

Characterization of Cellulose Microfibers Isolated from Rubberwood (*Hevea brasiliensis*)

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Abstract— Cellulose microfibers were isolated by chemical treatment followed by acid hydrolysis using sulphuric acid. The chemical compositions for extractive, holocellulose, cellulose and lignin were determined. The functional group of raw particles and cellulose microfibers of rubberwood were determined using fourier transform infrared spectroscopy (FT-IR). Morphological studies were viewed using Scanning Electron Microscopy (SEM) to investigate physical changes of the fibers after acid hydrolysis. The results show that cellulose content was increased to 63 % from 52 % after hydrolysis was conducted to the raw particles. Particle size distribution of cellulose microfibers falls in the range of below 100 µm. The removal of lignin and other extractives during chemical and acid hydrolysis can be seen by the absence of certain band in the FTIR spectra. The individualization of the fibers can be seen after hydrolysis with sulphuric acid. The removal of the surface impurities along with defibrillation were also shown in the cellulose microfibers.

Keywords— cellulose microfibers; rubberwood; raw particles; chemical properties; morphological

I. INTRODUCTION

Cellulose provides strength and stability to the plant cell walls and the fiber. The amount of cellulose in a fibers influence the properties, economics of the fiber production and the utility of the fiber in various applications [1]. Cellulose micro- and nanofibers include a variety of particles from microfibers and microfibrils to nano-sized whiskers. These kind of particles from cellulosic materials that having optimized strength properties can be used as a composites reinforcing agents [2], [3] and films [4]. Other than that, these cellulose micro and nanofibers having a bright future in various applications including papermaking additives, thickening agents for food and cosmetic products, and various medical applications [5],[6].

As abundantly available polymer on earth, cellulose has emerged as a very good candidate to provide such 'nanoparticles' to be used as a reinforcing agent. There are several advantages of this cellulose such as inherent stiffness and a high degree of crystallinity, which make it ideally suited for reinforcing and load bearing applications in composites. Other than that, cellulose is sustainable resource, biodegradable in nature, inexpensive and has a much lower density than most filler that are being used nowadays [7].

In Malaysia, rubberwood (*Hevea brasiliensis*) is one of the most important hardwood for the forest-products

industry. In order for rubberwood industry to maintain its competitive position in global market, producing a good quality wood to meet the required standard is important. Malaysia has become the most unbeaten country in using rubberwood throughout the world [8] for furniture making and wood- based products. Because of its favorable wood properties, there is great promising in the increasing use of this hardwood resource.

A previous study [9] isolated the cellulose nanofibers from rubberwood using only chemo-mechanical process. However, this study attempt to isolate the cellulose microfibers from rubberwood using chemo-mechanical followed by sulphuric acid hydrolysis. The chemical composition of rubberwood raw particles and cellulose microfibers were measured. The existence of functional groups in rubberwood particles and cellulose microfibers were also investigated. Scanning Electron Microscopy (SEM) and Light Microscope (LM) were used to observe the changes in anatomical properties of rubberwood raw particles and cellulose microfibers.

II. MATERIALS AND METHOD

Rubberwood sawn timber obtained commercially were cut into chips before grinding in Wiley Mill to form fine particles in the range 1000µm. The particles were sieved to measure the distribution of the particles.

A. Chemical Composition Analysis

Preparations of extractive free samples were conducted according to TAPPI 264 cm-97 [10] with a modification of the solvent ethanol-toluene ratio of 2:1. Holocellulose content was performed based on the method of Wise et al. (1946) [11] and cellulose content was extracted from the percentage of holocellulose with 17.5% sodium hydroxide. Lignin content of the samples was according to TAPPI 222 om-02 [12].

B. Preparation of cellulose microfibrils

The preparation of cellulose microfibrils were mentioned in our previous work [13] following Fahma et al. [14] with a slight modification. Briefly, the raw rubberwood fibers were weighed and the extractives were removed by Soxhlet extraction for 4 hr using ethanol/toluene (v/v 2:1). Then, the bleaching were done four times in sodium chlorite (NaClO_2) solution under acidic conditions (pH 4 to 5) at 70°C for 1 hr. The fibers were then washed with deionized water before 6 wt % potassium hydroxide (KOH) solution was added to the fibers at 20°C for 24 hr. The fibers then washed with deionized water until neutral. Then, 210 mL of sulfuric acid (H_2SO_4) solution (64%) were subjected to the cellulose fibers with stirring at 45°C for 1 hr before terminating the hydrolysis by adding 400 mL of cold water. The precipitate was resuspended in water with strong agitation, centrifuged for 3 days until the pH became constant. It was then homogenized, sonicated, and freeze dried.

