

Research Article

Effect of Addition Surfactant on Properties of Bacterial Cellulose Based Composite Foam Reinforced by Copper Oxide NanoparticleHeru Suryanto^{1,2,*}, Uun Yanuhar³, Jibril Maulana¹ and Yanuar Rohmat Aji Pradana¹¹Centre of Excellence for Cellulose Composite (CECCom), Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia²Centre of Advanced Material for Renewable Energy (CAMRY), Universitas Negeri Malang, East Java, Indonesia³Department of Aquatic Resources Management, Faculty of Fisheries and Marine Sciences, Brawijaya University, Jl. Veteran Malang, East Java, Indonesia

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Abstract

Pineapple waste is one of the problems in Indonesia as a larger producer country of this fruit. Pineapple waste is used as a fermentation medium for bacterial cellulose synthesis. The study aims to obtain the effect of the addition of surfactant on the properties of bacterial cellulose (BC) based composite foam with the addition of Copper Oxide (CuO) nanoparticles. The methods were conducted using pineapple peel extract as a medium of BC synthesis. BC pellicle product was disintegrated using a high-pressure homogeniser, and then BC composite foam was produced in the presence of CuO nanoparticles. The surfactant of Polyethylene glycol (PEG) 4000 and Cetyltrimethylammonium Bromide (CTAB) was used. The foaming structure was produced using freeze-drying methods. The foam structure was observed by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR). The SEM result showed that the CTAB as a surfactant makes a more homogenous porosity in the bacterial cellulose. The diffractogram indicates presented crystal peak found at 14°, 16°, 22°, and 28° as cellulose fingerprint structure, and there is a new peak in 28°, 35° and 38° after the addition of surfactant. The FTIR test showed that the surfactant treatment did not significantly change the bacterial cellulose bonds.

Keywords: Bacterial Cellulose, Composite Foam, FTIR, Surfactant, XRD**1. Introduction**

The pineapple (*Ananas comosus L. Merr*) is a popular tropical fruit in the United States and overseas. In the climate of the tropics, this fruit is very easy to cultivate, and the climate in Indonesia is great for it. Indonesia's inclusion in the top ten pineapple exporting countries in the world, with a production of 1.39 million tons in a single year [1]. This large-scale production has a negative impact on pineapple waste, such as peel, core, and crown. As a raw material for the manufacture of bacterial cellulose, more generally known as nata, one of the efforts that may be made to lessen the impact of waste generated is to use it. This is due to pineapple peel's low sugar, fiber, and protein content [2].

Through the fermentation process, *Acetobacter xylinum* or *Gluconobacter xylinum* produce cellulose. Bacterial cellulose (BC) is mainly composed of glucose monomers with the chemical formula $(C_6H_{10}O_5)_n$ [3], [4]. It has a three-dimensional structural matrix with a diameter of 20-50 nm that is constructed by hydrogen bonds [5]. The BC structure is identical to that of plant cellulose, but BC has advantages such as great purity, mechanical strength, and crystallinity, as well as unique physical qualities and biodegradability [3], [5]–[8]. BC can be used to build high paper, photocatalysts, sensors, artificial skin, diet food, biodegradable packaging, artificial blood vessels, water filters, and air filters because of its diverse properties [5], [8]–[12]. However, to increase the mechanical strength and produce these characteristics,

cellulose also needs to be combined with metallic materials such as titanium oxide [13], [14], silver [15], [16], copper oxide [9], [17], [18] and others.

