The Effect of Chemical Pretreatment Process on Mechanical Properties and Porosity of Bacterial Cellulose Film

Tito Arif Sutrisno[1], Heru Suryanto[2,*], Retno Wulandari[2], M. Muhajir[1], Shikh Mohd Shahrul Nizan Shikh Zahari[3]

[1]Master Student of Mechanical Engineering Program, Graduate School, Universitas Negeri Malang, Jl. Semarang 5, Malang, East Java, Indonesia
[2]Mechanical Engineering Department, Engineering Faculty, Universitas Negeri Malang, Jl. Semarang 5, Malang, East Java, Indonesia
[3]Industrial Chemical Technology Program, Faculty of Science and Technology, Universiti Sains Islam Malaysia, Bandar Baru Nilai 71800, Negeri Sembilan, Malaysia
**Corresponding author: heru.suryanto.ft@um.ac.id*

ABSTRACT

Bacterial cellulose (BC) is a natural polymer which have superior properties, like high porosity, high purity, and high permeability. The study objective is to determine the influence of chemical pretreatment on tensile strength and the porosity of BC. The method was to make BC films from pineapple peel extract through fermentation process for 14 days. The pretreatment was conducted by immersion of BC in BmimCl, H_2O_2, and NaOH solution with a concentration of 2.5%; 5%; and 7.5 %, heated at 80 °C then dried in the oven, and the samples were then tested by a tensile test using ASTM-D636-V standard, morphology analysis using Scanning Electron Microscope, and porosity analysis. The results indicate that the tensile strength of control sample was 123 MPa, whereas after chemical pretreatment, the tensile strength was decreased with the greater reduction occurred using NaOH pretreatment compared than the other solutions that having a lower tensile strength of 8.54 MPa at 7.5 % of NaOH. The results of porosity show that the value increased after being treated chemically. The BC film porosity was 87.13% after NaOH treatment of 7.5% while BC film untreated had porosity of 19.15%. This phenomenon was occurred due to the increasing pore, so the absorption of water increased.

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I. Introduction

At present, natural materials, like fiber, has been applied as materials for various biodegradable technology equipment. Cellulose produced by bacteria had a specific character and more purer than plant cellulose [1]. Plant cellulose is impure because of containing a complex carbohydrates like cellulose (35-50%), hemicellulose (20-35%) and lignin (10-25%)[2][3].

Nata, known as bacterial cellulose (BC), able to be produced using fruit extracts [4][5]. BC pellicle is produced from the glucose fermentation by *Acetobacter xylinum* bacteria for resulting the cellulose. BC films have advantages as paper, food, biomedicine, and filtration

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membranes [6]-[8]. BC is a natural polymer which have superior properties, like high degree of porosity, high purity, high permeability relative to gases and liquids, strength and ultrafine tissue, and high water absorption [8]. BC has a high surface activity because of its fibril; its tensile modulus can reach 16-30 GPa. Viewed from its structure, BC has a very fine band-shaped fiber network with a fiber diameter of 20-100 nm [9]. The BC contents are glucose, fructose, sucrose, and mannitol [10]. BC, with its hydrophilic properties, can absorb a high level of water content [11]. BC forms a thin and transparent layer on the surface, and its thickness can be increased over time, forming thick white sheets after 10-15 days [5].

Cellulose films can be modified using several methods, including mechanical, enzymatic, and chemical treatment. The chemical pretreatment method applied to reduce amorphous constituents and increasing its thermal stability [12]. The benefits of chemical treatment are to clean and modify the surface chemically, increase the surface roughness and to stop the moisture absorption process [13][14]. The four main classes of solvents are NaOH solution, ionic liquids, and hydrogen peroxide (H_2O_2). NaOH is dissolving, which causes the breaking of hydrogen bonds in the structure of BC pellicle network so that it can increase the surface roughness [15]. The hydrogen peroxide ussualy used as bleaching agent [16]. The ionic liquid is an organic solvent that is harmless and environmentally friendly [17]. The study objectived for describing influence of pretreatment of NaOH, H_2O_2, BmimCl on the strength, porosity and morphology of BC surface synthesized by fermentation of pineapple peel waste.

II. Methods

A. Materials

The study used pineapple peel extract and *A. xylinum* for fermentation process for 14 days, aquades, and chemical solution (NaOH, H_2O_2, BmimCl).

