Morphology and structure of bacterial cellulose film after ionic liquid treatment

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Abstract. Chemical treatment like ionic liquid is known as a green solvent had developed to improve the compatibility of bacterial cellulose in many composite applications. This study aimed to know the influence of treatment using the ionic liquid on the morphology and structure of bacterial cellulose film (BCF). The methods used a BCF made of pineapples peels waste. Pellicle, as fermentation product as long as 14 days, washed by distilled water then immersed to an ionic liquid solution such as 1-Butyl-3-methylimidazolium chloride (BmimCl) for 2 h with concentrations of 0%, 2.5%, 5.0%, and 7.5%. Treated BC pellicle was dried in an oven for 6 h for obtaining bacterial cellulose film (BCF) then observed by XRD and SEM. The result showed that the treatment using BmimCl change the surface morphology and structure of BCF. BmimCl solution with a concentration of 5.0% and 7.5% show cause some holes in the surface of bacterial cellulose film. BmimCl solution treatment changed the structure of BCF, indicated by the increasing the peak intensity of diffractogram at a diffraction angle of 14.4° and 22.7°. Crystalline content after treatment by BmimCl with concentrations of 0%, 2.5%, 5.0%, and 7.5% were 73.85%, 73.50%, 71.33%, and 72.81%, respectively.

1. Introduction

Recently, natural materials have been applied as materials for various biodegradable technology equipment. The bio-based product has increased in the application. The cleaner production and green technologies adopted as a universal goal for the preservation of natural resources. The microorganisms have a critical role in green technology processes [1].

Cellulose is a renewable material that abundant availability and widely known as natural polymers. It has interested because of its main properties, such as chemical and thermal stability, biodegradability, and biocompatibility. Product cellulose has been applied for textile, pulp, and paper production. Besides the plant, some microbes, including diverse aerobic bacteria, fungi, and algae used as an alternative agent to produce cellulose. Bacterial cellulose (BC) is a secretion from bacteria, and the most famous bacteria used for it is Acetobacter xylinum [2]. As a product of bacteria, BC has purity close to 100% with high crystallinity [3] and has nano-sized particles in the form of nanofiber, similar to silk natural fiber.

Ionic liquid (IL) is molecules that have a composition of cations and anions containing at least one component is an organic molecular structure. They comprise organic salts with any additives such as water or other solvents over a wide range of temperature. IL technology applied in cellulose processing to obtain cellulose-based materials and to produce cellulosic fibers [4]. The unique features of
conventional IL (such as wide excellent thermal stability, large electrochemical window, extremely low vapour pressure, stable liquid range, and but most particularly their molecular tailorability) are responsible for their exploration for a wealth of purposes including those pharmaceutics, battery technology, crystal engineering, CO\textsubscript{2} capture, biodiesel synthesis, liquid fuel desulfurization, and separations [5]. IL consist of anions and cations that different in size and possess conformational flexibility. These different anions and cations have different reactions to the reacted compounds. Therefore, this study purpose of obtaining the effect of IL in the form of BmimCl on morphology and structure of bacterial cellulose film (BCF).

2. Methods

2.1. Production of BC Pellicle

BC pellicle production refers to Suryanto (2018) [6]. It used a medium containing extract of pineapple peel of 2.0 L, acetic acid of 5\%v/v, ammonium sulphate of 0.5\%, and sugar of 10\%. The medium was fermented by A.xylinum of 10\%(v/v), adjusted at pH 4.5. Under static conditions, the process of fermentation was done for 14 days at 30 °C. Product of BC pellicle harvested then washed using distilled water until clean.

2.2. Ionic liquid treatment

BC pellicle was dissolved in BmimCl with various concentrations of 2.5\%, 5\% and 7.5\% on a magnetic stirrer hotplate then heated 80 °C for 120 min. At the end of the process, BC pellicle is washed with distilled water, then dried in the oven at 70°C for 6 h and kept into the desiccator.

2.2.1. XRD Analysis

The biocomposite structure was scanned by XRD analyzer (PanAnalytical X-Pert Pro Diffractometer) using CuK\textalpha radiation (\(\lambda = 1.540598\) Å) at 30 mA, 40 kV in the room temperature. Biocomposite film had a dimension of 10x10 mm\textsuperscript{2} in the area and 200 μm in thickness. Scanning step was done at a rate of 0.02°/scanning at range from 10° to 60° [7]. The Segal’s equation (Eq. 1) was applied to calculate the crystallinity (%Cr) [8]:

\[
\text{%Cr} = \frac{I_{(110)}}{I_{(am)} + I_{(110)}} \times 100\%
\]

where: \(I_{(110)}\) = diffraction intensity peak of crystal plane (110) at about 22°

\(I_{(am)}\) = lowest diffraction intensity of amorphous at about 18°

2.3. SEM Observation

Before observation, coating process using 10 nm gold on the BCF was conducted in the sputter coater (SC7-620 Emitech). The surface morphology of BCF was observed by Scanning Electron Microscopy (SEM) (FEI, Inspect-S50) at 30.00 kV.

