Microfibrillated cellulose (MFC) isolation based on stalk sweet sorghum through alkalinization-bleaching treatment: effect of soaking temperature

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Microfibrillated cellulose (MFC) isolation based on stalk sweet sorghum through alkalinization-bleaching treatment: effect of soaking temperature

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Abstract. In the current research, the effect of soaking temperature in sequence of chemical modification on the characterization of micro fibrillated cellulose (MFC) from stalk sweet sorghum waste fibres was carried out. Chemical treatment sequences through alkalization followed by bleaching treatment. The treatment was objected to unbundle the lignocellulose networks into MFC with less amorphous part and higher of crystallinity. Evaluation of the soaking temperature effect on crystallinity index of sorghum fibres was measured with X-ray diffraction (XRD) and supported by morphological image from field-emission scanning electron microscope (FE-SEM) and chemical characterization from Fourier transformation infra-red (FTIR) Spectroscopy. The experiments showed that production MFC from stalk sweet sorghum waste with alkaline-bleach treatment was successfully carried out and enhanced crystallinity index from 41% to 77.55% due to removal of amorphous part include hemicellulose and lignin.
Keywords: micro-fibrillated cellulose (MFC); sorghum waste; chemical treatments; crystallinity index; FE-SEM; FTIR

1. Introduction

Natural fibres lignocellulose such as sugarcane, coconut, rice husk, pineapple, bamboo, "ijuk" and bagasse are consisting of three main organic compounds of cellulose, hemicellulose, and lignin. The main constituent that responsible to strength and stability of the plant cell wall is cellulose, resource derived from plant stalk, trees and agricultural waste, that higher potential to be used as substitution of glass fibres or other synthetic reinforcing fibres in polymer composite materials. Besides that, this material has high specific properties such as stiffness, impact resistance, flexibility, and modulus. Cellulose is also available in abundant quantities in nature, renewable and recyclable caused it is friendly to the environment. Other properties possessed by cellulose from natural fibres lignocellulose are cheap, light, abrasion to low-process equipment, low skin and respiratory risks, dampening vibrations, and increasing recovering energy [1-4].

Cellulose is a long chain carbohydrate compound composed of D-glucopyranose units linked by β-1,4-glycosidic bonds with semi-crystalline structures and it is combined with other substance in plants [5]. Therefore, to utilize it they must first be separated, one of the methods is through chemical treatment.

Some of the preliminary researched according to isolation of micro-fibril cellulose from plant fibres through chemical treatment methods have been done in our research group. From these studies it was found that chemical methods through the alkalinisation, bleaching, acetylation and acid hydrolysis treatments could increase the crystallinity index of cellulose natural fibres and change fibrillated fibres into micro-fibrils cellulose [6-9].

One of the potential natural ingredients which are currently being developed in Indonesia is sorghum [10]. It is the fifth largest tropical and subtropical food crop produced in the world after wheat, rice, corn, and barley. Currently sorghum is widely researched to increase cellulose content that will be used as raw material for bioethanol which produced from juice extraction process containing cellulose (40-44%), hemicellulose (27-35%), and lignin and waste will remain. There are some researchers that have found the potential of sorghum fibres as a reinforcing material candidate in the matrix of thermoplastic and bio-polymeric polymers [11-14].

Alkalinisation is widely method used by researchers in the stage of cellulose isolation from plants by dissolving hemicellulose, pectin, waxes, minerals and a little lignin [15-18]. Besides being used in the isolation stage, alkalinisation can also be carried out on cellulose to make the fibre surface coarser and to increase mechanical interlocking when the fibre is combined with the thermoplastic polymer into a composite [19]. Bleaching is a process of dissolving the lignin of fibres so that increasing the brightness level of the resulting fibre [20]. Actually this bleaching emphasizes the removal of lignin content in fibre without damaging the cellulose present in the fibre [9, 21].

In this study, our objective is to prepare cellulose from sorghum by alkalinisation followed by bleaching treatment with two variables of soaking temperature and to investigate their composition, morphology and crystallinity. Variations were made to find the treatment series for cellulosic fibre isolation that was considered the most optimal in terms of these properties.

2. Material and Methods

2.1. Material

Stalk sweet sorghum fibre waste was obtained from the research institute of BIOTROP Bogor, West Java. Chemicals are sodium hydroxide in pellet form, acetic acid solution and sodium chlorite purchased from Merck.