C. Fourier Transform Infrared

Fourier Transform Infrared (FT-IR) analysis was performed to detect the presence of a functional group that exists in rubberwood raw particle and cellulose microfibrils. Two types of samples were used in this determination which include raw material sample and cellulose extractive sample were used to analyze and compare the elements. The mixture was then inserted into a mould and compressed with to form a disk sample about 1mm thick. The disk was inserted into a Perkin Elmer 1600 Infrared Spectrometer machine where the samples will be run under the infrared light and the spectra that produced was recorded for further analysis between a range of wave numbers of 4000 cm^{-1} and 500 cm^{-1} with resolution of 4 cm^{-1} to detect the functional group of the compound.

D. Morphological study

Scanning Electron Microscope (SEM) was used to scan image of rubberwood raw particles and cellulose microfibrils to obtain the information of physical structure of the fibers. A ultra-high resolution, LEO Supra 50 Vp field emission scanning microscope were used for this purpose. Light microscope was also used to view the raw particles and cellulose microfibrils.

III. RESULT AND DISCUSSION

A. Particle Size Distribution

Particle size of the substrate is important. It affects the performance of solid state fermentation. It affects the reactivity of solids participating in chemical reactions and needs to be controlled in many industrial products. Fig. 1

shows the particle distribution ratio of rubberwood particles and cellulose microfibrils. In this study, the particles size used was fixed in the range of 0-1000 μm . Generally, particle size that been used in this study was below 500 μm . The particle size ratio ranged of 100 μm for rubberwood particles and cellulose microfibrils obtained were 67% and 63%. Particle size of cellulose microfibrils majority falls in the range of below 100 μm .

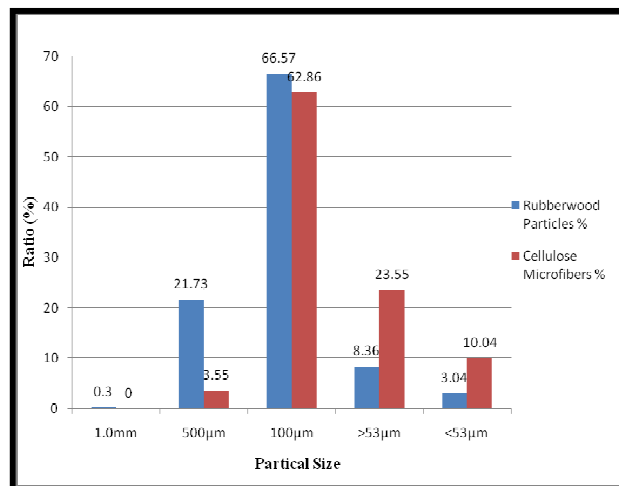


Fig. 1 Particle size distribution of rubberwood raw particles and cellulose microfibrils

B. Chemical Composition

Generally, chemical analysis of wood used to determine the chemical composition contained into a species. Chemical composition varies due to the differences of geographic locations, aged, climates and the soil conditions [15]. The chemical composition of rubberwood raw particles and cellulose microfibrils was studied to determine the percentage of its compositions. Table 1 displays the result of the chemical compositions of the rubberwood particles and cellulose microfibrils.

Generally, the data shows decreasing in the percentage of extractives, lignin, and hemicelluloses contents while the holocellulose and the cellulose had increased after chemical treatment. Based on Table 1, rubberwood contained only 2.24 % of extractives. During chemical treatments, hemicellulose and lignin will be removed from the fibers. After the treatment, rubberwood was found to contain a high percentage of cellulose and holocellulose. Holocellulose consists of α -cellulose (not dissolve in strong alkali) and hemicelluloses (dissolve in weak alkali). The presence of hemicelluloses will reduce wet wood strength but increase the dry wood strength.

Originally, the cellulose content found in rubberwood was higher in comparison to other researcher [9] that is 52.41% to 45%, respectively. After the rubberwood fiber under chemical treatment, the cellulose content was found increased to 63.35% (Fig. 2). The higher cellulose content will provides strength and stability to the plant cell wall and the fiber [1]. The differences of chemical composition percentage for both rubberwood particles and cellulose microfibrils were shown in figures. The chemical composition of rubberwood raw particles was higher in the case of holocellulose and cellulose whilst lower in lignin content when comparing to data reported by Jonoobi et al.

(2011) [9] that are holocellulose (65%), cellulose (45%) and lignin (29%), respectively.