Antibacterial characteristics are found in some types of metal such as silver, copper oxide alumina, titania, zinc oxide, etc. Copper oxide can also be utilised to improve BC mechanical strength. Copper is a relatively inexpensive metal, especially when compared to silver. CuO nanoparticles have the ability to reduce the bacterial population to zero, and when incorporated into the polymer, the release of ions makes it possible to kill bacteria optimally. Copper can also affect the bacterial cell membrane directly, causing it to enter the bacterial tissue. Copper releases Cu^{2+} ions that cause local pH and conductivity changes. Cu^{2+} ions are also small enough to disrupt bacterial cell membranes and gain entry in order to disrupt enzyme function [19]. Surfactants, which can strengthen the bond between metal and cellulose, can be added to increase the bond between cellulose and metal [20]. Surfactants have a molecular structure and an amphiphilic feature that allows them to influence the material's orientation and surface growth. Surfactants are required as a catalyst for the bonding of cellulose and metals, as well as serving additional functions such as defoaming agents, wetting agents, cleansers, and solubilising agents [21]. Surfactants can also help the material have a more steady absorption capacity and be more disseminated, reducing the likelihood of metal agglomeration [22]. The purpose of this research was to observe the effect addition of Polyethylene Glycol (PEG) 4000 and Cetyltrimethylammonium Bromide (CTAB)

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surfactants on bacterial cellulose-based porous membranes with the presence of CuO.

2. Research method

2.1. Materials

Pineapple skin was taken from a honey pineapple vendor's garbage at Malang City's market in East Java, Indonesia. *Acetobacter xylinum* is the bacteria that is utilised to make cellulose. Sugar (C₁₂H₂₂O₁₁) and urea were utilised as bacterial fermentation reagents (CH₄N₂O).

2.2. Bacterial Cellulose Synthesis

Bacterial cellulose synthesis was referred to Sardjono et al. (2018) [8]. A high-speed blender was used for crushing 300 g of pineapple peel waste to extract the juice. Extract of pineapple peel waste added with water until having volume 2 litres then boil it at 100°C for 30 min. The extract was added 150 grams of sugar, and 5 grams of urea, then adding acetic acid to adjust the pH to 4.5. After boiling, the solution is cooled at a room to 30°C. The culture was then supplied with 20% *A. xylinum* bacteria, and the culture was fermented for ten days. The cellulose will float on top of the fluid as a clear pellicle. After harvesting, the pellicle was cleaned with distilled water to remove germs and other residues, then boiled in 1 mol of NaOH for 2 hours at 90°C to eliminate contaminants. The boiled pellicle was rinsed using distilled water until pH 7.0.

2.3. Homogenisation Process

The homogenisation method referred to previously published articles [23]. Fifty grams of pellicle were cleaned before being placed in a high-speed blender with 1 litre of water for homogenisation. Cellulose was blended for 5 minutes at a rotating speed of 26,000 rpm utilising (ICH-DS7, Fomac, China). A High-Pressure Homogenisation (HPH) (AH-100D, Berkley Scientific) machine is used in the fibrillation process. The process was conducted for five cycles and a pressure of 150 bar. After that, nanocellulose was obtained by filtering the bacterial cellulose solution.

2.4. Bacterial Composite Foam Synthesis

By dry weight of BC, 1% CuO and 1% surfactant (PEG4000 and CTAB) were added to a BC solution containing 5 grams of cellulose and 40 ml of distilled water. The BC was stirred for 45 minutes on a magnetic stirrer and was homogenised for 1 hour with an ultrasonic homogeniser. Solution poured into a mould then dried using a vacuum freeze-dried (Berkley Scientific, China) at a pressure of 1 Pa, -62°C for 3-5 days. The dried sample was stored in a desiccator after being inserted into a plastic clip.

2.5. SEM Observation

Scanning Electron Microscope (SEM) testing using an SEM apparatus (Inspect-S50 type, FEI). Prior to testing, the surface of bacterial cellulose was coated with 10 nm gold using a sputter coater (Emitech SC7-620). This test serves to determine the morphology of bacterial cellulose resulting from the addition of PEG4000 and CTAB to the specimen. In addition, the porosity of the specimen can also be further analysed using ImageJ software.

2.6. Structure Analysis

The BC crystallinity structure was analysed using XRD (PANalytical Expert-Pro). Diffractogram of XRD was

conducted to determine BC's degree of crystallinity and crystalline index. XRD scanning was carried out in the range of 2θ of 5° to 50° at parameters of CuKα (λ) radiation from 1.54, at 30 mA and 40 kV [23]. The crystallinity index (CI) and degree of crystallinity (Cr) were calculated using the Segal method:

$$Cr = \frac{I_{(002)}}{I_{(002)} + I_{(am)}} \times 100\% \quad (1)$$

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100\% \quad (2)$$

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

The changes in functional groups in BC composite foam were analysed using the Fourier Transform Infra-Red spectrometer/FTIR (Shimadzu IR Prestige-21). BC composite foam samples of 0.1 mg were ground into powder, added KBr powder of 1 mg, and pressed into a pellet for measurement. The spectrum was recorded using a resolution of 4 cm⁻¹ in the range of 400-4000 cm⁻¹.

