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Preparation of micro-fibrillated cellulose based on sugar palm ijuk (*Arenga pinnata)* fibres through partial acid hydrolysis

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Abstract. The aim of this study was to isolate and characterized micro-fibrillated cellulose (MFC) from sugar palm/ijuk fibre (*Arenga pinnata*) by partial sulfuric acid hydrolysis. Cellulose fibre was prepared by repeated treatments with 5 wt% sodium hydroxide 2 h at 80 ^{o}C, followed by bleaching with 1.7 wt% sodium chlorite for 2 h at 80^{o}C in acidic environment under stirring. MFC was prepared by partial hydrolysis with sulfuric acid in various concentrations (30, 40, 50, and 60 % for 45 min at 45 ^{o}C) under stirring. Fourier Transform Infrared, Field Emission Scanning Electron Microscope, Thermo Gravimetric Analyzer and X-ray Diffraction characterized cellulose fibre and MFC. FTIR measurements showed that alkaline and bleaching treatments were effective to remove non-cellulosic constituents such as wax, lignin and hemicellulose. FESEM observation revealed conversion into more clear surface and defibrillation of cellulosic fibre after pre-treatments. XRD measurement revealed increase in crystallinity after pre-treatments and acid hydrolysis from 54.4 to 87.8%. Thermal analysis showed that increasing acid concentration reduced thermal stability.

1. Introduction

Cellulose is the main constituent component responsible for the strength and stability of the plant cell wall. Cellulose has a linier chain of ringed glucose molecules created by repeating link of β-D-glucose [1]. This is confirmed by presence of hydroxyl groups (-OH) are participated the formation of strong inter- and intra-molecular bond [2, 3]. Cellulose has a wide range of potential application due to, low cost, renewable and biodegradability. It can be used as, reinforcing agent, biomaterials (drug delivery), energy harvesters, energy storage, and nanostructure via templating with nanocellulose [4-8]. Since cellulose has such big potential applications, several developmental efforts to convert cellulose into various forms such as microfibrillated cellulose (MFC), microcrystalline cellulose (MCC), nanofibrillated cellulose (NFC), and nanocrystalline cellulose (NCC) is still being conducted. There are two routes for conversion of cellulose into micro/nanocellulose, chemical route and mechanical route. Since the energy consumption of the mechanical route is rather high, chemical route seem a promising research topic [9].

Sugarcane, coconut, rice husk, pineapple, bamboo and bagasse are mostly used resource in Indonesia. Widely applied in Indonesia is also a kind of natural fibres isolated form sugar palm fibre *(Arenga pinnata)* or locally knows as ijuk. Ijuk fibres can be used as a broom, binders, filters and

rooftop. Ishak *et al.,* (2013), previously reported chemical and physical properties of ijuk fibre [10]. Mechanical properties were also reported such as; tensile strength (276.6 MPa), tensile modulus (5.9 GPa), and elongation (22.3 %) [10]. With superior mechanical properties, sugar palm fibre is expected to replace the use of synthetic fibres. Sahari *et al.,* (2013) made bio-composite of the sugar palm fibre reinforced with starch [11]. Bachtiar *et al.,* (2008) also reported effect of alkalinisation on mechanical properties sugar palm fibre reinforced epoxy [12]. Chalid *et al.,* (2015) reported that sugar palm fibre could be reinforced on PLA and act as a nucleating agent of for making polypropylene composite [2,13,14]. However, effects of partial acid treatment on cellulose ijuk fibre have not been exploited before. The aims of this paper are to analyse the effect of chemical treatment (pre-treatment and various concentration acid hydrolysis treatments) on cellulose ijuk fibre followed by characterization of the properties of the isolated MFC.

2. Materials and Methods

2.1. Materials

Ijuk *(Arenga pinnata)* fibre was purchased from PD Markum Jaya, South Tangerang, and Indonesia. Analytical grade sodium hydroxide (NaOH) pellet, 99% acetic Acid (CH_3COOH), 96.1% sulfuric acid (H_2SO_4), 25% sodium chlorite ($NaClO_2$) were purchased from Merck, German.