B. Bacterial Cellulose Synthesis

The synthesis methods of BC pellicle was addapted from Suryanto (2017) [18]. BC production used fermentation media containing 2000 ml extract of pineapple peel, ammonium sulphate of 0.5%, acetic acid of 5% (v/v) sugar of 10%, and the fermentation medium with pH 4.5. Medium was added by *A. xylinum* of 10% (v/v) for fermenting process conducted for 14 days at 30°C. The pellicle was collected then washed by fresh water to remove the dirt.

C. Bacterial Cellulose Pretreatment

BC pellicles were boiled to remove bacteria and acid content, afterward, they were rinsed using water then took BC pellicles to be and treated in all chemical solutions (NaOH, H_2O_2, and BmimCl). After that, BC was put into 250 mm^3 beaker glass with four variations of a chemical solution (control, NaOH, H_2O_2, and BmimCl) each with different chemical solution concentration of 2.5; 5; and 7.5 % into solution with a total volume of 100 mm^3,

thus, the BC pellicles can be fully immersed and took the glass on a hot plate (SP131320-33 type, Thermo Scientific) then heated until 80°C and stirred by 100 rpm. BC pellicles were rinshed using water until netral and then drying process conducted in an oven for four hours at 80°C. Before putting them to the oven, BC pellicles were clamped to get smooth sheets.

D. Tensile Test

The strength of the BC film were observed by tensile test in Techno Lab. Indonesia based on ASTM D638-V standard. The samples having a length of 26.35 mm were attached at the clamping system of the tensile test machine and tested with a pulling speed of 0.025 mm/s. Each sample was tested for five repetitions. Tensile strength was calculated by formula [19]:

$$\sigma = \frac{F}{A_o} \tag{1}$$

Where: F is force (N), σ is tensile strength (MPa), A is cross-sectional area (mm^2).

E. BC Porosity Test

The porosity of samples was tested before and after chemical treatment. The samples were immersed for 4 hours at a temperature of 25^0C. W_d is defined as sample weight measured at dry condition (weighed in the air) while W_w is defined as sample weight measured by submerging them in the water. The porosity was calculated using equation [20]:

$$Porosity(P) = \frac{(Ww - Wd)}{(dxAxD)_o} x100\% \tag{2}$$

Where: W_w and W_d is the wet film weight (g) and dry film weight (g), respectively, d is the pure water density at ambient temperature (1 g/cm^3), D is the film thickness, and A surface area (4 cm^2).