3. Results and Discussion

3.1 Morphology Analysis

The morphology of BC composite foam synthesised without surfactant (a), PEG4000 (b), and CTAB (c) are shown in Figure 1. Surfactants can change the shape of the resultant BC composite foam. According to the porosity quantification data, the control treatment, the addition of PEG4000, and CTAB resulted in porosity of 55.23%, 44.8%, and 92.63%, respectively (Figure 2). The percentage of porosity created was reduced by 10.43% when PEG4000 was added. PEG has also been linked to a reduction in porosity homogeneity. This is due to PEG's ability to fill gaps between cellulose fibres (swelling) and its ability to induce the formation of cellulose fibres, resulting in a large number of holes being filled by PEG [24].

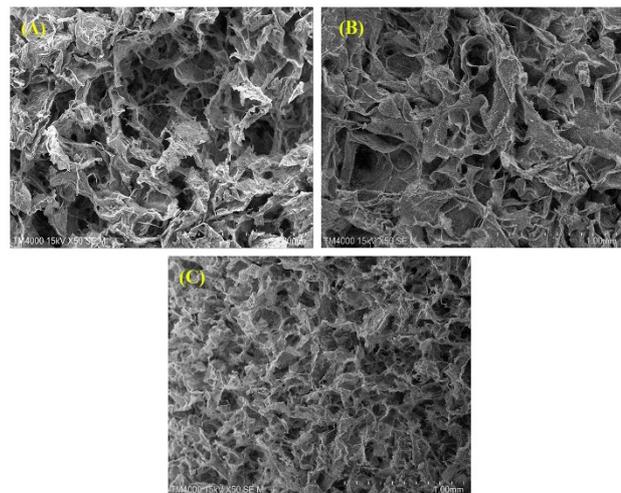


Fig. 1. Bacterial cellulose foam morphology without the addition of surfactant (a), 1% PEG4000 (b), and 1% CTAB.

CTAB could provide a more homogenous porosity when used as a surfactant. It will dissolve and disappear from the substance, resulting in the formation of mesoporous [25]. The

addition of CTAB causes the creation of more homogenous porosity in micelles, spherical or cylindrical structures [26]. It can migrate into the cellulose bond to produce a porous structure material [27]. Besides increasing the porosity homogeneity, the addition of CTAB improves the percentage of porosity by up to 92.63%. This finding is consistent with the previous study, which found that the material's porosity was greater than 80% [28], but the finding porosity is higher than the porosity of surgical filter masks in a range from 77-88% [29].

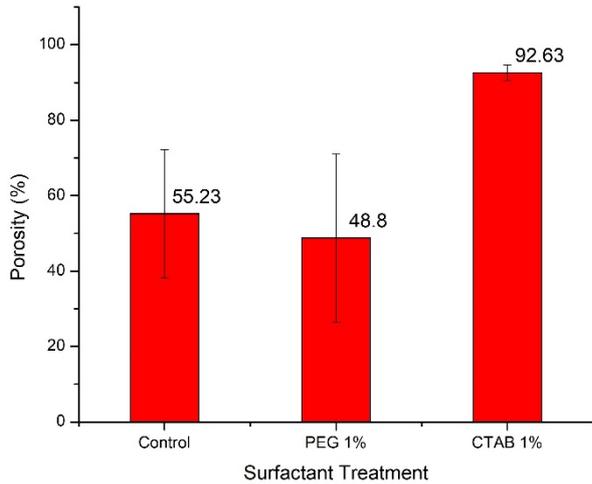


Fig. 2. Porosity of bacterial cellulose foam

3.2 Crystallinity Analysis

Figure 3 illustrates the structure of the nanocomposite foam with the addition of PEG4000 and CTAB with the addition of copper oxide (CuO). The identified peaks in the BC composite foam, the crystallinity degree (Cr), and crystallinity index (CI) of bacterial cellulose with copper oxide are shown in Table 1.

