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Characterization of the microfibrillated cellulose from water hyacinth pulp after alkali treatment and wet blending

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Abstract. In this study, the effect of mechanical treatment on the characterization of microfibrillated cellulose (MFC) from water hyacinth pulp was carried out. Chemical and mechanical treatments were used in this experiments. Chemical treatment such as cooking fibers into the high-pressure reactor.While, the mechanical treatment that provides shear stress on the fibers by means of the wet blending process. The experiments were conducted at the time of wet blending namely 15, 20, and 25 min respectively. The final products were characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD), and tensile test. SEM observation was carried out on the surface of the film. XRD shows that the crystallinity index of MFC with wet blending 15, 20, and 25 min are 56.24, 78.41, and 85.97% respectively. The maximum value of tensile strength was 23.21 MPa at 25 min of wet blending.

1. Introduction

The last two decades, the potential of natural fibers reinforced biocomposites become interest topics to replace conventional composite materials due to its environmentally, friendly, and availability. The availability of natural fibers and their use in the micro to nano size fibers as a reinforcing agent becomes a main focus of researchers [1].

The natural fibers usually consist of cellulose, hemicelluloses, and lignin. Cellulose is a fibril component of the plant cell. Chemically, cellulose is a linear polymer of residual impurities (1 => 4) - linked β-D-glucopyranose. In nature, cellulose chain is packaged in the form of microfibril which is stabilized by intermolecular and intramolecular hydrogen bonds [2].

Cellulose with a new morphology was developed by Turbak et al. (1983) which is known as micro fibril cellulose (MFC) [3]. The fabrication of MFC pulp through a mechanical process able to produce cellulose with large surface area. The advantages have been used for any aspect such as additives in food, paint, cosmetics, and medical product. The MFC can also be used as reinforcement to the thermosetting polymers and thermoplastic polymers [1,4].

The most fiber in form of pulp has a degree of polymerization in range 600-1500. Cellulose can be found in cell walls and woody parts of plants. Cellulose has an important role in determining the fiber properties in the fabrication of paper. Making pulp fibers with high cellulose content have to observe the properties of cellulose content especially on degree polymerization of the cellulose molecule [5,6].

The shape of pulp fiber is usually produced by using mechanical methods. However, the method for the destruction of natural fiber can damage the microfibril structure by reducing molar mass and degree crystallinity of natural fibers [7].
Takashi Taniguchi and Yano report on how to produce the microfibrils by the simple mechanical method by means of the super grinding method. This method works by giving shear stress to the longitudinal sample of fiber. The size of fiber was produced by this method is in the range of 20-90 nm diameter [8,9].
Moreover, Herrick, Nakagito, and Henrickson produce pulp fibers by passing a suspension of cellulose pulp fibers through the mechanical homogenizer. This process can increase the degree of fibrillation [4,10,11].
However, according to our best knowledge, no studies have reported on the effect of wet blending time on the characteristics of microfibrillated cellulose (MFC) from water hyacinth pulp. In this study, a tensile test was carried out to evaluate the tensile strength. The surface morphology of the MFC was investigated by scanning electron microscopy. XRD experiment was performed to know the index crystallinity.

2. Materials and Methods

2.1. Materials
The water hyacinth plants were obtained from Payakumbuh, Indonesia. The content of lignin and cellulose were 5% and 43% respectively. Sodium Hydroxide (NaOH) technical grade was obtained from Bratachem Company, Padang, Indonesia. Distilled water was supplied from the Faculty of Mathematics and Natural Science, Andalas University.