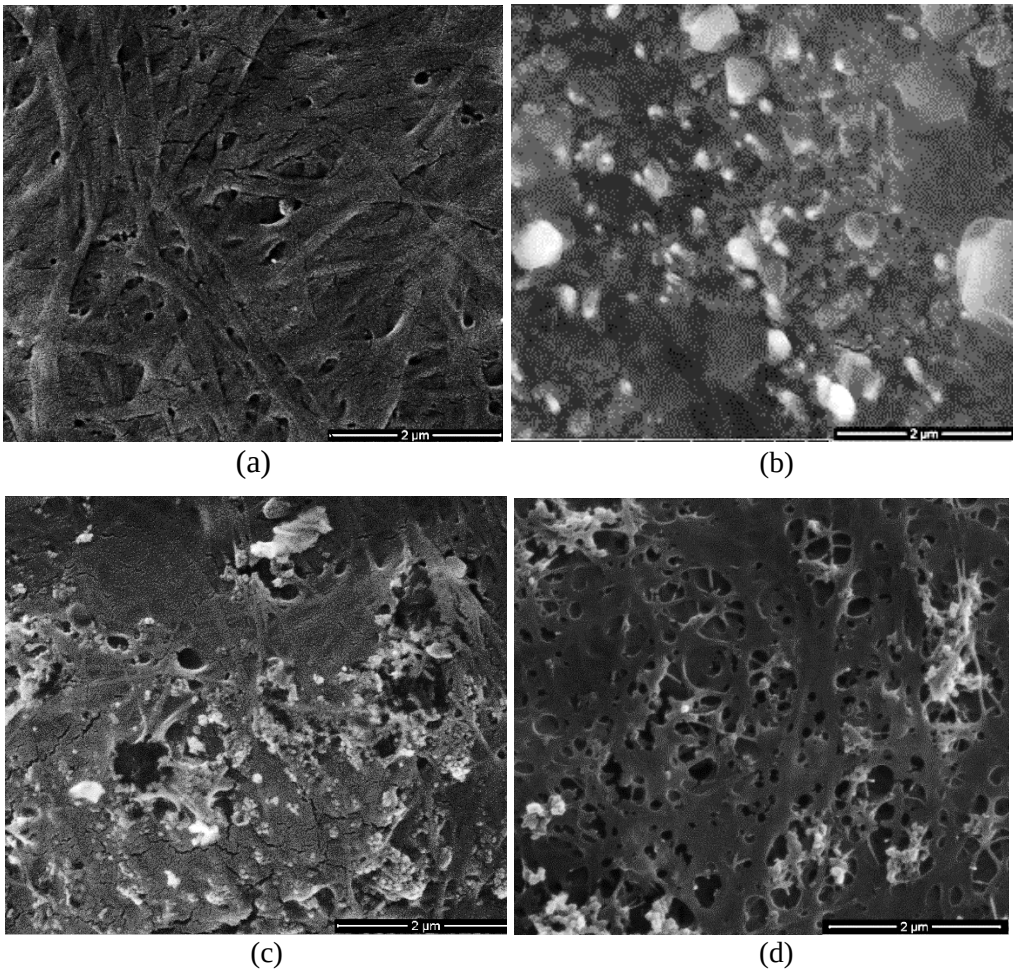
III. Results and Discussion

A. Morphological Analysis

The surface morphology of BC film formed after chemical pretreatment using the concentration of 2.5; 5; and 7.5 % were analyzed using scanning electron microscopy (SEM) with 50000 times of magnification. The SEM analysis was utilized to compare the morphology of all chemically-treated sample and untreated sample (control). The SEM images of BC film are presented in Figure 1.

Chemical pretreatment of cellulose aimed to clean the surface, modify the surface chemically, increase the surface roughness, and reduce the moisture absorption [13],[14]. BC films were formed from fiber networks arranged irregularly or randomly in three dimensions during the fermentation process produced by bacteria [18]. Morphological

changes after the chemical pretreatment caused expansion of cavity size and decrease in fiber size. Based on research that has been carried out, the morphology of BC fibers formed by interconnected fibril tissue containing bonds. If BC films were observed, there were fibrils appearance having three-way branching points. This type of branching caused the BC film to have a unique nature. NaOH is in the form of white crystals and is dissolving, causing the rupture of hydrogen bonds in the structure of BC pellicle networks. Therefore, it can increase the surface roughness [15]. Pretreatment using NaOH can be harmful to the BC fiber because of its extremely high degradation [21]. Alkali pretreatment of cellulose affects the fiber structure, pore size, and particle size of cellulose, the cellulose of excess NaOH concentration causes damage to the cellulose surface [22]. Hydrogen peroxide also has several advantages such as fiber treatment which has a high resistance and a tiny decrease in fiber strength [23]. Cellulose fiber can be dissolved by using an ionic liquid of 2% at a temperature of 110-150 °C. Because the nature of BmimCl is a solvent, it can cause cellulose fibers to break down from hydrogen bonds to produce particles and fibers that look irregular and fragile.



(a) (b)

(c) (d)

Fig 1**.** The **s**urface of the BC Film (a) control (b) 7.5% NaOH (c) 7.5% H_2O_2 (d) 7.5% BmimCl

B. Mechanical properties

Figure 2 shows a bar chart of tensile strength, as mechanical properties indication, before and after pretreatment using BmimCl, H_2O_2, and NaOH. The value of the tensile strength of BC with aquades (control) is 123 MPa. In general, the tensile test value decreased after being treated chemically. At 2.5% NaOH concentration showed a tensile strength value of 33.02 MPa. The 2.5% H_2O_2 treatment was 44.62 MPa, and 2.5% BmimCl treatment was 83.37 MPa. At 5% concentration NaOH treatment tensile test value of 11.8 MPa, with H_2O_2 treatment tensile test value of 29.9 MPa, and BmimCl treatment tensile test value of 42.25 MPa. At a concentration of 7.5% BC with NaOH treatment tensile test value was 8.54 MPa, with H_2O_2 treatment equal to the tensile test value of 16.84 MPa, and with BmimCl treatment tensile test value was 22.36 MPa.