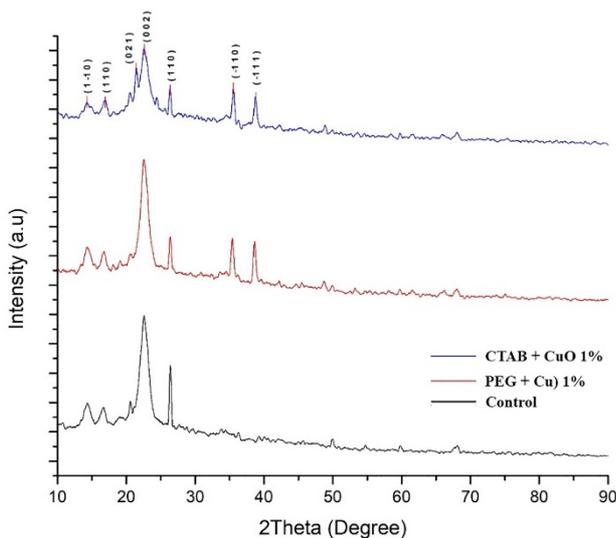


Fig. 3. Diffractogram of bacterial cellulose foam.

X-ray Diffraction was used to investigate the freeze-dry crystallinity of bacterial cellulose reinforced with copper oxide and treated with surfactant. Peaks in the 2θ of 14.3° ,

$16.6-16.9^\circ$, and 22.6° reveal bacterial cellulose structure with crystalline planes of $[1 -1 0]$, $[1 1 0]$, and $[2 0 0]$, respectively [24]. The range of diffraction peaks observed is also compatible with Cai's research in 2010 [30]. At a 2θ of 22° , CTAB surfactant produced the lowest intensity with a value of 192, followed by control material with a value of 266, and finally PEG4000 with a value of 268. Among the crystals formed were cellulose I crystals [31]. Copper oxide (CuO) is responsible for the formation of two peaks at 35.5° and 38.7° angles. This peak appears as a fingerprint in CuO [32].

The effect of PEG 4000 and CTAB as surfactants on the structure of BC composite foam can be seen in Table 1. PEG 4000 treatment resulted in a crystal index (CI) of 81.21% and a degree of crystallinity (Cr) of 76.86%. However, the CTAB treatment resulted in a crystallinity index of 75.88% and a degree of crystallinity of 68.22%. The lower crystallinity of BC composite foam of CTAB treatment result in the foam being more flexible compared to the other treatment. The introduction of carbon bonds resulted in a decrease in the use of CTAB surfactants. The crystallinity index value of the material will drop as the elongation of the carbon bond increases [33]. It formed amorphous based on earlier studies for peaks with a sloping shape of approximately 21.5° [34]. The addition of CTAB results in a new peak at a 21.45° angle to the plane $[0 2 1]$. The presence of new bonds at the molecular level that affects cellulose's structure is assumed to be the cause of the appearance of new crystalline peaks.

