Preparation of micro-fibrillated cellulose from sorghum fibre through alkalization and acetylation treatments

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Abstract. Recently, the pollution due to non-degradable materials including plastics, has led to needs on the development of environmental-friendly material. Owing to its biodegradability nature, sorghum fibres are interesting to be modified with petro-polymer as a composite. These materials are also expected to reduce the impact of environmental pollution. Surface modification of sorghum through chemical treatment was aimed to enhanced crystalline part of micro-fibrillated cellulose, thus increased compatibility to petro-polymer, as mean to improve composite properties. The experiments were conducted by alkalization process (10% NaOH) followed by acetylation with acetic acid glacial and acetic anhydride $(CH_3CO_2)_2$ with additions of 1 and 2 drops of 25% H_2SO_4. Fourier transform infra-red (FTIR) spectroscopy, field-emission scanning electron microscope (FE-SEM) and x-ray diffraction (XRD) were used to characterize the treated and untreated fibres. The results of investigation showed that the chemical treatments have effectively produced MFC with the smallest fibre size around 5.5 – 6.5 microns and reduced lignin and hemicellulose where the highest crystalline part up to 80.64% was obtained through acetate acid treatment of 17.4 M, followed acetic anhydride with 1 drop of H_2SO_4 addition. Based on the current results, it is promising that the synthesized composites can be improved for their compatibilities.

1. Introduction

Cellulose, available on earth, is the most abundant natural polymer that renewable, biodegradable in nature, has a lower density than synthetic filler and inexpensive so hence it is considered an alternate to non-degradable fossil-based polymers. In the most recent decades, several examinations have spent their considerations on how to obtain scale micro fibrillated cellulose (MFC) from natural fibres. This objective has been driven by finding suitable uses of MFC in material designing. The inherent stiffness and high level of crystallinity make it preferably suited for strengthening and load bearing application in composite [1-3].

Sorghum is an ancient, old world cereal that was domesticated in Africa, became an important food crop and ranked after wheat, rice, corn, and barley, and it is cultivated in many countries [4]. One of the distinctive properties of sorghum is its resistance to drought and tolerance to water logging. Sorghum also has a great potential to be developed in Indonesia because of its natural adaptation. It

can be used as industrial raw materials such as sugar ants, amino acids, starch, etc., or fuel as bioethanol, and animal feed [5].

Previous studies have proposed that natural fibres like flax, hemp, jute and sisal can provide great potential as reinforcements in composite materials [6]. In 2015, E Yuanita *et al*., (2015) [7] investigated the preparation of MFC obtained from Arenga Pinata or "ijuk". Another research, in the same years, reported that sorghum has higher cellulose and lowest lignin contents compared to the other agro-waste materials such as bagasse and rice straw [8]. Based on the result investigations be related to sorghum , which might a chance to be candidate as source to obtain MFC as reinforcing fibres in polymer composite.

Among all techniques preparation of MFC, chemical treatments such as alkalization and acetylation are known as simple and cheap methods. The alkalization using sodium hydroxide solution is aimed at reducing the impurities on the surface of the fibre including lignin, wax oils, and hydrophilic functional group (-OH), in order to increase fibre resistance to water. On the other hand, the acetylation or esterification using a solution containing acetyl functional group (CH_3CO^-) aims to reduce the hygroscopic properties of natural fibres and to increase the dimensional stability of the fibre with the result that expectable increasing compatibility in the composite [9].

The solid waste from sorghum extraction process is abundant; however its usage for reinforcing material is still limited. Therefore, the current research is focused on obtaining micro-fibrillation cellulose fibres from sorghum to be used further as bio-composites. More specifically, the investigation aims to determine the effect of alkalization followed by acetylation on several properties of the fibres, such as sorghum bicolor fibres, compound composition, morphology, size and the crystallinity of the fibre.

2. Materials and Methods

2.1. Materials

Sorghum waste was obtained provided from a traditional market. Sorghum fibre was dried in room temperature (25°C) for 3 days. The dried sweet sorghum were cut into ± 5 cm and crushed to pass a 40 mesh. Sodium hydroxide in pellets form, acetic acid, acetic anhydride and sulfuric acid solution was purchased from Merck.

2.2. MFC preparation

The alkalization samples were prepared by soaking 7 g of size reduced sorghum fibre in 50 mL of 10 % sodium hydroxide agent solution with continuous agitation. The mixture was kept at 80°C for 1 h. Acetylation treatment was carried out after alkalization by soaking in 50 mL of 17.4 M acetic acid

in agitated condition at 25°C for 1 h. Sample from acetylation treatment was filtered and soaking in 20 mL acetic anhydride solution for 10 min with adding one and two drops of 25% sulfuric acid as a catalyst, and sample AGA2 was followed by soaking in 25% sulfuric acid at room temperature during 2 h. After each cycle of the treatment, sample were washed in three times with tap water and then dried in air at 25°C for 3 days to ensure the wash medium already reached neutral and filtered. Aside from hydrolysis, the sample was soaking in water distillation while 1 h for left out acid concentration which still adhere. The experiment procedure in this work is summarized in Table 1.