2.2. Preparation of Micro-Fibrillated Cellulose from Ijuk Fibre

Raw ijuk fibres were previously cut and crushed into small pieces around 30-40 mesh were washed thoroughly with tap water and dried at room temperature for 24 h. The fibres were treated with 5 w% sodium hydroxide solution at 80ºC for 2 h in a solid to liquid ratio of 1:20 (w/v) to remove non-cellulosic components. This alkali treatment was repeated four times. After treatment, alkali-treated ijuk fibres were recovered by filtration and washed with deionized water until neutral pH. Afterwards, ijuk fibres were treated with acidified 1.7 wt % sodium chlorite solution at 80ºC for 2 h in a solid to liquid ratio of 1:20 (w/v). After addition of sodium chlorite for four times, bleached ijuk fibres were recovered as described above. The bleached ijuk fibres were then partially hydrolysed with aqueous sulfuric acid solutions having four different concentrations 30, 40, 50 and 60 w% at 45ºC for 45 min under stirring. Then, each suspensions was diluted for 5 fold with cold water. Materials remained unhydrolyzed were separated by decantation, and pH of the remained suspension was adjusted to 2-3. The samples were filtered; the filtrate was washed with 0.1 M sodium hydroxide until pH reaches 6-7. Samples were dried at 60 ºC for 24 h. The samples abbreviation are presented in Table 1.

Table 1. Samples code

Sample Code	Treatments
Native ijuk	Without chemical treatment
Alkali-treated ijuk	Treated with 5 w% sodium hydroxide for 2 h, 80 ºC, repeated 4x
Bleached ijuk	Treated with 1.7 w% sodium chlorite for 2 h, 80ºC, repeated 4x, pH 4-4.5
Hdr 30	Treated with 30 w% sulfuric acid for 45 min at 45 ºC
Hdr 40	Treated with 40 w% sulfuric acid for 45 min at 45 ºC
Hdr 50	Treated with 50 w% sulfuric acid for 45 min at 45 ºC
Hdr 60	Treated with 60 w% sulfuric acid for 45 min at 45 ºC

2.3. Characterizations

Fourier transform infrared (FTIR) spectroscopy was used for functional group analysis of ijuk fibres. FTIR spectra at 450-4000 were recorded using a PerkinElmer UATR Two. Thermo Gravimetric Analyzer using Perkin Elmer STA 6000 under an argon atmosphere with gas flow of 10 mL/min and heating rate 10 ºC/min from room temperature until 500 ºC, analyzed the thermal behavior. The crystallinity index of the ijuk fibres were estimated by X-Ray Diffraction (Phillips *X ray Diffractometer*) under the condition with monochromatic Cu K-α radiation of λ= 15.418 nm; 40 kV, 40 mA with step size 0.02º and time/step around 20 s from 10º to 40º (2θ). The crystallinity index (CrI) was determined by an empirical method using the following equation by Segal, L *et al.,* (1959) [15];

$$CrI\ (\%) = \frac{(I_{002} - I_{am})}{I_{002}} x100\% \quad (1)$$

Where I_{002} is the maximum intensity of the (002) lattice diffraction at 2θ = 22.5º and I_{am} is the intensity of the scattered diffraction by the amorphous part of the sample at 2θ = 18º. The morphology of ijuk fibre was observed by INSPECT F50 Field Emission Scanning Electron Microscope (FE-SEM) (FEI Co., part of Thermo Scientific, Oregon, USA) after sputter coated with AuPd.

