Effect of the Homogenization Process on Titanium Oxide-Reinforced Nanocellulose Composite Membranes

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ABSTRACT

Indonesian pineapple production can reach 200 tons per day; however, pineapples generate a significant amount of waste. Pineapple peel waste can be used to make membranes. Composite membranes containing TiO_2 have dense properties, low porosity, and increase the mechanical strength of the cellulose sheet. This research uses various ultrasonic homogenizers to homogenize the distribution of nanocellulose and TiO_2 (50% and 100% power with 30, 60, and 90 minutes). The casting method is used to shape the membrane. The SEM test shows that the higher the power used and the longer the sonication time, the less agglomeration of about 1.63%/ cm^2 and a thickness of 16.56 µm. Identification of X-ray diffraction (XRD) results shows that sonication treatment for too long causes the peak at an angle of 25° to disappear. The analysis revealed no new peaks in the diagram pictures that were found using Fourier Transform Infrared Spectroscopy (FTIR) to analyze the functional groups, but it is known that changes occur in the O-H bonds of cellulose and C=C. The 50% sample with a power of 60 minutes had the lowest roughness value of 1.008 µm. Furthermore, as the power and time on the sample are increased, the roughness increases.

Keywords: *Bacterial cellulose, tensile strength, TiO_2 nanoparticles, ultrasonic homogenizer*

I. Introduction

Cellulose is a naturally occurring polymer that accounts for approximately 1.5 x 10^{12} tons of total annual biomass production [1]. Cellulose comprises glucose bonds arranged in a linear chain, with the C-1 of one glucose binding to the C-4 of another [2]. Fruit extracts such as oranges, apples, pears, pineapples, tomatoes, and coconuts can be used to produce bacterial cellulose. Because of their high strength, rigidity, and low density, cellulose-based biofibers such as banana, pineapple leaf, coir, cotton, hemp, hemp, kenaf, sisal, and wood fibers are commonly used to reinforce plastics. Agricultural crop waste has the potential to become a valuable source of natural fiber due to its favorable properties and characteristics [3], [4].

Bacterial Cellulose (BC) is widely known as a natural polymer, one of them is a membrane [5]. The membrane from cellulose has character with a thin layer that acts as a barrier to a specific species, BC membrane can separate substances of different sizes and

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limit the transport of different species based on their physical and chemical properties. Membrane separation can occur due to differences in pore size, shape, and chemical structure.

Titanium oxide is frequently used in manufacturing as both an additive and a reinforcement of biofiber, especially cellulose [6]. The composite membrane mixed with TiO_2 on the surface has the characteristics of being dense, having low porosity, and having spherical grains approaching a diameter of about 10 nm, as well as having a uniform size, implying that the addition of TiO_2 can later increase the mechanical strength [7].

Homogenization is the process of uniformizing particle size in order to maintain the stability of a mixture formed from two incompatible phases, also known as an emulsion [8]. Size uniformity is achieved by decreasing particle size in the dispersed phase [9]. The size reduction process occurs as a result of the force generated by the mechanical treatment, which causes the dispersed particles to break down. Sonicators are homogenizers that work on the principle that the ultrasonic sound waves produced by the sonicator destroy cell tissue by causing the mechanical breakdown of cell walls, so the study aims to describe the effect of the homogenization process on titanium oxide-reinforced nanocellulose composite membranes.

II. Material and Methods

1. Materials

Pineapple peel was used as waste pineapple peel in Malang, Indonesia; Acetobacter *xylinum,* which was purchased from the Agricultural laboratory UMM, Indonesia, was used as starter fermentation, sugar as a carbon source, ammonia acid as a nitrogen source; acetic acid was used to adjust pH, and TiO_2 as a reinforcement of membrane that was bought from Sigma Aldrich.

2. *Bacterial Cellulose Synthesis*

The Suryanto method was used to create bacterial cellulose pellicles in 2021 [10]. Bacterial cultivation media were 1000 ml of pineapple peel extract, 100 g of sugar, 5 g of ammonia acid, and acetic acid to achieve a pH of 4.5. Then, 100 ml of bacterial starter was added and incubated for another 10 days. The formed pellicle was harvested and neutralized (pH 7) with water for further testing.