2.2. Preparation of MFC
The roots and leaves of the water hyacinth plant were separated from the rod and cleaned from dirt. Then, the rods were dried in plastic home UV (ultraviolet) for 5 days and cut along ± 1 cm before being alkalization processed into the high-pressure reactor. The water hyacinth rods, distilled water, and sodium hydroxide (NaOH) 25% for alkaline treatment were added into the high-pressure reactor with a ratio 1 kilogram, 10 liters, and 250 grams respectively, then stir the mixture. After that, they were heated at temperature and pressure of 130 ℃ and 2 bars respectively for 6 h. Finally, we produce soft MFC with pH of about 12-13. Then, the MFC was neutralized with distilled water until pH 7. After alkalization treatment into the high-pressure reactor, the MFC was blended in wet condition at 25000 rpm using ice blender under the Philips brand. Varied time of wet blending treatment was 15, 20, and 25 min respectively. After that, they were cast in a pulp paper into screen printing 30 x 40 cm with sieve mesh of 62T. And then dried in the sun for one day before being characterized.

2.3. Surface morphology analysis
The surface morphology of the sample films was investigated by using a Scanning Electron Microscope (SEM) ZEISS EVO MA10 with an acceleration voltage of 10 kV. The surface of the sample was coated with Palladium-Gold (Pd-Au) using an Emitech SC7620 Sputter Coater machine and then observed.

2.4. Crystallinity index analysis
Wide angle of X-Ray Diffraction (XRD) was measured using a PANalyticalXpert PRO. Cu Kα radiation (λ=0.1542 nm) operating at 40 kV and 35 mA. The range of scattering angle was recorded at (2θ = 10-30^{o}) (θ is the Bragg's angle). Crystallinity index was calculated by using Segal's method [12]:

$$I_{cr}=\left(\frac{I_{200}-I_{am}}{I_{200}}\right) \text{ x } 100\% \quad (1)$$

Equation (1) indicates that I_{200} is the maximum intensity of the diffraction peak 200 ($2\theta = 22.6^{o}$) and I_{am} is the intensity of diffraction ($2\theta = 18^{o}$). I_{200} was indicated crystallinity and amorphous regions. Meanwhile, I_{am} was indicated only amorphous regions.

2.5. Tensile strength

There were three specimens were tested for every sample. The test was carried out after 2 days of releasing samples from the screen printing mold. The standard of the sample for testing was ASTM D638. Tensile tests were conducted with an Equipment Com-Ten testing machine of 95T Series. Both speed and temperature during testing were 3 mm/min and room temperature, respectively.

3. Results and Discussion

3.1. Surface morphology studies

SEM was used to know the morphological change of MFC by wet blending treatment at 15, 20, and 25 min, respectively. SEM images of MFC from water hyacinth pulp is presented in figure 1(a-c) with the same magnification (x25000).