Table 1. Summarized of step experiment and sample code sweet sorghum fibres preparation.

Sample code	Alkalization	Acetylation	
SV	Un-treated		
AGA1			$(CH_3CO_2)_2O$ + 1 drop H_2SO_4 25 %;10 min;25°C
AGA2	10 % NaOH; 1 hour;80°C	CH_3COOH 17,4 M;1 hour;25°C	$(CH_3CO_2)_2O$ + 2 drop H_2SO_4 25 %;10 min;25°C
AGA2H			$(CH_3CO_2)_2O$ + 2 drop H_2SO_4 25 %;10 min;25°C + hydrolysis 2 h;25°C

Note: SV: Sorghum Virgin; AGA: Acetic Glacial Anhydride; H: Hydrolysis

2.3. MFC characterization

The characterizations were carried out in the Universitas Indonesia, Department of Metallurgy and Materials Engineering's, using Spectrum Two™ Infrared Spectrometer Perkin Elmer (ASTM E 1252) was used to determine composition of untreated and treated sorghum with chemical treatment. The morphologies of used untreated and treated sorghum fibres were analyzed using Field-Emission Scanning Electron Microscope (FE-SEM) FEI Inspect F50 with gold using a vacuum sputter coater. An X-Ray Diffraction (Shimadzu XRD-700 X-Ray Diffractometer) was used to study crystallinity of untreated and treated sorghum fibres. Crystalline parts of the fibres were determined based on reflected intensity data from method of Segal *et al* [10]:

$$Cr.I = \frac{(I_{002} - I_{amp})}{I_{002}} x\ 100 \quad (1)$$

Where I_{002} is the maximum intensity which located at angle around 2θ = 22° and I_{amp} is the intensity scattered by the amorphous part of the sample at the diffraction angle around 2θ =18°.

3. Result and Discussion

3.1. Compound in Un-treated and Treated Sweet Sorghum Fibres

The FTIR spectra of untreated sweet sorghum are presented in Figure 1. As shown in Figure 1, FTIR spectrum of untreated sweet sorghum fibre (SV) shows some peaks. The peaks are 1245, 1510, and 1607 cm^{-1} wavenumbers that indicate the occurrence of phenolic C-O stretch, aromatic rings, and C=C chemical bond of lignin. Peak at 1735 cm^{-1} wavenumber, indicates the occurrence of chemical bonding C=O stretch of hemicellulose and at 3344 cm^{-1} wavenumber indicates the occurrence of chemical bond O-H stretch part of lignin, hemicellulose and cellulose fibres that indicate sorghum fibres hydrophilic properties [11-14].

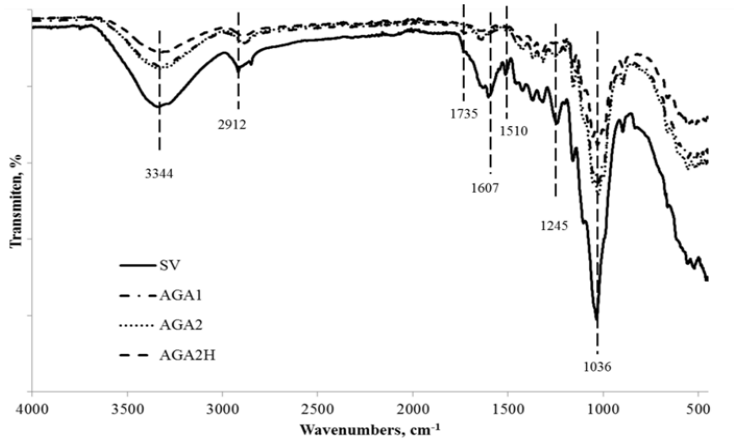


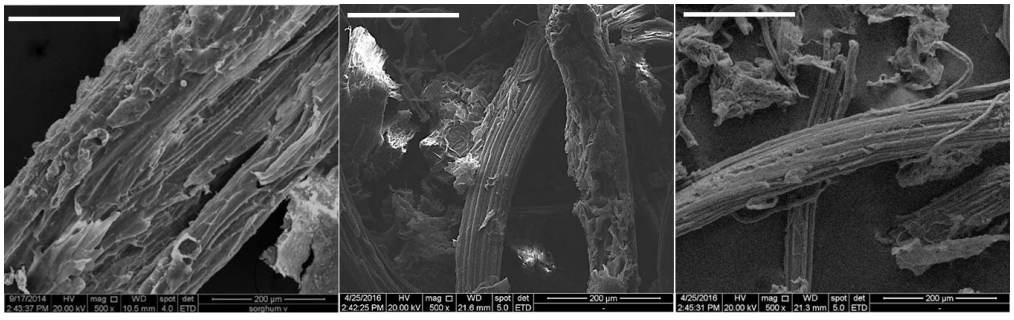
Figure 1. FTIR spectra of untreated sorghum and alkalization-acetylation glacial-anhydride-catalyst –with and without hydrolysis treated sorghum