3. Synthesis Bacterial Nanocellulose

The procedure begins with cleaning up to 5 kg of pineapple skin, which is then thoroughly washed and cut into small pieces. The pineapple skin is then blended until smooth and filtered to extract the juice from the pineapple skin. The pineapple skin juice is then mixed with 10 L of water and cooked until boiling, then added 10% (w/v) sugar, 0.5 ammonium sulfate percent (w/v), and acetic acid to adjust the acidity of the media to pH 4.5. The boiling solution was then cooled to room temperature. The culture media was then placed in 5 plastic pans, each of which held 1800 ml. Then, add 20% bacterial starter, cover with newsprint, tie with rubber, and ferment for 10 days until it becomes nata de pina (pelicle BC) [11],[12].

4. *BC/TiO_2 Homogenization Process*

For the homogenization process nata de pina was crushed with blender and filtered to obtain cellulose. After that, 20g of cellulose was stirred with 125 ml aquades in 30 minutes. After mixing the nanocellulose and 1% nanoparticles TiO_2 particles solution with the stirring

method, the mixture will be sonicated using an Ultrasonic homogenizer (Ningbo Lawson, China) until the nanocellulose and TiO_2 mixture become homogeneous. In this study, sonication power varied with 150 watts (50%) and 300 watts (100%), and sonication time variation was used with 30, 60, and 90 minutes.

5. *Membrane Nanocomposite*

The membrane was done by the casting method, with 125 ml of a mixture of nano-bacterial cellulose and nano TiO_2 particles placed in a 250 ml biker glass. The mixture was dried vacuum for 18 hours at 60 °C. The membrane was placed in a plastic clip and stored in a desiccator at 58 percent RH and 25°C [13].

6. SEM Observation

Sample evaluation based on a Scanning Electron Microscope (SEM) using an SEM instrument (Inspect-S50 type, FEI). Bacterial cellulose was coated with 10 nm gold using a sputter coater (Emitech SC7-620) before testing. This study proposes to ascertain how sonication affects the shape of bacterial cellulose. Additionally, ImageJ software features additional analysis of the specimen's morphology.

7. Crystallinity Analysis

Analyzing the crystallinity of a material has been performed via XRD testing. The findings of this test, which employs PANalytical XRD to calculate the crystallinity index and degree of crystallinity of bacterial cellulose, are presented. CuKα (λ) radiation from 1.54 was subjected to XRD scanning in the range of 10^o to 40^o at 30 mA and 40 kV. [14]. The crystallinity index (CI) and degree of crystallinity (Cr) were calculated using the Segal method:

$$Cr = \frac{I_{(002)}}{I_{(002)}+I_{(am)}} x100\% \quad \text{.....} \quad (1)$$

$$CI = \frac{I_{(002)}-I_{(am)}}{I_{(002)}} x100\% \quad \text{.....} \quad (2)$$

Whereas $I_{(am)}$ refers to the diffraction intensity at an angle of 18°, and $I_{(002)}$ is the highest diffraction intensity at a 22° angle.

8. FTIR Analysis

The FTIR test is used to determine the changes in functional groups that occur in bacterial cellulose. The Shimadzu IR Prestige-21 Fourier Transform Infra-Red Spectrometer (FTIR) was used to determine the transformations on the functional group of the membrane. The spectrum was recorded using a resolution of 4 cm-1 in the 400-4000 cm-1 range.

9. Surface Roughness Analysis

The surface roughness of the specimens was analyzed using the SurfTest SJ301 instrument at the State University of Malang's Mechanical Engineering metal laboratory. The parameters to consider are 0.8 mm λc profile filter, 0.75 mN gauge precision, average maximum height (Rz), average roughness (Ra), and total length of 4 mm. 200.0 µm/cm in the horizontal direction and 5.0 µm/cm in the vertical direction were the roughness measurement rates.

III. Results and Discussions

1. SEM Observation

Figure 1 depicts the findings of Scanning Electron Microscopy (SEM) observations. It can be seen that increasing the power and sonication time on the BC/TiO2 composite membrane can reduce the resulting agglomeration, with the distribution of TiO_2 nanomaterials increasing as the power and sonication time increase. This is due to the ability of an ultrasonic homogenizer to break particle bonds, resulting in improved particle distribution [15].