TABLE I
CHEMICAL COMPOSITION OF RUBBERWOOD

| Sample | Extractives (%) | Holo-Cellulose (%) | Cellulose (%) | Lignin (%) |
|----------------------|-----------------|--------------------|---------------|------------|
| Raw particles | 2.24 | 78.74 | 52.41 | 14.31 |
| Cellulose Microfiber | - | 96.36 | 63.35 | 1.08 |

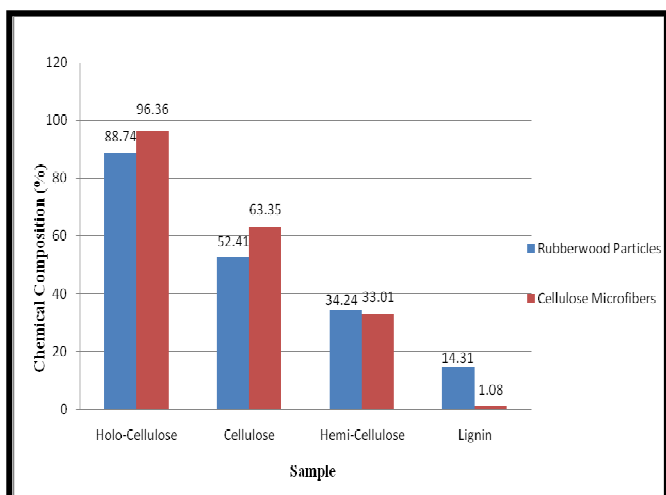


Fig. 2 Chemical composition of rubberwood raw particles and cellulose microfibers

C. Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FT-IR) spectroscopy was used to detect the presence of functional group that existed in rubberwood and cellulose microfibers. The infrared spectra of cellulose, hemicellulose and lignin are mainly composed of alkanes, esters, aromatics, ketones and alcohols, with different oxygen-containing functional groups [16]. The FT-IR spectra for rubberwood raw particles and cellulose microfibers was shown in Figs. 3a and b. All samples presented two main transmittance regions. Lignin presented characteristic peaks in the range 1200–1300 cm^{-1} corresponding to the aromatic skeletal vibration. In addition, due to the presence of functional groups such as methoxyl -O-CH₃, C-O-C and aromatic C-C, peaks in the region between 1830 cm^{-1} and 1730 cm^{-1} were observed [1]. The -OH bending of absorbed water at 1640 cm^{-1} is reported [17]. All the FTIR spectra were developed after the same carefully drying process, however the water adsorbed in the cellulose molecules is very difficult to extract due to the cellulose-water interaction. The peak present at 1736 cm^{-1} in the spectrum corresponding to the raw fibers could be due to the presence of C-O linkage, which is a characteristic group of lignin and hemicellulose, at 1736 cm^{-1} .

When fibers subjected to sodium hydroxide treatment, hydrogen bonding will be reduced due to the removal of the hydroxyl groups resulting in the increase of the -OH concentration. This can be observed with the increased in intensity of the peak between 3300 and 3500 cm^{-1} bands in

cellulose microfibers compared to the rubberwood particles [17]. It is reported that in most lignified plant cells, lignin and hemicelluloses are deposited between the microfibrils to give an interrupted lamellar structure.

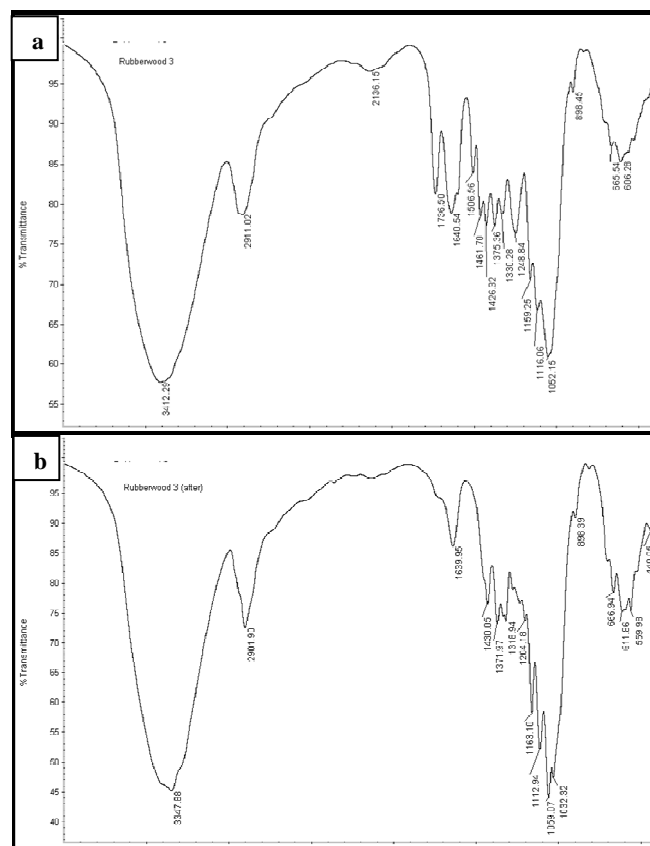


Fig. 3 FTIR spectra of rubberwood (a) raw particle (b) cellulose microfibers

With the chemical treatment subjected to the rubberwood raw particles, the lignin was removed resulting the increasing of the degree of crystallinity. This may be due to the removal of lignin which acts as a cementing material and on delignification, an ordered arrangement of the crystalline cellulose in the structure takes place. From the FTIR spectra, one can conclude that there is a reduction in the quantum of binding components present in the fibers due to the process of chemical treatment [18]. These peaks are chiefly responsible for the hemicellulose and lignin components. These characteristic peaks are completely absent in the final cellulose microfiber.