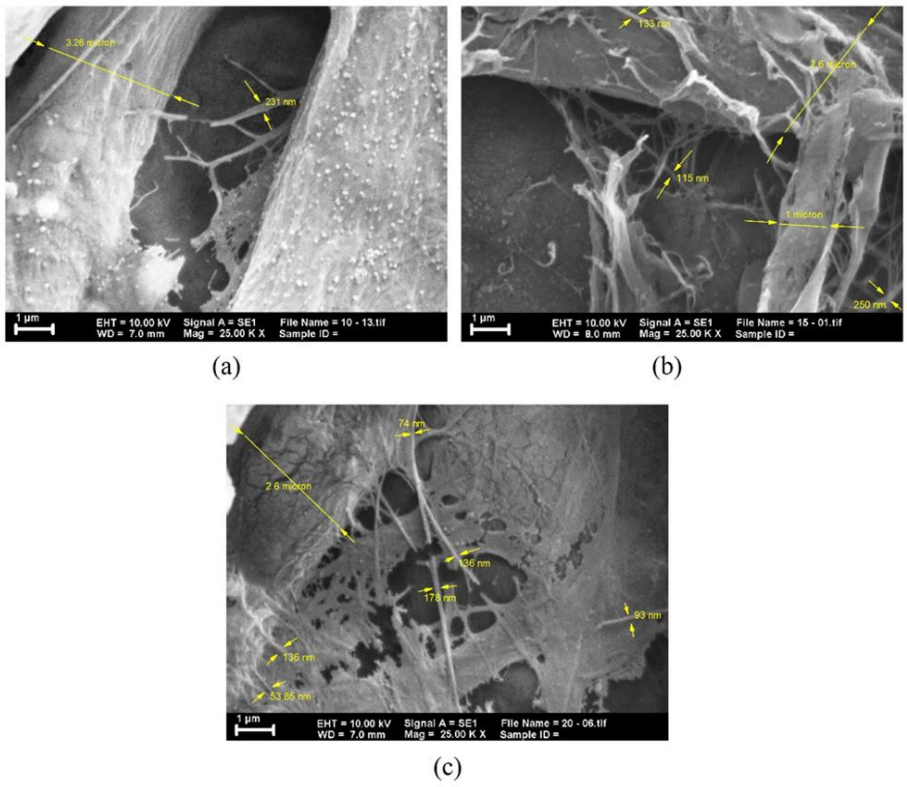

Figure 1. SEM on surface morphology of MFC from water hyacinth pulp: (a) wet blending time for 15 min; (b) wet blending time for 20 min; (c) wet blending time for 25 min.

As shown in figure1, MFC shows diameter around 3 µm on the surface of the sample with blending time for 15 min. Those fibers, showed by SEM images for MFC samples figure 1(b-c) are disintegrated from micro to nano-size after 20 and 25 min of wet blending were performed, respectively. It was indicated, the degree of fibrillation of MFC from water hyacinth pulp was increased with the increased time of wet blending treatments. However, the amount of MFC from water hyacinth pulp in nano-size is minimum. A substantial part of fibrils is around 50 – 100 nm in diameter. This phenomenon similar with previous report [1,4,9].

3.2. Cristallinity index studies

Figure 2 shows the diffraction pattern of the MFC from water hyacinth pulp with wet blending treatment for 15, 20, and 25 min showed two sharp peaks at ($2\theta = 16^{o}$ and 22.6^{o}) respectively. On the XRD peak of ($2\theta = 22.6^{o}$) and ($2\theta = 16^{o}$) correspond with crystallinity and amorphous region respectively. This phenomenon was indicated the crystal structure of cellulose type I as reported by Sunil et.al. and Ahmad et. al. due to the formation of inter and intramolecular H-bonding in cellulose by the hydroxyl groups [13,14].

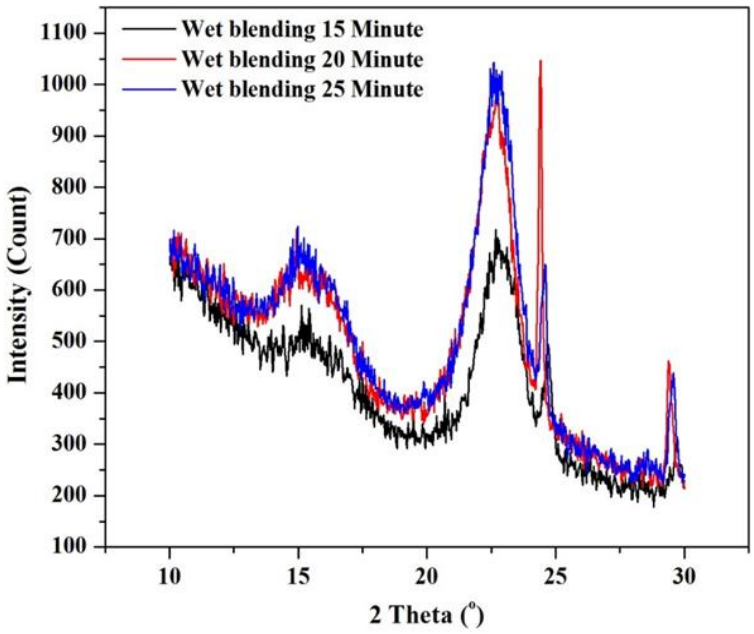

Figure 2. XRD pattern of MFC from water hyacinth pulp with different time of wet blending

The crystallinity value was calculated by using Segal's method. The estimated crystallinity value of MFC with wet blending time for 15, 20, and 25 min were 56.24, 78.41, and 85.97% respectively. It was indicated, the role of the alkali and wet blending treatments were very significant to improve the crystallinity of cellulose fibers due to the removal of the amorphous region such as hemicellulose and lignin contents during treatments. This result is in agreement with the Sunil et. al.'s report that chemical treatment such as alkalization, acid hydrolysis, and bleaching able to remove amorphous region and present a crystallinity component in the samples [13]. However, the higher crystallinity of the cellulose fibers can also increase the tensile strength as reported by Alemdar et. al. and Janoobi et. al. [2,12].