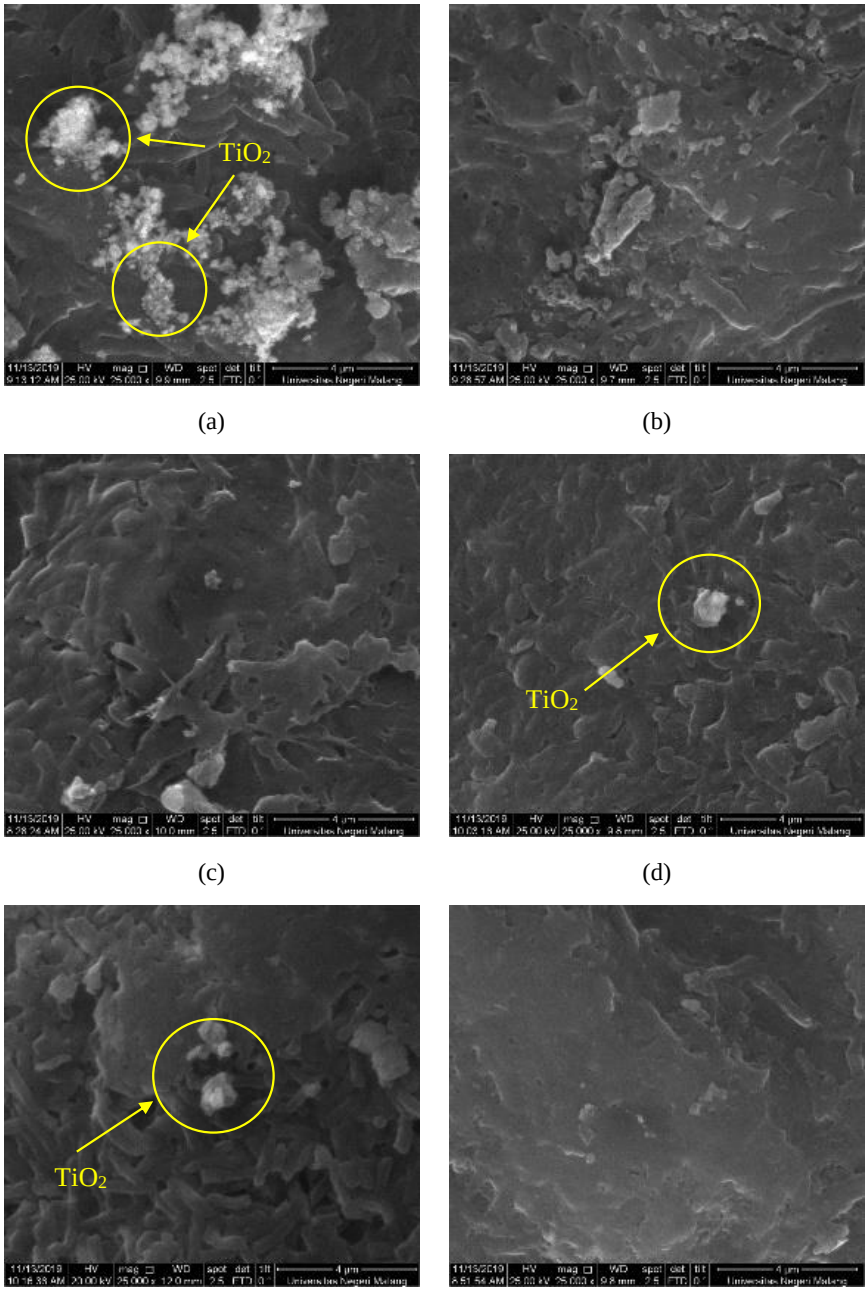

Fig. 1. BC/TiO membrane with 50% sonication 30 minutes (a), 50% of 60 minutes (b), 50% of 90 minutes (c), 100% of 30 minutes (d), 100% of 60 minutes (e), 100% of 90 minutes (f)