3.3 Functional Group Analysis

Figure 4 illustrates the functional group of the nanocomposite foam with the addition of PEG4000 and CTAB with the addition of copper oxide (CuO). Intramolecular and intermolecular hydrogen bonds (O-H group) identified at FTIR spectra range $3,200 - 3,400 \text{ cm}^{-1}$ [35]. CTAB treatment caused an increase in the percentage of infrared transmittance (22.4%) compared to control (19.7%) and PEG treatment (13.2%). It indicates that the presence of OH group in nanocomposite foam reduced, so hydrophobicity properties improved after CTAB treatment. CTAB is a surfactant with symmetric and asymmetric CH_2 alkyl chain vibrations at $2,850$ and $2,917 \text{ cm}^{-1}$, respectively. The presence of CTAB bonds adsorbed on single cellulose fibrils caused changes in the FTIR spectra at $2,850 \text{ cm}^{-1}$ absorptions [36]. Satish et al. [37] observed that the peaks detected in the range of $2,924$ and $2,852 \text{ cm}^{-1}$ indicate the presence of asymmetric stretching C- CH_3 bonds and N- CH_3 symmetric stretching vibrations in CuO and surfactants. This bond demonstrates that CTAB and copper oxide have formed a bond. The use of CTAB and PEG4000 as surfactants reduces the wavenumber of $1,900 \text{ cm}^{-1}$, which is a C-H bending aromatic molecule. This indicates that the cellulose-cellulose link transforms into a surfactant-surfactant bond. The cellulose-CTAB linkages changed in the form of vibrations from symmetric H=C=H in the form of alkyl bonds from CTAB and the trimethyl groups from quaternary ammonium at wave number $1,480 \text{ cm}^{-1}$ [38]. Besides the cellulose bond, minor jagged peaks in the range of 572 , 524 , and 428 cm^{-1} imply CO_3^{2-} and Cu-O bonds, indicating the presence of surfactant-CuO-cellulose interconnections [37]. The addition of cationic surfactants, such as PEG4000 and CTAB, improves the hydrophobicity of the nanofibril surface [20], [34]. This surfactant's application will boost penetration by lowering surface tension, allowing it to bond two distinct materials [21].

Table 1. Crystallinity structure of BC composite foam

Sample	Peak at diffractogram						Crystallinity (%)	
							Cr	CI
BC	14.32	16.64	22.57	28.3	-	-	81.59	77.43
BC + PEG4000 + CuO	14.35	16.75	22.56	28.7	35.5	38.4	81.21	76.86
BC + CTAB + CuO	14.43	16.9	22.64	29.1	34.5	38.7	75.88	68.22

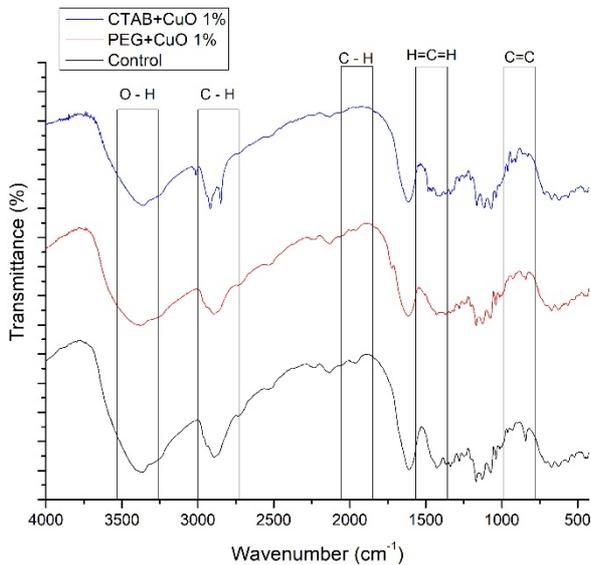


Fig. 4. FTIR result of bacterial cellulose foam

4. Conclusion

This work has successfully synthesised BC composite foam reinforced by copper oxide nanoparticles. The addition of surfactants affected their morphology. The addition of

PEG4000 successfully produces a homogeneous porous structure composite foam. Its porosity reaches 92.63%. XRD analysis show some distinct peak at 2θ of 14.3° , $16.6-16.9^\circ$, and 22.6° that belong to crystalline peak $[1 -1 0]$, $[1 1 0]$, and $[2 0 0]$, respectively. The crystallinity index of the composite foam with CTAB addition is lower than the PEG4000 addition. BC composite foam with CTAB addition has a new peak at 2θ 21.45° . There is a bond change indicated by peak change at $\sim 2,850 \text{ cm}^{-1}$ because of the presence of CTAB. The peak at wavenumber $2,924$ and $2,852 \text{ cm}^{-1}$ indicate that C-CH₃ bond asymmetric stretching and N-CH₃ symmetric stretching, respectively, belong to vibrations from the reaction between CuO and CTAB. In the future, these findings will be expanded as the candidate of material for air filtering systems for improving healthy human air.

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