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Influence of Copper Oxide Nanoparticles on Properties of Bacterial Nanocellulose **Membrane Made of Pineapple Peel Waste**

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Abstract

Indonesia is the larger pineapple producer country in the world, so they have the potential to generate biomass waste from the peel. Pineapple peel content is a carbon source in the fermentation process for producing bacterial cellulose. Some nanomaterials such as TiO2 and Graphene oxide has been increased the adsorption of ion metal and water purification in nanocomposite membranes. CuO nanomaterial has functioned as an antibacterial material in biomedical applications. So, this study aimed to evaluate the effect of adding CuO nanoparticles (CuO-NPs) to the characteristic of bacterial nanocellulose-based membranes made of pineapple peel waste. The methods include synthesizing bacterial cellulose from pineapple peels and producing bacterial nanocellulose in a high-speed blender and a nano-homogenizer. Raw materials such as BC, CTAB, and CuO-NPs (concentrations of 1.0% and 2.0%) were mixed and homogenized using an ultrasonic homogenizer, then filtered and freeze-dried at -62oC for two days to obtain a membrane. Using SEM, XRD, FTIR, surface roughness, and tensile tester we can see the addition of CuO-NPs can affect the characteristic of BC/CuO nanocomposite. SEM Results show that the surface morphology containing a lower concentration of CuO-NPs has better homogeneity dispersion. From XRD analysis, by addition, CuO-NPs can be appearing new peaks at 35.470 and 38.680, but it reduces the degree of crystallinity, crystallinity index, and Crystalline size of the membrane but increases its surface roughness. Adding CuO-NPs to the BC structure causes a shift and change of transmittance value that indicate the interaction of CuO to BC fibril. The highest tensile strength of nanocomposite membrane is 69.643 MPa, obtained from a lower concentration of CuO-NPs.

Keywords: Bacterial Cellulose, CuO, Nanoparticles, Tensile Strength, Surface Roughness,

1. Introduction

Pineapple (Ananas Camosus L.) is one of Indonesia's most promising types of fruit. Indonesia has a tropical climate that is suitable for pineapple breeding, so Indonesia has become the third largest in Southeast Asia, with a production of 2,447,243 tons [1]. The use of pineapples, in general, is only on the flesh of the fruit. Meanwhile, the peels and hump are thrown away and become garbage. Pineapple peels in various industries also do not undergo further processing. They are often disposed of as waste, with the amount of pineapple peel waste in Indonesia reaching 612 tons per year [2]. Even though this part also still contains sucrose, glucose, and other nutrients [3]. This content can be used as a carbon source in the fermentation process which can be used for the manufacture of bacterial cellulose.

Bacterial cellulose is a fermented product of bacteria and produces a three-dimensional structural matrix formed due to hydrogen bonds [4]. This material has a diameter ranging from 20 to 50 nm. Cellulose produced by bacteria has the same structure as cellulose in plants. For biodegradable packaging, bacterial cellulose can be used as a raw material.

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Bacterial cellulose is constructed of monomeric D-glucose chains, which can be up to 20 µm in length [5]. Because it consists of organic materials with high molecular purity, BC can decompose naturally for 1 month [4]. The production of organic-inorganic nanohybrids can also use BC as a matrix for filter material. This is due to the 3-dimensional network and structural porosity that BC possesses, which make it simpler for antibacterial materials to infiltrate into the cellulose network's deepest layers [6].

Some research has been conducted to support the application of bacterial cellulose as a multi-purpose material with the addition of nanoparticles needs such as TiO2[7], ZnO[8], Fe₃O₄[9], Graphite [10], Ag[11], CuO[12] and Al2O3[13]. Surface modification by nanoparticles with an appropriate method reduces the toxic reagents and enhances the eco-friendly conditions to develop the nanocomposite functions. Copper is one type of metal that has antibacterial properties by directly attacking the bacterial cell membrane and entering the bacterial tissue [14]. They are also a material that has a low price, especially when compared to silver. In addition, the addition of nanoparticles (CuO-NPs) can also affect the mechanical strength of the BC/CuO-NPs composite[15]. This study aimed to evaluate the effect of adding CuO-NPs on morphology, crystallinity, functional groups, mechanical strength, and surface roughness of bacterial nanocellulose membranes made of pineapple peel waste.