Figure 1 depicts the results of SEM observations. It can be seen that increasing the power and sonication time on the BC/TiO_2 composite membrane can reduce the resulting agglomeration, with the greater the power used and the longer the sonication time, the distribution of TiO_2 nanomaterials. This is due to the ability of an ultrasonic homogenizer to break particle bonds, improving particle distribution [1]. According to Figure 1, the sample with sonication treatment at 100% power for 90 minutes has the best distribution. Figure 1 (f) illustrates a 1.65 % agglomeration. The reduction in porosity value is caused by an increase in the density of the hydroxyl group (-OH) on the surface area, which builds strong interaction and generally makes a more even distribution of TiO2 and cellulose agglomeration [10].

2. Crystallinity Analysis

Figure 2 shows the effect of the different power and sonication time on the crystallinity of bacterial cellulose membranes. The figure shows that the higher the power and the longer the time used, the higher the crystallinity value of cellulose. This is illustrated in the top graph, where Miller's index [0 0 2] is higher in samples with other treatments. However, the crystallinity of TiO_2 at an angle of 2θ 25° disappeared in this treatment. This is most likely due to excessive sonication treatment, which it turns the agglomeration of TiO_2 into smaller particles and can improve the material's physical properties [16].

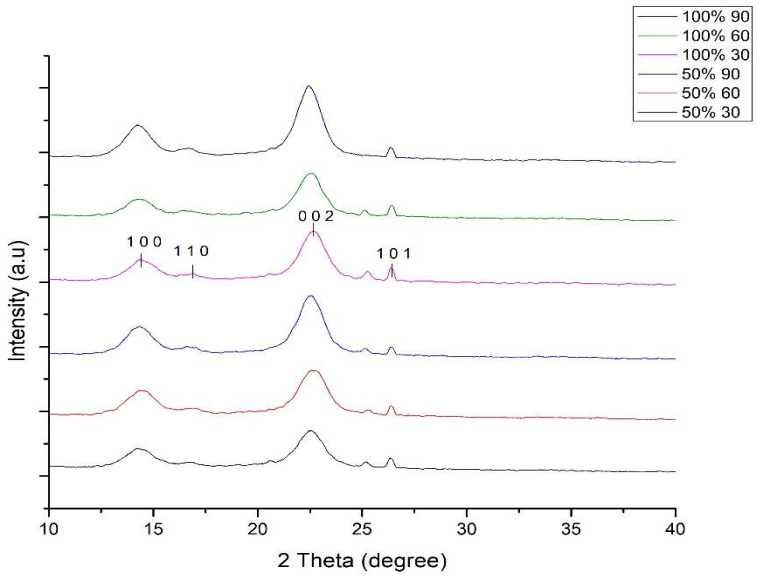

Fig. 2. Effect of power and sonication time on crystallinity cellulose

Table 1 demonstrates the impact of ultrasonic homogenization treatment on crystallinity in more detail. The presence of peaks at 14°, 16°, and 22° indicates that the membrane is made of cellulose I [17]. Sonication treatment increases the cellulose I, as indicated by an increase in the intensity value at angle 22°. It can be seen in Table 1 that increasing the power and sonication time tends to increase the intensity value and make the peak higher. The increase in intensity also indicates a change in the crystallinity index, and the difference in value that occurs in the crystallinity index value indicates the content of cellulose I crystals. Increasing the power and time of sonication also increases the amount of cellulose I crystals in the BC/TiO nanocomposite membrane. The addition of power and time of sonication also

affects the size of the cellulose crystals, which, with a smaller size, will make cellulose have a regular crystal structure and improve the physical properties of the membrane, and increase the purity of the cellulose [17].

Table 1. Crystallinity index and crystallite size BC/TiO_2

Sample	Power 50%			Power 100%		
	30 min.	60 min.	90 min.	30 min.	60 min.	90 min.
2θ	22.547	22.602	22.510	22.663	22.553	22.453
Peak Intensity	370	429	546	463	423	648
Crystallinity Index(%)	82.7027	85.0815	88.2783	86.1771	84.8699	90.1234
Crystal Size (nm)	12.862	12.863	11.453	11.435	8.575	8.574

3. FTIR Analysis

The FTIR test is intended to identify changes in functional groups in the membrane. Furthermore, the main objective of this test is to observe the chemical bonds that form and to determine the functional groups based on the graph formed and the FTIR table. Figure 3 shows FTIR graphic data of bacterial cellulose with sonication treatment at % power for 30 minutes, 60 minutes, 90 minutes, and % power for 30 minutes, 60 minutes, and 90 minutes.