2.2. Methods

The experiment was started by cutting the stalk sweet sorghum fibre waste by using the Crushing machine and followed by filtering process with a 40 mesh sieve size. A total of 7 grams of sorghum stalk sweet sorghum waste was passed from the filtration process were subsequently dissolved in an alkalinisation solution with 10% wt. NaOH for 2 h at 70°C and followed by bleaching process in a 100 mL solution of 1.7% $NaClO_2$ which added 50 mL of buffer (100 mL CH_3COOH 0.2 M and 0.291 gram NaOH) for 4 hours with temperature variation 50°C and 90°C. Table 1 summarized of chemical treatment which carried out in this study. After each cycle of the treatment, samples were washed with deionized water until reached neutral pH, filtered and agitated condition.

Table 1. Experiment conditions for sorghum fibres preparation.

Sample code	Sequence of experiments
SV	Untreated sorghum
AB1	10 wt. % NaOH 2 h; 70°C→ bleaching (50 mL Buffer (100 mL CH_3COOH 0.2 M+0.291 g NaOH)+100 mL 1.7% $NaClO_2$; 4 hour; 50°C.
AB2	10 wt. % NaOH 2 h; 70°C→ bleaching (50 mL Buffer (100 mL CH_3COOH 0.2 M+0.291 g NaOH)+100 mL 1.7% $NaClO_2$; 4 hour; 90°C.

Samples of stalk sweet sorghum waste resulted from treated and untreated chemical treatment process was characterized using FE-SEM (FEI INSPECT F50), XRD (Philip Analytical PW3710) and

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spectroscopy (Perkin Elmer Spectrum-ASTM E 1252). FE-SEM was used to obtain surface morphology from treated and untreated chemical treatment. The scanning images were obtained with an acceleration voltage of 20.00 KV and 1000× magnification. While the Perkin Elmer Spectrum FTIR and XRD instruments were used to obtain the FTIR spectrum and crystallinity index of treated and untreated of stalk sweet sorghum waste.

3. Result and Discussion

3.1. Analysis of compound composition

Fig. 1a-c illustrate the FTIR spectra of SV as an untreated sorghum and both AB1 and AB2 as treated sorghum fibres, recorded as the transmittance (%) versus wave number in the range of 4000–500 cm^{-1}. The spectrum of SV fibres (Fig. 1a) shows several important peaks in range 3200–3600 cm^{-1}, which corresponds to the OH- bonding stretching vibration, at 2900 cm^{-1} is related to C–H stretching in hemicellulose and cellulose and at 1734,1640 and 1514 cm^{-1} is due to carbonyl stretching of carboxylic groups in hemicelluloses-pectin. The peaks appeared at 896 cm^{-1} may correspond to β-glucosidic linkages between the sugar units in hemicellulose and cellulose [9, 22].

According to the spectrum of treated sorghum with alkalinisation-bleaching treatment (Fig. 1b and 1c) the –OH concentration are reduced and hemicellulose and cellulose content with decreased intensity at 3200–3600 cm^{-1} and 2900 cm^{-1}, respectively. Furthermore, the peaks at 1734, 1648 and 1514 cm^{-1} were disappeared that indicates loss of lignin and hemicellulose content in sorghum fibre. The disappearance of the 1734, 1648 and 1514 cm^{-1} peak after alkaline-bleach treatment indicate that oxidation by ClO^{2-} which destroyed the lignin aromatic chain and increases the brightness of the fibre. This is in line with the SEM image of Fig. 3, which implies that the binding materials on unbundle fibre of untreated stalk sweet sorghum waste were removed by alkaline-bleach treatment and its surface appearance is getting brighter. On the other hand, the peaks at 896 cm^{-1} also disappeared. This indicate that the treatment causes decreased cellulose content. This may be due to the degradation of cellulose by sodium chlorate solution. Cellulose which is most likely to be degraded is amorphous cellulose because it has a lower chemical resistance.