2. Research method

2.1 Materials

The pineapple peel was obtained from the city of Malang, East Java, Indonesia. The bacteria used as a starter for cellulose were Acetobacter Xylinum, Sugar ($C_{12}H_{22}O_{11}$), and urea utilized as bacterial fermentation reagents (CH₄N₂O). The surfactant used to assist material dispersion was Cetyl Trimethyl Ammonium Bromide (CTAB) with the Merck brand. The CuO-NPs used were purchased from the brand HW Nano, Guangzhou Hongwu Material Technology Co., Ltd, China.

2.2 Bacterial Cellulose Synthesis

The synthesis carried out refers to the method used in previous research by Suryanto et al. [16]. Pineapple peel juice was prepared using 300 grams of pineapple peel crushed in a high-speed blender with 2 liters of water. 150 grams of sugar and 5 grams of urea were added after boiling 2 liters of pineapple peel extract. Boiling water was used to dissolve the sugar and urea, and once the mixture had cooled to 30° C. The starter bacteria (*A. xylinum*) of 20% were added to the culture medium and kept for a 14-day for the fermentation process. With a thickness of around 1 cm, the produced bacterial cellulose pellicle will float on the surface of the culture.

2.3 Homogenization Process

Before homogenization, the pellicle was washed with 6% NaOH solution for two hours at 90(C) to eliminate impurities and fungus. The pellicle was subsequently cleaned until the pH was normal. Every 5 grams of clean pellicle are combined with 1 liter of water and crushed for 5 minutes at a speed of 26,000 rpm during the homogenization process. After that, a Nano-Homogenizer (AH-100D, Berkley Scientific) was used to homogenize the sample for five cycles at 150 bar of pressure. The solution was filtered using Whatman paper number 42 to produce bacterial cellulose.

2.4 Nanocomposite Synthesis

Three grams of bacterial cellulose, 1% and 2% CuO-NPs, and surfactant CTAB 1% were required to produce a nanocomposite. They were added to 200 ml of water and stirred with a magnetic stirrer for 1 hour. Forty-five minutes and homogenized for 30 minutes using an ultrasonic homogenizer. The solution was dried by filtering using a vacuum machine and Whatman paper no. 42. The membrane formed on paper was dried using the freeze-drying method at -62° C for three days.

2.5 Morphology Analysis

Surface observations were carried out using Scanning Electron Microscopy (Inspect-S50 type, FEI) with a magnification of 25,000 times. Before the test, the surface of the 10 nm gold composite membrane was coated using a sputter coater (Emitech SC7-620) to increase the membrane surface's conductivity to clarify the nanocomposite morphology surface.

2.6 Crystallinity Analysis

Bacterial cellulose nanocomposite was analyzed using XRD (PANanalitycal Expert-Pro) to show the diffraction angle and intensity values. The results were then analyzed using the Scherer and Segal equations to determine the crystal size, degree, and value of crystallinity formed. The test was carried out at 2Theta angle with an angle range of 5°-50° with parameters of CuK α (λ) radiation from 1.54, at 30 mA and 40 kV. Crystal size was measured using the Scherer equation shown in equation 1, while the degree of crystallinity (Cr) and crystalline index (CI) were calculated using the Segal equation shown in equations 2 and 3.

$$\mathsf{Dp} = \frac{(\mathsf{K} \times \lambda)}{\beta \times \mathsf{Cos}\theta} \tag{1}$$

Where:

Dp : Particle size (nm) K : Crystal form factor constanta = 0.94

 λ : Wavelength (nm)

 β : FWHM (°)

θ : diffraction angle (°)

$$Cr = \frac{I_{(002)}}{I_{(002)} + I_{(am)}} \times 100\%$$
⁽²⁾

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100\%$$
(3)

Where $I_{(am)}$ is the intensity of diffraction at an angle of 18°, and $I_{(002)}$ is the maximum intensity of diffraction at 22°-23°.

2.7 FTIR Analysis

Bacterial cellulose nanocomposite frequently changes in molecular bonds and functional groups that can be detected with the FTIR test. The Fourier Transform Infrared spectrometer (FTIR) was used to assess the alterations that took place (Shimadzu IR Prestige-21). The spectra were scanned with a resolution of 4 cm⁻¹ in the 400–4000 cm⁻¹ range. Afterward, the results were compared with the IR Correlation Table.

2.8 Mechanical Strength

The mechanical strength test was carried out using a tensile test with ASTM D638-V, which was used for testing samples with a thickness below 4mm. The test was carried out 3 times, and then the average tensile strength value was calculated. Tensile testing was carried out using a fiber tensile test machine (Techno Lab, Indonesia) with a maximum load is 50 N. Samples were cut following the ASTM D638-V using a scissor and mounted between tensile testing grips. The crosshead rate was set at 3 mm/min for each sample.