3. Results and Discussion

3.1. Compounds Composition

Figure 1 shows the FTIR spectra of the ijuk fibre samples recorded for (a) pre-treatments and (b) acid hydrolysis with sulfuric acid. The result shows that the peak at 3500-3390 cm $^{-1}$ wavenumber that represent C-H and O-H occur in every spectra, so do ~1635 and 2990-2880 cm^{-1} wavenumber also occur in every spectra. These functional groups are responsible to the water absorption and C-H stretch respectively [16, 17]. These three main peaks are hydrogen and hydroxyl bond, which occur in cellulose structure. This shows that the pre-treatment (alkali and bleached) and hydrolysis did not

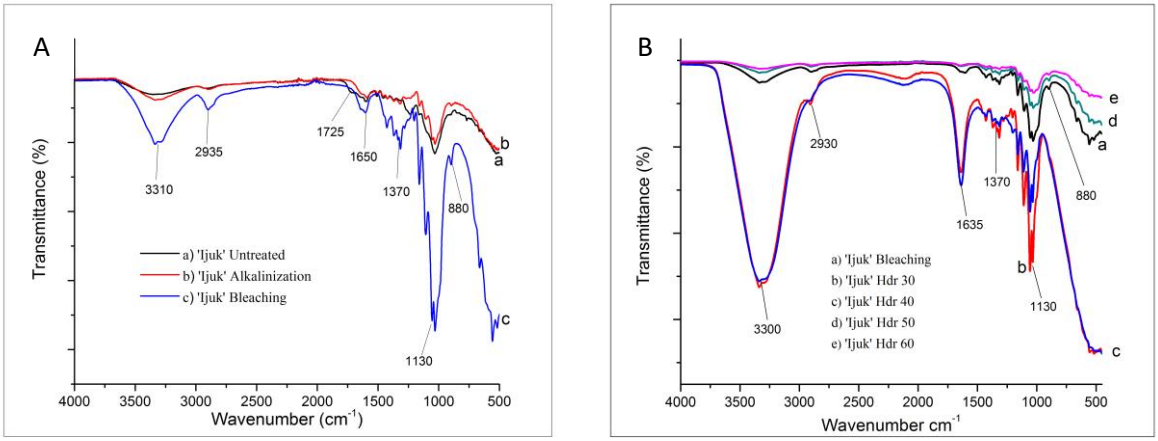

Figure 1. FTIR Spectra of ijuk fibre after (A) pre-treatments (B) various acid hydrolysis concentrations treatment

eliminate the cellulose from ijuk fibre [2,16,17]. Furthermore, 1700-1735 cm^{-1} wavenumber occur at untreated ijuk fibre. The wavenumber represent C=O functional group from acetyl and uranic ester group from hemicelluloses or ester linkage of the carboxylic group of lignin/hemicellulose [16,17]. As we can see, the prominent peak did not see at pre-treated fibre. It shows that pre-treatment was successfully eliminated lignin and hemicelluloses at certain amount. Same result reported by Kegarzadeh *et al.,* (2012) for kenaf fibre untreated and Johar *et al.,* (2012) for rice husk fibre untreated. Another peak at 1450-1330 cm^{-1} that occurs in every spectra show symmetric bending of C-H, also C-O and C-H from aromatic function group in polysaccharides [18]. The 1200-1030 cm^{-1} and ~880 cm^{-1} wavenumber peaks represent C-O and C-H function group from pyranose ring skeleton [19]. There are no significant differences between spectra and concentration in sulfuric acid except the intense of the absorption. This means there is no structure transformation of cellulose molecule after acid hydrolysis treatment [2,16,17].

3.2. Thermal Properties

Thermo Gravimetric Analysis (TGA) observed effect of multistage treatment in MFC preparation to thermal behavior of ijuk fibre. Figure 2 show TGA curve from untreated, alkalinization treated, bleach treated, and various acid hydrolysis concentrations treated of ijuk fibre. The result shows weight loss about 2-7 % happened at below 100 ºC in almost every sample. It is occurred by vaporize of moisture content from every sample. At higher temperature, the weight loss increased because the fibre were starting to degrade. Compared to untreated and alkalinization treated fibres (Figure 2), bleached ijuk fibre has highest stability of thermal behavior. Bleached ijuk fibre is start to degrade at ~225ºC while untreated and alkalinization fibre start to degrade at ~100 ºC. This degradation temperature difference because effect of the hemicelluloses and pectin elimination.