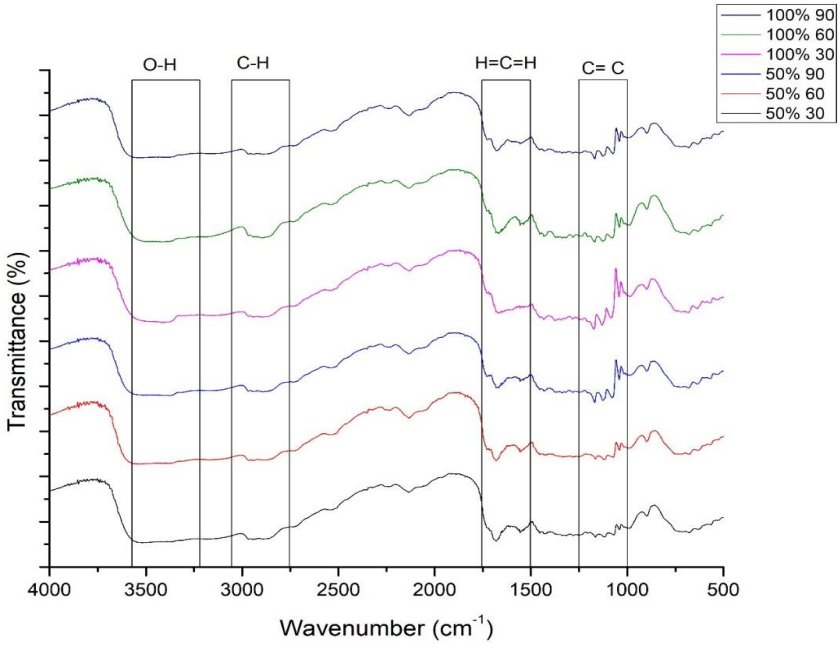

Fig. 3. FTIR graphic of cellulose

The graphical representation of the sample's FTIR spectrum is shown in Figure 3. The O-H group stretching vibration from cellulose I type caused the transmittance signal at ~3414 cm^{-1}. The frequencies of the signals resulting from the C-H stretching and bending modes were detected at around ~2875 cm^{-1}. While ~1600.92 cm^{-1} H=C=H and ~114.86 cm-1 for C=C out of plane bending vibration between glucose units and cellulose type I. For detail, the result of characterization is shown on Table 2. Table 2 presents a list of bonding results produced by the FTIR test to support understanding and indicates that there is no significant change in the resulting bond. The only difference is that the resulting peak value

is displayed on the graph by the peak inequality. Differences in sonication treatment show an increase or decrease in the number of bonds [18]. This also indicates that the sonication treatment does not result in the development of new bonds [19].

Table 2. Functional groups as a result of sonication

Bonding	Wavenumber (cm^{-1})					
	50%			100%		
	30 min.	60 min.	90 min.	30 min.	60 min.	90 min.
C=C	1114.86	1116.78	1126.43	1130.29	1126.43	1126.43
H=C=H	1681.93	1681.93	1732.08	1600.92	1614.42	1681.93
C–H	2875.86	2872.07	2873.94	2872.01	2872.01	2875.86
O–H	3498.87	3498.87	3414	3415.93	3415.93	3414

4. Roughness Test

Based on the graph, this test demonstrates the effects of sonication on the surface quality of the membrane. As shown in Figure 4, the highest roughness value was produced by a sonication treatment at full power for 90 minutes. While the minimum standard deviation value can be reached with a treatment of 50% sonication power and 60% time. Figure 4 shows the roughness results on every sample.