D. Scanning electron microscopy (SEM)

Scanning Electron Microscope (SEM) was used to scan the images of rubberwood particles to obtain the information about anatomical structure. The sample was observed under SEM at magnification 500X and 1.0 K X.

Figs. 4a and b showed the SEM micrographs of the rubberwood raw particles while Fig. 4c and d was cellulose microfibers. The fiber in Fig. 4a shows a compact structure; exhibiting an alignment in the fiber axis direction with some non-fibrous component in the fiber surface [19]. In Fig. 4b, the starch can be seen clearly in the fiber.

The defibrillation of fibers in cellulose microfibrils by chemical treatment was seen in Figs. 4c and 4d. The removal of the surface impurities along with defibrillation was observed in the figures. The micrograph also showed fiber in single form after the chemical treatment indicating that the treatment separate the bundle fiber into a single fiber. It was previously shown that during the chemical treatment most of the lignin and hemi-cellulose were removed, thus cellulose microfibrils of the original fibers were obtained.

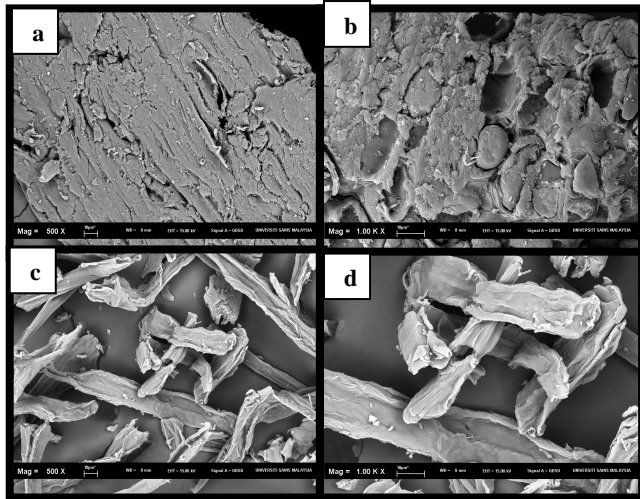


Fig. 4 SEM micrographs of rubberwood (a) raw particles (b) cellulose microfibrils

A clear change in the morphological structure of the whole cellulose fibers occurred upon acid hydrolysis and it can be observed via SEM. The larger bundles from which the microfibrils can be seen released after a hydrolysis, ultrasonication and homogenization process. During the preparation of samples for SEM, a broad distribution of fiber lateral dimensions is evident showing that some of the microfibrillar bundles were still not completely dispersed and/or reaggregated [7].

The sample of morphology also viewed through light microscopy. The sample was observed under LM at 4X and 10X. Figs. 4a and b show the LM images of the rubberwood raw particles while Fig. 5a and b are cellulose microfibrils.

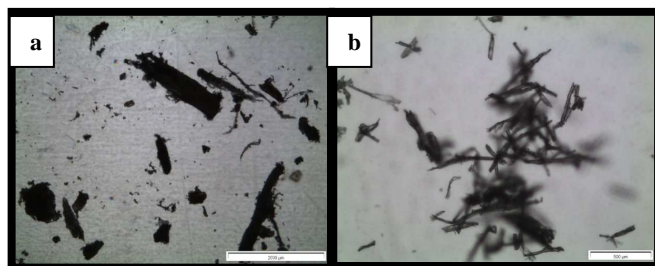


Fig. 5 LM images of rubberwood (a) raw particles (b) cellulose microfibrils

IV. CONCLUSIONS

The chemical composition of rubberwood particles for extractive and lignin content were 2.24% and 14.31% respectively. Meanwhile, holocellulose and cellulose content were 78.74% and 52.41% respectively. The increments of cellulose and holocellulose components percentage were detected after the fibers been treated with chemical which are 63.35% and 96.36% respectively. On the other hand, a reductions were found on lignin, 1.08% and hemicelluloses, 33.01% components from cellulose microfibril. FTIR analysis shows that changes in the spectra of cellulose microfibrils indicating the removal of lignin and hemicellulose from the fibers after hydrolysis compared to rubberwood raw particles. From the observation on the rubberwood raw particles, impurities and starch can be seen on the surface of the fibers. Individualization of microfibrils were observed after acid hydrolysis and raw particles in bundle form can be seen in the LM images.

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