3. Results and Discussion

3.1. Morphology

Testing materials with SEM was the surface appearance of cellulose bacteria film formed with variations in the ionic liquid of 2.5\%, 5\% and 7.5\% was shown in Figure 1. In the control sample, the surface morphology of BCF is smooth and many BC fiber appearance (Figure 1a). After treated by 2.5\%, BC fiber is more clearly appearance (Figure 1b). Increasing concentration of BmimCl cause surface of BCF is rough and show high porosity (Figure 1c and 1d). It indicates that a higher concentration of IL for treatment make damage on the surface morphology of BCF.

Chemical treatment of cellulose aimed to clean the surface, and modify the surface chemically, stopping the process of moisture absorption, increasing the roughness of surface [9], [10]. Bacterial
cellulose films were formed from fiber networks arranged irregularly or randomly in three dimensions during the fermentation process produced by bacteria. Network ribbons of BC build a dense reticulation structure with extensive hydrogen bonds as a structure stabilizer and have 1 to 9 μm in length [11]. Morphological changes after the chemical treatment caused the expansion of cavity size and decrease in fiber size. Based on research that has been carried out morphology of bacterial cellulose fibers formed with interconnected fibril tissue containing bonds. If bacterial cellulose films being observed, there were fibrils appeared that have three-way branching points, this type of branching caused the bacterial cellulose film has a unique nature. Cellulose fiber treatment using ionic liquid can dissolve by 2% using a temperature of 110-150 °C. Because the nature of BmimCl is a type of solvent, it can cause cellulose fibers to break down from hydrogen bonds to produce particles and fibers that look irregular and fragile.

![Figure 1. Surface of the BCF after BmimCl treatment: (a) control (b) 2.5% (c) 5.0%, (d) 7.5%](image)

The chemical treatment of bacterial cellulose film was able to increase porosity because this bacterial cellulose film was broken down which caused the amount of pore was increase and water could be absorbed into the film [12].

3.2. Structure of BCF
The diffractogram of BCF after treatment with BmimCl is shown in Figure 2. There are three peaks that appear in diffraction peaks of 14.4°, 16.7°, and 22.7°. These peaks are similar with BNC film that treated with high-pressure homogenization at peaks of 14.3°, 16.4°, and 22.5° that indicate the plane crystal of (100), (010) and (110), respectively [13].

After treatment with BmimCl, BCF do not undergo change structure. BCF has a crystal structure of cellulose Iα [14] that formed triclinic structure with $\alpha = 117^\circ$, $\beta = 113^\circ$, $\gamma = 81^\circ$; $a = 0.674$ nm, $b = 0.593$ nm, $c = 1.036$ nm [13]. Crystallinity of BCF after treatment in ionic liquid BmimCl are 73.85%, 73.50%,
71.33%, and 72.81% at concentration of 0%, 2.5%, 5.0%, and 7.5%, respectively. It shows that the crystallinity of BCF is decreased and correlated with the morphology of BCF that show damage. IL treatment in a concentration of more than 2.5% able to able to dissolve cellulose, break down the cellulose bond so that decreasing regularity of cellulose bond. The fibrillation, shortening, and degradation of the cellulose fibers cause a reduction of the quantity and quality of the cellulose product [15]. This results in strengthened by Zhang et al. that adding pretreatment process using ultrasound can reduce the crystallinity of cellulose, improve the enzymatic hydrolysis effect and damage of the surface morphology and chemical structure [16].

4. Conclusion
Synthesis and characterization of BCF and the effect of IL of BmimCl treatment have been made to investigate. The treatment using BmimCl change the surface morphology and structure of of BCF. The higher concentration of BmimCl for treatment make damage on the surface morphology of BCF. Analysis using XRD indicate that BmimCl treatment decreasing the degree of crystallinity of BCF and correlated with the morphology of BCF that show damage. In the future, this optimum treatment can be adopted as pretreatment in polymer composite reinforced by bacterial cellulose.

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Acknowledgment
A great appreciation was delivered to the LP2M Universitas Negeri Malang with a research grant of PNBP 2020.