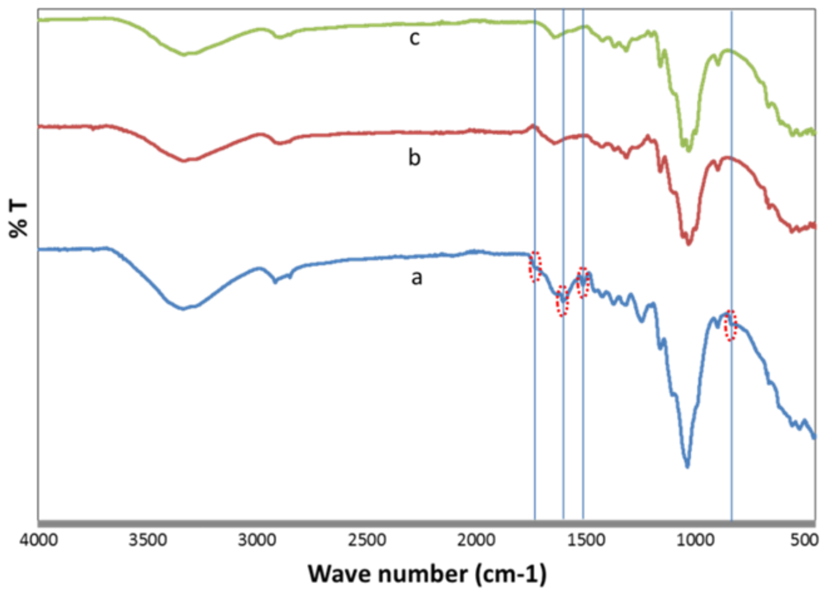

Figure 1. FT-IR spectra of stalk sweet sorghum waste fibre; a) SV, b) AB1, and c) AB2.

Other than that, Fig. 1b and 1c shows the effect of soaking temperature of bleaching treatment after alkalization process. The figure implies near identical FT-IR spectra and the higher the soaking temperature causes cellulose to degrade. This result was supported by XRD observation.

3.2. Analysis of Crystallinity Index (CI)

Plant fibre consists of hemicellulose and lignin which have amorphous structure and cellulose that have semi crystalline structure. The crystallinity of cellulose was an important characteristic since the crystallinity correlates with fibre strength and stiffness. Fig. 2 shows the comparison of XRD diffractograms of untreated and alkali-bleach with variation soaking temperature treatment stalk sweet sorghum waste fibre. As seen in Fig. 2, the pattern treated fibres implies four peaks at 15.62, 22.04, 30.56 and 34.28°. The 15.62° reflections correspond to the (10$\bar{1}$) crystallographic planes. The other peaks at 22.04 and 30.56° correspond to the (002) and (004) planes, respectively. The (002) reflection is the major crystalline peak of cellulose I [23].

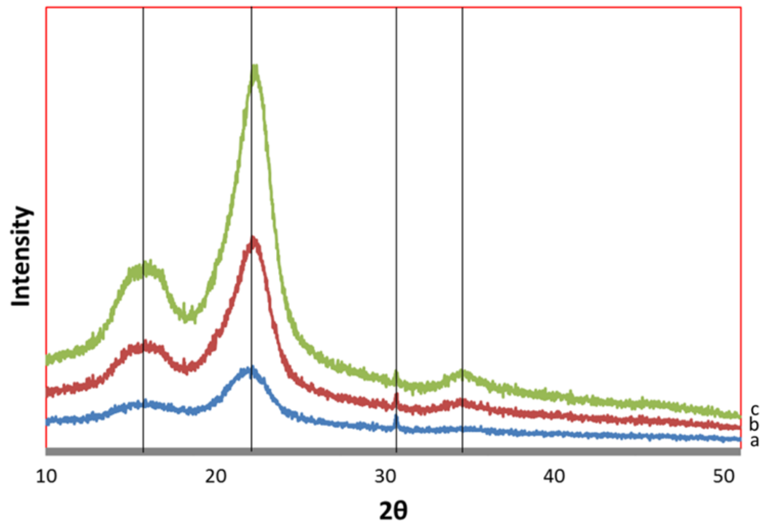

Figure 2. XRD diffractograms of stalk sweet sorghum waste fibre bundles; a) SV, b) AB1, and c) AB2.

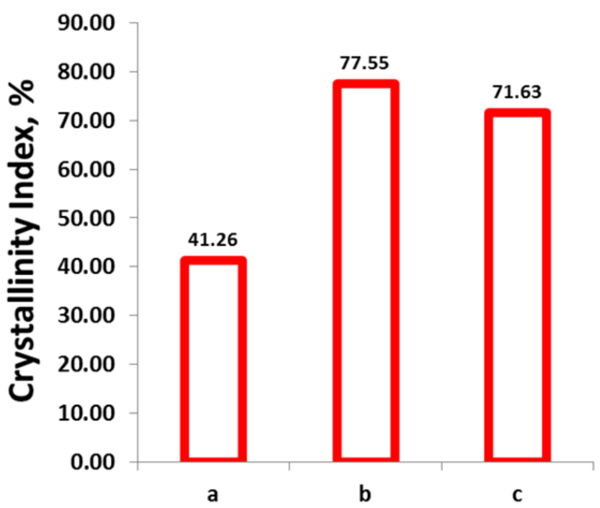

Figure 3. Crystallinity index of untreated and alkali-bleach treatments of sorghum fibres: a) SV, b) AB1, and c) AB2.