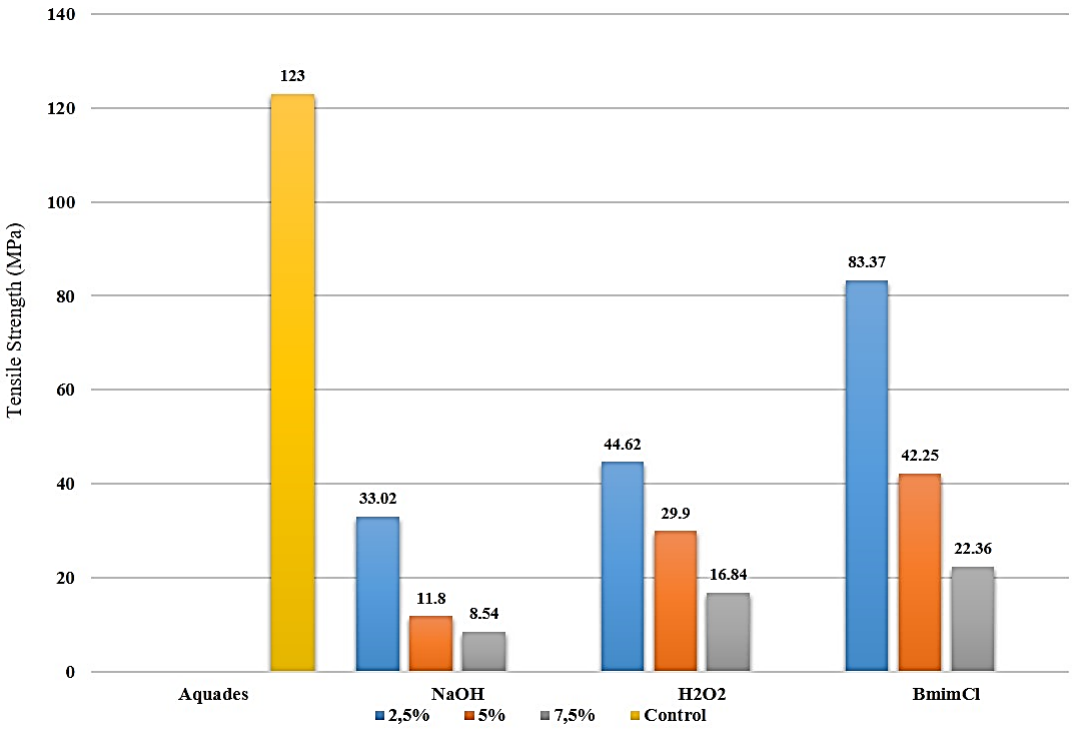


Fig. 2. The Tensile Strength of BC Before and After Chemical Treatments

After the chemical treatment, a reduction in tensile strength was caused by the dissolution or exfoliation occurred on BC fiber, so the binding capacity between fibers becomes brittle. The improvement and reduction of tensile strength were influenced by fiber network structure interaction between hydrogen bonds [24]. The results of tensile strength in the control sample showed the highest tensile test value because BC pellicles remained intact, or the solubility does not occur. Therefore, the fibers in BC had stronger surface bonds. Cellulose consists of a large number of hydrogen bonding networks with intra- and inter-molecular H bonding networks insoluble in water [24][25].

High chemical and mechanical stability of cellulose and its hydrophobic properties were caused by strong glycoside bonds and very high levels of hydrogen bonds [26]. In this study, it shown that the chemical treatment of BC causes the tensile strength to decrease. Treating cellulose using NaOH caused transformation of cellulose I to cellulose II, which caused a reduction of the modulus [27]. The use of hydrogen peroxide in BC treatment caused tensile strength to drop because of the nature of hydrogen peroxide could cause the dissolution of BC pellicles. The treatment of H_2O_2 against cellulose caused oxidation [28]. The ionic liquid is considered a harmless organic solvent because it can be recycled and is environmentally friendly [17]. The application of ionic liquids on chemical treatment of BC led its tensile strength to decrease because BmimCl is a type of organic solvent.

C. Porosity Analysis

Analysis of film porosity as shown in Figure 3 that show the results of porosity testing from BC before and after chemical pretreatment using BmimCl, H_2O_2, and NaOH at a concentration of (a) 2.5%; (b) 5%; and (c) 7.5%.