2.9 Surface Roughness

The surface of the bacterial cellulose composite membrane was analyzed using a portable surface tester (Surftest SJ-301 type, Mitutoyo Co, Japan) to determine the effect of adding CuO-NPs. The parameters used are 0.75 mN gauge precision, 0.8 mm λc profile filter, average maximum height (Rz), roughness average (Ra), and 4 mm total length. The

roughness measurement rate was 200.0 μ m/cm in a horizontal direction and 5.0 μ m/cm in a vertical direction.

3. Results and Discussion

3.1 Morphology Analysis

Using SEM analysis and 25000x magnification, Figure 1 represents the morphology of the addition of copper oxide to bacterial cellulose nanocomposites. A porous surface was observed in the BC/CuO-NPs nanocomposite membrane synthesized using the freeze-dry drying technique. This porosity happens because the water content in the wet nanocomposite will be frozen to limit the material's mobility and then sublimated, preventing form changes, in the freeze-drying methods after the filter sample is processed under vacuum.

Especially in comparison to bacterial cellulose, bacterial cellulose nanofibers have a larger surface area because cellulose will be able to handle an increase in the number of contact angles when fiber size decreases. This increase in surface area will make it easier for copper oxide and bacterial cellulose fibers to bond. Figures 1(b) and 1(c) show a connection between CuO-NPs and cellulose. The spherical, black, aggregated CuO-NPs are readily apparent.







Fig. 1. Surface Morphology of nanocomposite Bacterial Cellulose: Control (a), 1% CuO-NPs (b), and 2% CuO-NPs (c)

In Figure 1 (b), the addition of 1% copper oxide is well dispersed. This is due to the help of CTAB as a surfactant on the bond between bacterial cellulose and CuO-NPs, as happened in previous studies [10]. While the addition of 2% CuO-NPs, it appears that the nanocomposite agglomeration occurs at several points. This indicates a high increase in surface area and van der Waals forces, so 1% CTAB is considered less capable of accommodating 2% CuO-NPs dispersion.

3.2 Crystallinity Analysis

Figure 2 demonstrates the diffraction pattern that comes from the X-ray diffraction characterization. In the control sample, four primary peaks were observed: 14.4° , 16.7° , and 22.6° . Cellulose I is indicated by these peaks. While cellulose II will occur at an angle of 12.1° and 20° , cellulose I would most likely represent three primary peaks at 14.5° , 16.8° , and $22.6^{\circ}[17]$.



Fig. 2. XRD Result of BC/CuO-NPs Nanocomposite

Bacterial cellulose is a form of cellulose I having crystal planes [110], [1 10], and [200]. Cellulose I has several polymorphs, including triclinic structure (I) and monoclinic structure (I). The strength of the CuO-NPs peaks obtained at 35.4° and 38.6° increased as CuO-NPs % increased [13, 21]. These two peaks represent the type of bonding of monoclinic

crystal planes with [111] and [111] planes on CuO-NPs [12]. Index Miller and XRD testing may be used to estimate a material's crystallinity properties. This crystallinity value will impact the mechanical quality and strength of the nanocomposite. Table 1 provides more information on the crystallinity of the BC/CuO-NPs nanocomposite.

 Table 1. Crystallinity and Peak of nanocomposite BC/CuO-NPs

Sample	Peak in Diffraction Pattern (Degree)					Crystallinity %		BC Crysta
						Cr	CI	l Size (nm)
Control	14.6 7	16.6 4	22.5 7	-	-	88.84	87.4 4	12.86
BC/CuO -NPs 1%	14.3 0	16.7 7	22.5 9	35.4 3	38.6 5	84.12	81.1 2	9.35
BC/CuO -NPs 2%	14.4 5	16.8 6	22.6 5	35.4 7	38.6 8	83.33	80.0 0	9.35

Table 1 illustrate the addition of CuO-NPs into the bacterial cellulose network. CuO-NPs are sufficient to affect the value of the degree of crystallinity and the crystalline index of bacterial cellulose [20], [21]. The crystallinity of a membrane is described by its degree of crystallinity or crystalline index. It is known that a bacterial cellulose control sample without the addition of CuO-NPs has a degree of crystallinity of 88.84% and a crystal index of 87.44%. The degree of membrane crystallinity of BC/CuO-NPs 1% and 2% decreased to 84.12% and 83.33%, respectively. The crystal index decreased to 81.12% and 80%, respectively. The additional substance penetrates the bacterial cellulose network and breaks the crystal chain links. It might decrease the crystallinity value of the cellulose [22] [23]. This reduction in crystallinity also indicates that there is indeed a molecular interaction that occurs between bacterial cellulose and copper oxide.