The peak at 22.04° which resulted from alkali-bleach treatment became sharper than the untreated fibre. These assume that its treatments enhancement the fraction cellulose crystallinity by removing some part of amorphous component, such as lignin, hemicellulose and pectin. Crystallinity index value of untreated and treated sorghum fibres was measured by Segal *et al.* [24] equation (1):

$$CI(\%) = \frac{I(002) - I(amp)}{I(002)} = 100 \quad (1)$$

Where I(002) is the maximum of the lattice diffraction peak for plane (002) which is lie at a diffraction angle around 2θ=22° and the lowest of the intensity scattered by the amorphous part is measured at the diffraction angle around 2θ=18°.

The calculation results of crystallinity index for each sample are shown in Fig. 3. The degree of crystallinity index increased after sorghum fibres was treated with alkali-bleach. Interestingly, increasing on soaking temperature treatment caused decreased of degree of crystallinity index. This is caused by the higher temperatures lead to excessive oxidation reactions that influence the cellulose fibre content [21].

3.3. Analysis of Surface morphology
Morphologies of untreated and treated stalk sweet sorghum through alkali-bleach at soaking temperature 50°C has been observed under scanning electron microscope as shown in Fig. 4. Fig. 4 (a) represent surface of an untreated stalk sweet sorghum waste fibre (SV) directly after fibre was crushing using crushing machine. The fibre was still a bundle and it's covered with non-cellulosic gummy contents namely wax and pectin, rough surface and the diameter more than 100µm. This may occur as a result of the process of crushing sorghum into fine fibres.

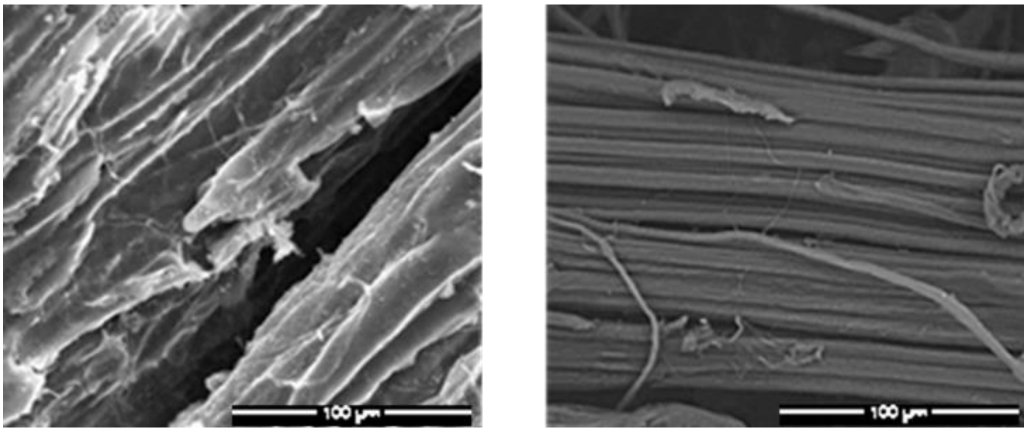

Figure 4. FE-SEM morphology of stalk sweet sorghum waste fibre; a) SV, and b) AB1.

Fig. 4 (b) shows a surface treated stalk sweet sorghum waste fibre through alkali-bleach at soaking temperature 50°C with higher crystallinity index as shown in Fig. 3. It is showed that the surface of the fibres was becomes smoother, brighten and become unbundle fibre as compared to the untreated fibres. This indicates that the alkali-bleach treatment at soaking temperature 50°C can remove the wax and impurities part on the surface of fibre. Loss of binder materials on surface untreated sorghum after treatment caused the fibre become unbundle or fibrillation. This result was in line with FTIR characterization. The treatments resulted micro fibril cellulose with diameter size of separate fibres was around 6 µm.

4. Conclusion
The effect alkali-bleach treatment and soaking temperature of bleaching on crystallinity of stalk sweet sorghum waste fibres has been investigated. The chemical isolation method through alkalization

followed by bleaching treatment has successfully obtained micro fibril cellulose from stalk sweet sorghum waste fibres. In the bleaching process, higher of soaking temperature treatment, crystallinity index which is obtained will be lower due to the excess oxidation reaction to cellulose.

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