Figure 1 also shows the treatment of sorghum with alkalization-acetylation and alkalization-acetylation-hydrolysis. The purpose of treatments are removing impurities such as a wax and oil that adhere on the surface of the fibre, as well as number of amorphous fractions (lignin and hemicellulose) in the cell wall of sorghum. Significant change in peak IR-spectra occurred at 1735 cm^{-1}, which is indicates the occurrence of chemical bonding C=O stretch of hemicellulose, disappear after alkalization-acetylation and alkalization-acetylation-hydrolysis treatment. The same occurrence at peak around 1245, 1510, 1610 cm^{-1} which is associated with phenolic C-O stretch, aromatic rings, and C=C chemical bond of lignin, also disappear after alkalization-acetylation-hydrolysis. Another important peak are at 1036, showing a decrease in intensity which is indicate reducing of lignin and hemicellulose after alkalization-acetylation and alkalization-acetylation-hydrolysis.

3.2. Morphology in Untreated and Treated Sweet Sorghum Fibres

Structure of sorghum fibre are constitutes of cellulose microfibrils are binding together with lignin, pectin and hemicellulose, as well as joining adjacent fibres together to form fibre bundles. SEM

evaluation were applied to untreated sorghum fibre and MFC that was obtained from the modification treatments of sorghum fibres are displayed in Figure 2. The micrograph in Figure 2(a) implies the untreated sorghum fibres (SV) are covered with a layers, it is likely that waxy composition substances, evenly that the layers not distributed along the fibres surface but its thickness varies from point to point. The diameter of untreated sorghum fibre around 100µm. on the other hand, alteration in the morphology structure sorghum virgin occurred after preparation with 10 % NaOH solution and 17.4 M acetic acid followed soaking in acetic anhydride with or without hydrolysis solution. It was observed that the treatments removal of the layers on surface fibres as seen in Figure 2 (b) and Figure 2 (c), with the result that, the surface of treated fibres became smoother as compared to that untreated fibres. A loss of the waxy substance on the surface of lignocelluloses materials and substitution of surface hydroxyl groups by acetyl groups could make clear something of the fibre surface after acetylation. It is according with Tserkia *et al.,* (2005) and Zafeiropoulos *et al.,* (2002) that study of the effect of acetylation surface treatments on natural fibres [15,16].



(a) (b) (c)

Figure 2. SEM image of sorghum fibres; (3a) untreated sorghum fibre surface (SV), (3b) alkalization-acetylation glacial anhydride-2 drop catalyst sorghum fibre surface (AGA2) and alkalization-acetylation glacial anhydride-2 drop-hydrolysis (AGA2H). White bar scale represents 200µm.

Figure 2 (b) and 2(c) affirmatively display the fibre became fibrillated after treatments. It is peer that sorghum fibre bundle separate into individual fibres. It was also observed from Figure 2 (c) that hydrolysis with 25 % sulfuric acid during 2 h after acetylation make fibre damage and crack. The diameter of treated sorghum fibres decreased to an average of around 5.5-6.5 µm resulted from acetylation without hydrolysis treatment. It indicated that the waxy which bind the fibril structure were removed after treatment. It was verified also that with removed of shallow layer can improve increased contact area which make more interesting for application as reinforcement in composite materials.

3.3. Crystallinity in Untreated and Treated Sweet Sorghum Fibres

Most of the natural fibre are polymer that having amorphous and crystalline parts, where the lignin and hemicellulose as amorphous and cellulose as semi-crystalline. Only the crystal polymorph I of cellulose was appear in both untreated and treated fibres, as usual for native cellulose [15]. The

XRD pattern of untreated and alkalization-acetylation-hydrolysis sorghum fibres are showed in figure 3. As seen in Figure 3 the pattern treated fibres implies four peaks at 15.1, 22.1, 34.0 and 47.5°. The 15.1° reflections correspond to the $(1\bar{1}0)$ crystallographic planes. The other peaks at 22.1 and 34.0° correspond to the (200) and (023) or (004) planes, respectively [15]. Referred to Segal's empirical equation (1), I_{002} is the maximum of the lattice diffraction peak for plane (002) which is lie at a diffraction angle around $2\theta = 22°$ (for this case the peak is at $2\theta = 22.1°$) and the lowest of the intensity scattered by the amorphous part is measured at the diffraction angle around $2\theta=18°$ (for this case the peak is at $2\theta = 15.1°$) [10, 17]. If the fibre within high amounts of amorphous materials, as in this case of sorghum fibres, such as lignin, hemicellulose, and amorphous cellulose, the peak at around 15°-16° appearing as one broad peak [15].