3.3 Functional Group Analysis

Figure 3 shows the BC/CuO-NPs nanocomposite's FTIR test results. It demonstrates the presence of OH stretching bonds in the valley at a range of 3200-3400 cm⁻¹, where there are loose O-H bonds with the ability to attach to other substances. The C-H bond of bacterial cellulose is represented as a peak in the region of 2900 cm⁻¹; at this wavelength, the transmittance value varies as the amount of CuO-NPs applied grows. The carbon double bond occurs in the wavelength range of 2200 cm⁻¹, indicating a slight change in the peak value, which means that adding CuO-NPs has a slight effect on this bond. The addition of CuO-NPs also affects the transmittance value that occurs at the wavelength of 675 cm⁻¹.

The change in transmittance value in question is the initial value in the control sample is 50.94%. After adding 1% CuO-NPs, the value in the range of 675 cm⁻¹ changes to 28.77%, and the addition of 2% CuO-NPs changes the transmittance value to 33.51%. This shift in transmittance value suggests the presence of CuO-NPs material in the BC/CuO-NPs nanocomposite molecular network. The variations in wavelength between 400 and 700 cm⁻¹ reveal the presence of CuO-NPs [6].

3.4 Mechanical Strength

Figure 4 shows the tensile strength of bacterial cellulose nanocomposites with variations in the addition of CuO-NPs. Based on the bar graph presented, the highest tensile strength was shown by a 1% BC/CuO-NPs nanocomposite

of 69,643 MPa. Then the control material was 40,652 MPa, and in the end, the 2% BC/CuO-NPs nanocomposite was 26.707 MPa. Molecular interactions of BC/CuO-NPs nanocomposites have an important role in the changes in the mechanical strength values. This is due to the effect of adding CuO-NPs to the C-H bonds of bacterial cellulose. Not only C-H bonds but the addition of CuO-NPs also affected the O-H molecular bonds of bacterial cellulose at a wavelength of 675cm⁻¹. Due to its effect on the hydroxyl bonds of bacterial cellulose, it significantly influences the mechanical strength of the nanocomposite [10].



Fig. 3. FTIR Result of the BC/CuO-NPs Nanocomposite



Fig. 4. Tensile Strength of The BC/CuO-NPs Nanocomposite

3.5 Surface Roughness

The results of surface analysis of bacterial cellulose composite membranes using a portable surface tester (Surftest SJ-301 type, Mitutoyo Co, Japan) are presented in Figure 5, and the quantification of surface profile roughness (Ra) is shown in Figure 6. The roughness test was carried out by random sampling at three different points to determine the roughness value of the entire membrane. The addition of CuO-NPs to bacterial cellulose nanocomposite was able to increase the surface roughness value. In bacterial cellulose without the addition of CuO-NPs, the roughness indicated by the Ra value was 2.68 µm. Then there was an insignificant increase in the addition of 10% CuO-NPs to 2.93 µm. The addition of 2% CuO-NPs increased the roughness by 79%. This significant increase caused the roughness value to be 4.8 µm. The increase in surface roughness is believed to be caused by the addition of additives to the less completely dispersed bacterial cellulose

network [24]. The added CuO-NPs are believed to be unable to enter the bacterial cellulose tissue due to agglomeration and collect on the surface of the nanocomposite as shown by the results of morphological tests with SEM [25].



Fig. 5. Roughness Profile of the BC/CuO-NPs Nanocomposite: Control (a) CuO-NPs 1% (b) CuO-NPs (c)



Fig. 6. Surface roughness (Ra) BC/CuO-NPs Nanocomposite

4. Conclusion

Research on the synthesis of bacterial cellulose nanocomposite and copper oxide nanocomposites has been successfully carried out. The method used is a vacuum filtration process and freeze-drying to maintain the porosity. The addition of CuO-NPs nanoparticles can affect the morphology of the nanocomposite by filling the gap in its porosity. In addition to influencing morphology, CuO-NPs are also able to reduce crystallinity values and affect C-H and O-H bonds when analyzed based on the resulting FTIR graph. Mechanically, the addition of 1% CuO-NPs has a significant effect by increasing the tensile strength to 69.643 MPa. The resulting roughness due to the addition of CuO-NPs increased by 79%. The agglomeration of CuO-NPs resulted in filling the porosity gap, which was not well spread, so the roughness continued to increase.

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