Hemicelluloses and pectin have lower degradation temperature. So do the alkalinization, it has lower degradation temperature due to partial removal of non-cellulosic ijuk fibre [16]. Afterward, the effect of various sulfuric acid concentrations to thermal behavior of the ijuk fibre was observed. The results show that hydrolysis treatment with 60 % sulfuric acid has the lowest stability of thermal behavior, around ~140ºC. It is caused due to the residual of sulfuric function group. Sulfuric function group gives lower the degradation temperature of ijuk fibre. Same result reported by Fahma *et al.,* (2011) that shows nanowhiskers cellulose from coconut husk, hydrolysis treated, has degradation temperature ~135ºC with 65 % acid concentration. It also shows that the highest stability of thermal behavior occur with 30 % acid concentration [20]. The 30 % acid concentration has highest thermal behavior stability due to successfully removing sulfuric function group on MFC by sodium hydroxide. At high temperature, >350 ºC, residual weight of native and alkalize fibre are higher than bleached, hydrolysis at 50-60 % due to non-cellulosic composition is higher in untreated, and alkalinization treated fibre than bleached, and hydrolysis treated. The pyrolysis of non-cellulosic produces higher residual weight than pyrolysis of cellulose [20].

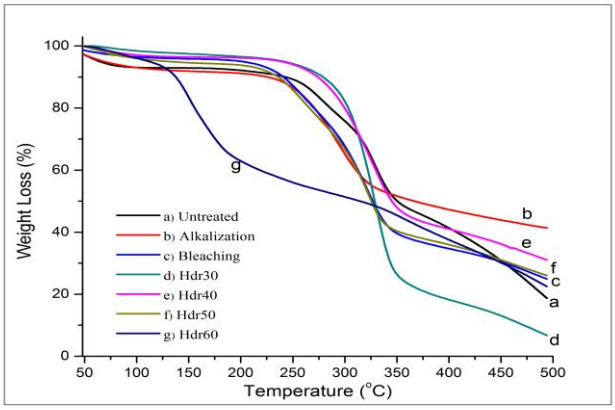

Figure 2 Thermal behaviour of ijuk fibre with various

3.3. Crystallinity

Observation of X-ray result to every chemical treatment and crystallinity index (CrI) which calculated using Segal equation (1) could be seen in Figure 3a-b. Figure 3a show the effect of pre-treatments to the crystallinity of ijuk fibre. The results show a significant enhancement of crystallinity compared to the crystallinity of untreted ijuk fibre. Based on Figure 3b, crystallinity of native ijuk fibre is 57.1 %, increased to 63.1 % by alkalinization, and increased to 85.7 % by bleaching treatment. It shows that the pre-treatment was effectively eliminating the non-cellulose compounds (pectin, hemicelluloses and lignin) which have amorphous structure due to the complexity of the molecule structure. In Figure 3a,

all diffraction has the same pattern, and pre-treatment of ijuk fibre increase the sharpness of the peak, which indicates the increase of crystallinity.

Its peak can see the typical of cellulose. At peak about 2θ = 18º indicates amorphous zone and 2θ = 22.5º, 34-35º indicates crystalline zone. The increase of crystallinity by pre-treatment is consistent with our previous observation before [2]. Effect of hydrolysis concentration on crystallinity of ijuk fibre can be seen in Figure 3a-b. Based on calculation, sulfuric acid with 60 % concentration has highest crystallinity index compared to 30, 40, and 50% concentration. Hydronium ion from sulfuric acid was expected to penetrate amorphous region of cellulose, causing hydrolytic cleavage of glycoside bond and the release of individual crystallite [21]. Hydrolysis with 30 and 40%, concentration do not cause any significant change to the crystallinity of ijuk fibre [16,17,20,22].