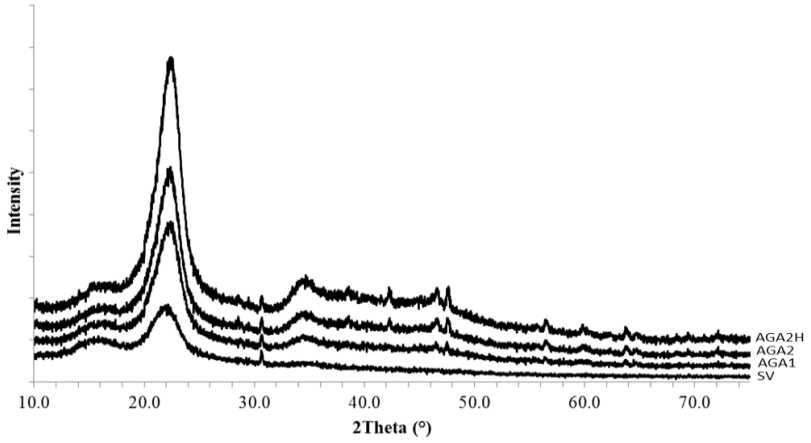


Figure 3. X-ray diffraction patterns of untreated and alkalization-acetylation-hydrolysis sorghum fibres

Table 2 was presenting the calculated results of crystallinity index which extracted from XRD curve for the both untreated and alkalization-acetylation-hydrolysis treatment, based on the equation (1). As seen in Table 2, that the alkalization-acetylation-hydrolysis treatment point out significantly remove the amorphous parts in sorghum fibres and the alkalization-acetylation with acid hydrolysis treatment has the best effectiveness in removing the amorphous part. This result is according with the data obtained from FTIR spectroscopy.

Table 2. Crystallinity Index of untreated and chemical treated sorghum

	SV	AGA1	AGA2	AGA2H
Crystallinity Index (%)	41.12	80.64	76.18	82.61

4. Conclussion

This study has effectively acquired micro-fibrillated cellulose from sorghum as a matter of fact potential source which is large in number in nature. The MFC was set up by alkalization and acetylation. The both modification treatments demonstrated that the chemical treatments have adequately diminished lignin and hemicellulose where the most astounding crystallinity up to 82.6% was acquired through alkalinization and acetate acid treatment of 17.4 M acetic anhydride with 2 drop of H_2SO_4 addition followed by 25 % sulfuric acid hydrolysis and the treatments result MFC with the lowest fibre sized around 5.5-6.5 µm. In view of the present results, it is promising that the integrated composites can be enhanced for their compatibilities.

References

[1] Lavoine N *et al* 2012 *Carbohydr. Polym.* **90** 735-764.
[2] Bhattacharya D *et al* 2008 *Carbohydr. Polym.* **73**, 371-377.
[3] George J, Sabapathi SN 2015 *Nanotechnol. Sci. and Appl.* **8** 45-54.
[4] Dahlberg J *et al* *Maydica* **56** 1750.
[5] Bambang I, Nana S 2011 *Forum Penelitian Argo Ekonomi* **29** (2) 99-113.
[6] Bakker B *et al* 2013 *Eng. J.* **4** 265.
[7] Yuanita E *et al* 2015 *Procedia Chemistry* **16** 608-615.
[8] Kumar A *et al* 2014 *Mat. Phys. and Chem.* **2** (1) 1-8.
[9] Xue L *et al* 2007 *J. Polym. Environ.* **15** 25-33.
[10] Segal L *et al* 1962 *Text Res. J* **29** 786-794.
[11] Yan Z *et al* *Fuel* **158** 152-158.
[12] Ridzuan M J *et al* 2016 *Mater. and Design* **89** 839-847.
[13] Kabir M M *et al* Cordana F 2013 *Appl. Surface Sci.* **276** 13-23.
[14] Bledzki A K *et al* 2008 *Express Polym. Let.* **2**(6) 413-422.
[15] Tserki V *et al* 2005 *Composites Part A* **36** 1110–1118
[16] Zafeiropoulos N E *et al* 2002 *Composites Part A* **33** 1083.
[17] Uma C *et al* 2012 *Biomat. Bioener.* **46** 555-563