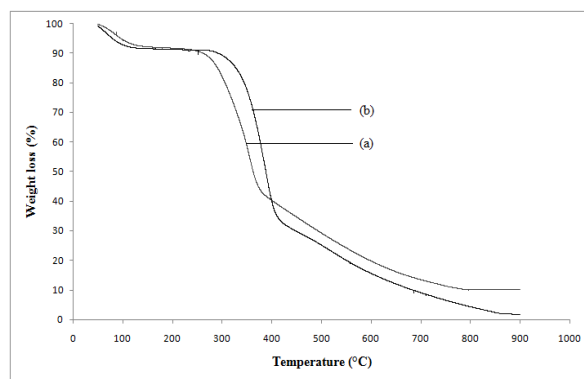


Figure 3 Thermogravimetric curves of (a) untreated fiber; and (b) cellulose

As seen in Figure 3, all the TG curves showed the small weight loss from 50 to 100°C corresponding to the mass loss of water or low molecular weight compound remaining from the isolation procedures [5]. The figure also showed that the raw EFB fiber started to degrade at around 240°C due to the early decomposition of hemicelluloses. Meanwhile, the onset of the thermal degradation of cellulose fiber occurs at a higher temperature than raw fiber, which is around 320°C. This trend of rise in decomposition temperature can be explained due to removal of hemicelluloses, pectin and lignin in the cellulose obtained after the chemical treatments.

The main thermal decomposition step for the untreated EFB fiber and alkali treated fiber occurs at 370 and 390°C, respectively, corresponding to the decomposition of cellulose. This is due to the fact that the decomposition of cellulose is mainly occurring in the range of 315 to 400°C [20]. As a final remark, it can be concluded that the cellulose from EFB fibers which were extracted in this study had better thermal stability than their respective raw EFB fiber.

4.0 CONCLUSION

In this study, cellulose was successfully extracted from EFB fiber, which is an abundant biomass in Malaysia. EFB fiber was firstly treated with alkali and it has been confirmed that NaOH treatment seems to be effective in the removal of lignin and hemicelluloses components. Evidence of non-cellulosic components loss can be observed in the FTIR spectra, whereby there is no main absorption band of lignin and hemicelluloses at 1500–1600 cm^{-1} and 1730–1740 cm^{-1} after treating with NaOH. Alkali treatment of the fiber make cell wall swells in order to enable chemical molecules to penetrate through the crystalline region of the cellulose, thereby causing the cementing substances like lignin and hemicelluloses to be removed. On the other hand, the XRD analysis, the crystallinity index of the fiber increases after treatment. The crystallinity index of the raw EFB fiber was 38%. After alkali treatment, the crystallinity index of the cellulose increased to 63% due to the removal of most non-cellulosic components. Based on the results of the TG curves, the main thermal decomposition step for the untreated EFB fiber and alkali treated fiber occurs at 370 and 390°C, respectively. Therefore, cellulose had better thermal stability than their respective raw EFB fiber. In conclusion, it can be concluded that the chemical treatments used in this study can achieve improvement in the properties of cellulose, compared to that observed in previous studies.

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