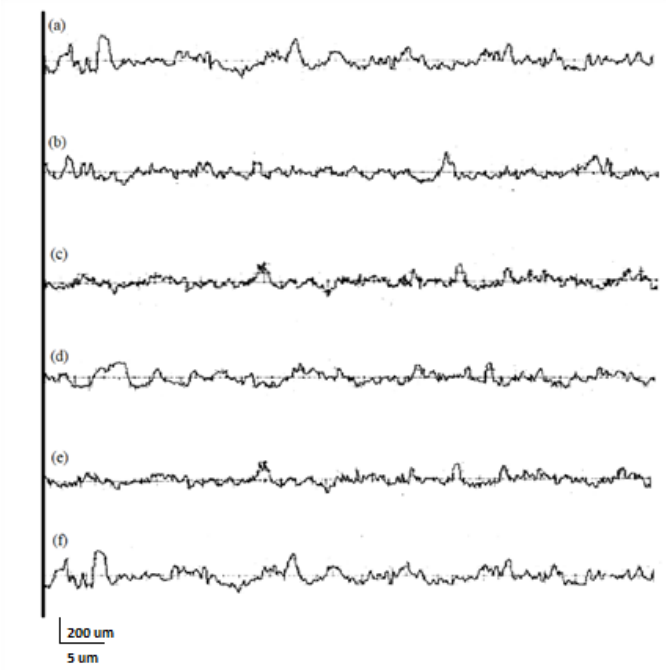

Fig. 4. BC/TiO_2 membrane roughness results at 50% power with time of 30 (a), 60 (b), 90 minutes (c) and 100% power with time of 30 (d), 60 (e), and 90 minutes (f)

During sonication, the shock waves tend to dissolve surrounding filler particles, resulting in the creation of intense turbulence. When the clusters of TiO_2 nanoparticles break down, they are evenly spread out in the matrix, inferring that fewer loose hard TiO_2 nanoparticles are found on the surface in this case. Thus, the roughness of the surface tends to go down as the sonication time goes up [20]. However, sonication is not able to prevent

the aggregation of nanoparticles in the long term and to establish stability at good dispersivity, and as a result, the use of sonication with too long a time gives TiO nanoparticles to move and bind to each other and leads to higher agglomeration and increased membrane surface roughness [21]. The details of the surface roughness of membrane BC/TiO_2 are presented in Table 3.

Table 3 Effect of power and time of ultrasonic homogenizer on surface roughness BC/TiO_2

Power of ultrasonic (%)	Surface roughness (μm)		
	30 min.	60 min.	90 min.
50	1.120	1.008	1.105
100	1.073	1.075	1.205

From Table 3, we can see the roughness value in the 50% sample with a time of 30 minutes is 1.12 μm with a standard deviation of 0.391, as shown in the figure. The lowest value was 1.008 μm with a standard deviation of 0.036 in the 50% sample with a power of 60 minutes. This is because TiO_2 improves the bond's quality, producing it more regular. Furthermore, the roughness continued to increase with increasing power and time in the sample until the roughness was 1.205 μm with a standard deviation of 0.193 for a 100% power sample with a time of 90 minutes. This result is caused by the spread-out nanoparticles fillers are more evenly and end up meeting with other nanoparticles and producing new clumps that finally increase surface roughness [22].

IV. Conclusions

Several conclusions can be drawn based on the data from the testing and analysis of titanium oxide-reinforced nanocellulose membranes, such as that the sonication treatment can affect the distribution and thickness of bacterial cellulose/TiO_2 membranes. The XRD crystallinity results show that the sonication treatment affects the cellulose crystals. The increased sonication treatment significantly caused the peak at an angle of 25^o to disappear. This is due to the fact that solutions-based will break the cellulose/TiO_2 bonds. Because no new peaks were created in the FTIR graphic image, it can be determined that the sonication treatment seemed to have no significant effect on the existing bonds in cellulose. The graph shows that the modifications occur in the O-H bonds of cellulose and the C=C bonds. The lowest roughness value was 1.008 μm with a standard deviation of 0.036 in the 50% sample with a power of 60 minutes. Furthermore, once the power and duration on the sample increased, the roughness increased until it reached 1,205 μm with a standard deviation of 0.193 for a 100% power sample with a length of 90 minutes.

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