3.3. Tensile strength studies

As shown in figure 3, the tensile strength of the MFC from water hyacinth pulp in membrane films with different time of wet blending (15, 20, and 25 min). The tensile strength of the MFC with wet blending time for 15 min was about 18.41 MPa. The tensile strength slightly increased with the increased time of wet blending up to 23.21 MPa at 25 min. The MFC did improve the tensile strength due to the formation of inter and intramolecular H-bonding by the hydroxyl groups as reported by Janoobi et al and Sunil et al. [12,13]. The results are in agreement with the SEM and XRD observations that the higher degree of fibrillation and crystallinity of fibers can increase the tensile strength.

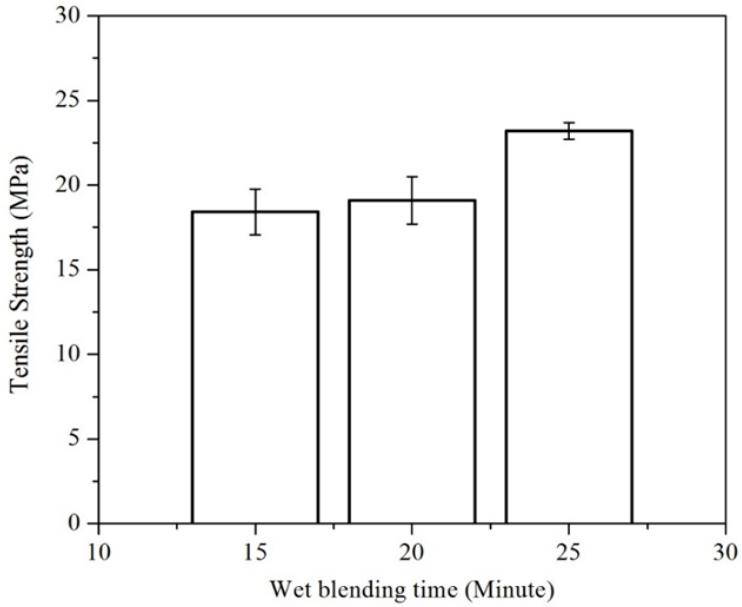

Figure 3. The tensile strength of MFC from water hyacinth pulp with different time of wet blending

4. Conclusion

The fabrication of MFC can be done with chemical and mechanical methods. A chemical method such as cooking fibers into the high-pressure reactor with a 25% sodium hydroxide solution at temperature and pressure was about 130^{o}C and 2 bars respectively then proceed by mechanical treatment such as wet blending treatments with ice blender. The tensile strength slightly increased with the increased time of wet blending. The maximum value of tensile strength was 23.21 MPa at 25 min of wet blending time. XRD shows that the crystallinity index of cellulose MFC with wet blending time for 15, 20, and 25 min are 56.24, 78.41, and 85.97% respectively. It was indicated that the alkali treatment and wet blending were successful to removal of the amorphous region such as hemicellulose and lignin contents in WH fibers. These results are in agreement with the tensile strength observations that higher crystallinity of fibers can increase the tensile strength as reported by Janoobi. SEM micrograph on surface morphology shows a reduction size of fiber in diameter with 15 to 25 min of wet blending time was from $\geq$ 1 μm to 50-100 nm respectively. In this study, the bleaching and acid hydrolysis processes were not performed. Therefore, this study need to be studied further in terms of its chemical treatment, especially in the alkalization, acid hydrolysis, and bleaching processes. However, the diameter size, crystallinity, and mechanical properties of the natural fibers were very significantly determined by chemical and mechanical treatments.

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