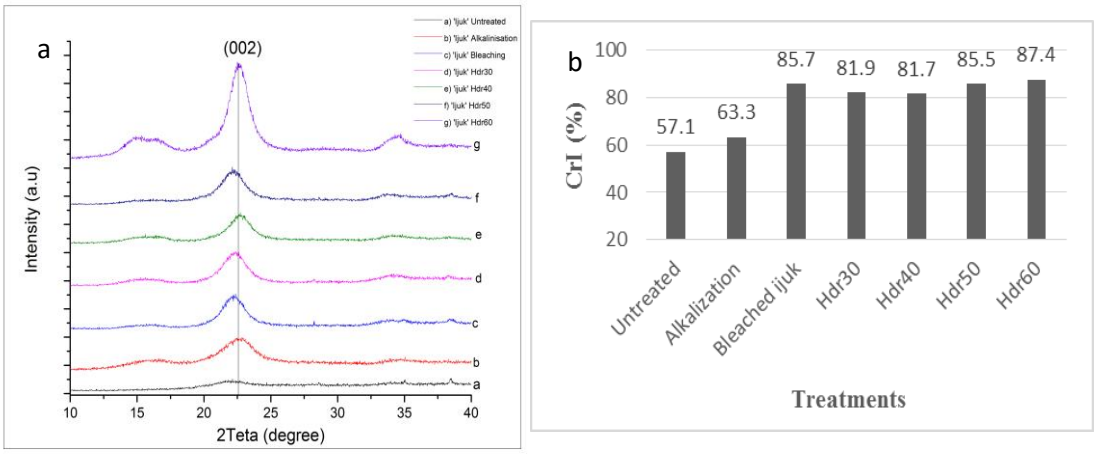

Figure 3. a) X-ray diffactogram b) Crystallinity Index calculations of ijuk fibre with various treatments

3.4. Morphology

The microscopic evolution of the ijuk fibre after each stage of chemical treatment is present in Figure 4a-g. The images show that pre-treatment of ijuk fibre clearly modified the fibre surface (Figure 4a-c). Figure 4a is the image of native ijuk fibre. Native ijuk fibres still contain impurities and wax layer. The diameter size of untreated ijuk fibre is around 50-80 μm. Alkalinization-treated ijuk fibres produce an impurities-free surface (Figure 4b). Alkalinization treatment also promotes the defibrillation phenomena. Defibrillation phenomena decrease the diameter size of ijuk fibre caused the size of the fibre decreased from 100 μm to 10-20 μm but not entirely. Cleaner surface of ijuk fibre increase the effectiveness of chlorite to oxidation hemicelluloses and lignin. Figure 4c shows ijuk fibre after oxidation process. It shows clear image of ijuk fibre, and as we can see, the diameter size reduce to <20 μm entirely. Pre-treatment process has reduced the ijuk fibre size to MFC. The size reduction of ijuk diameter is also consistent with our previous report before [2]. The diameter size is decrease from

native cause the separation of the fibre primary cell wall due to removal of non-cellulosic contents [23].

The effect of different hydrolysis concentration can be seen in Figure 4d-g. Increasing sulfuric acid concentration leads to decreasing diameter of ijuk fibre. Figure 4d-g shows the size of ijuk with 30, 40, 50, 60 % of hydrolysis concentrations are ~15 ; 10 ; 2.5 ; 2 μm respectively. This shows an increase in the concentration of sulfuric acid, has also increased the content of hydronium ion (H^+), which responsible for penetrating amorphous area compared crystalline structure during 60% acid hydrolysis

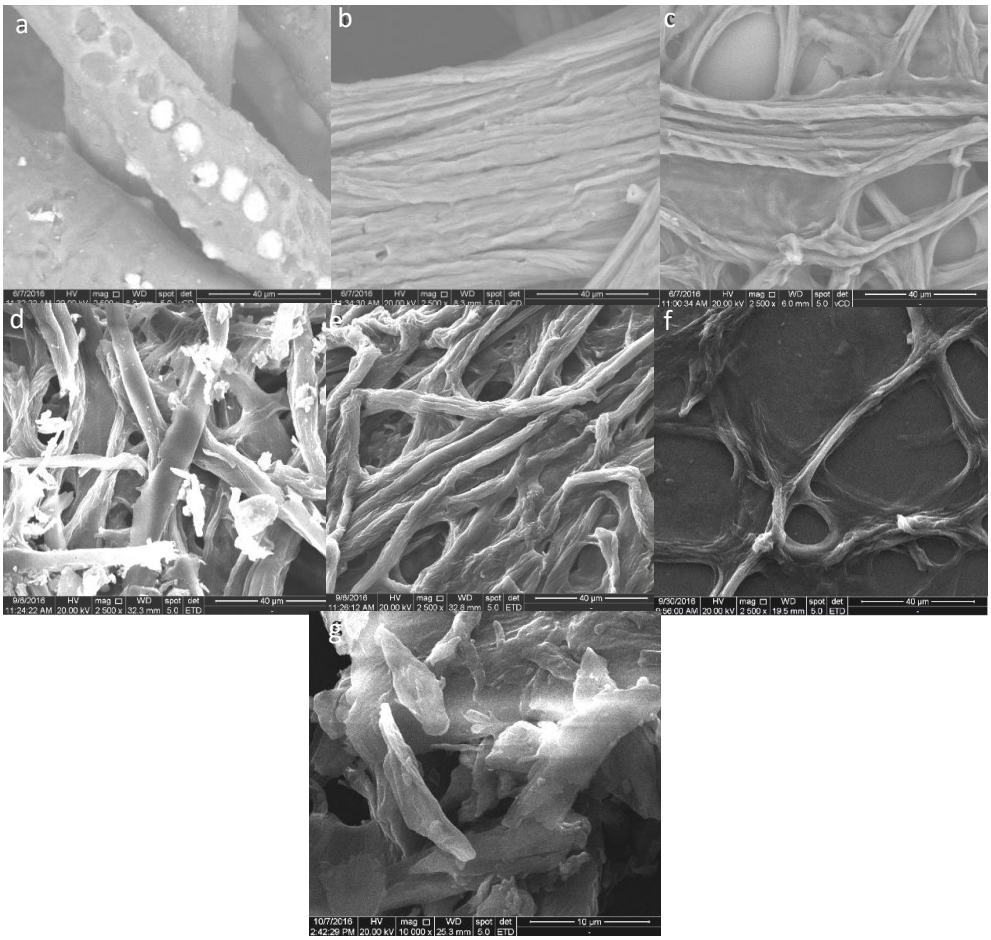

Figure 4. FESEM images of ijuk, a) untreated, b) alkalinization, c) bleaching, d) hdr30, e) hdr40, f) hdr50 and g) hdr60

concentration [24]. However, there is no significant difference to the morphological behaviour of ijuk fibre. Nevertheless, the change is which occur only in the fibre hydrolysis 60% (Figure 4g). This expected to the start of the nanocellulose formation due increasing amount hydronium ion (H^+) promotes hydrolytic cleavage of the amorphous region, but not enough to separate fibre into nanosize

[24]. The addition of temperature, time, and a higher concentration suggested capable to form nanocellulose fibre.

4. Conclusion

Cellulose fibres were extracted form ijuk fibre by alkalinisation followed bleaching treatment. Cellulose characterized by FTIR spectroscopy, thermal behaviour, X-Ray diffraction and Electron microscope examination. The results show pre-treatments has successfully removed non-cellulosic contents, increased thermal stability, enhanced crystallinity and caused defibrillation of cellulose. The effect of different concentration of sulfuric acid causes size reduction of ijuk fibre and increase crystallinity around 87.1%. In contrast, sulfuric acid (60%) reduce thermal stability of ijuk due the present of sulphate group. Electron microscope examination showed hydrolysis with a concentration of 60% has not enough to reduce microfibrillated cellulose into nano size.

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