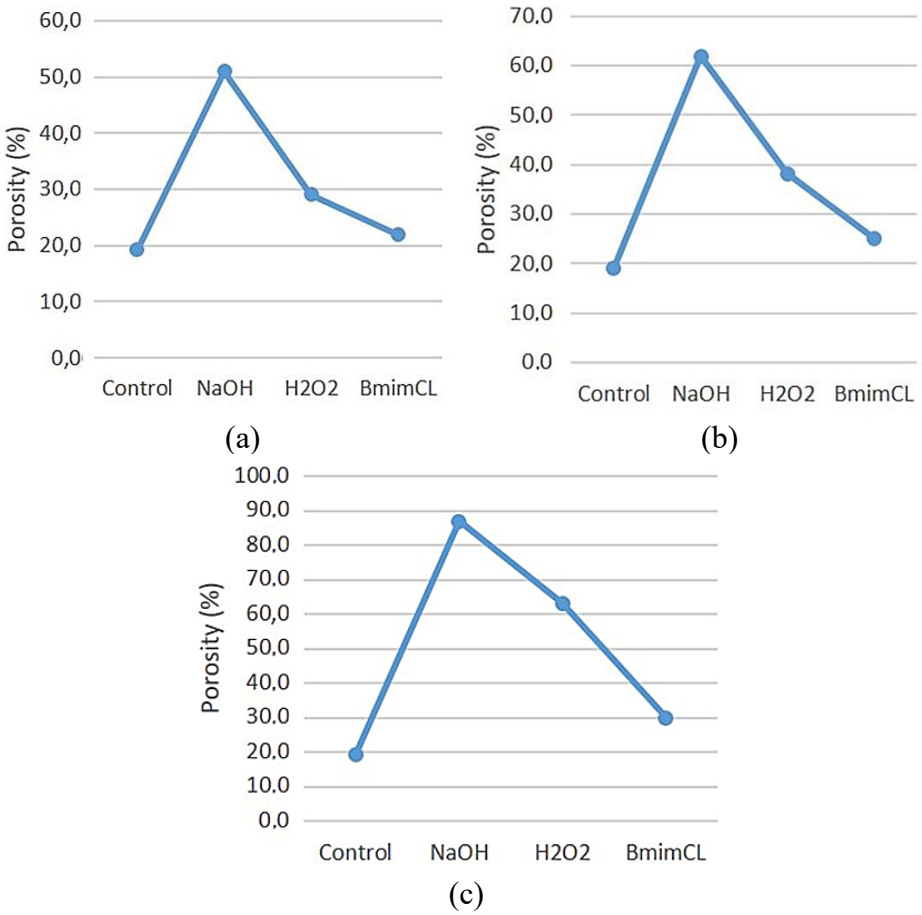


Fig 3. The Porosity of BC film before and after treatment at the concentration of (a) 2.5; (b) 5; and (c) 7.5%

The porosity of the control was 19.15%. In general, after the chemical pretreatment, the amount of porosity increased. The pretreatment of BmimCl, H_2O_2, and NaOH with concentration of 2.5% resulted porosity by 21.88%, 28.99%, and 50.94%, respectively. The pretreatment of BmimCl, H_2O_2, and NaOH with concentration of 5% resulted 25.08%,38.18 %, and 61.90%, respectively. The pretreatment of BmimCl, H_2O_2, and NaOH with concentration of 7.5% resulted porosity by 30.06%, 63.32%, and 87.13%, respectively. Porosity was influenced by the transport of oxygen and water diffused into BC [29]. The chemical treatment of BC caused the particles in BC to be chipped and more damaged, causing water to be easily diffused. Narrowing the inter-cavity could reduce water vapor transmission, so the water vapor transmission rate affected the ability of the film to hold the water vapor [30]. The chemical pretreatment of BC film was able to increase porosity because BC tissue was broken down, causing an increasing number of pores and water could be absorbed into the film. After the pretreatment, the porosity produced was higher because BC had a network of nano and microfiber with a porous structure, so it provided space for diffusing water. Thus, the more pores formed made, the easier absorbability on water.

IV. Conclusions

Morphological analysis, porosity, and mechanical properties with variations of chemical solutions were carried out. On the whole, the chemical pretreatment affected the character of BC. The results of the tensile test showed that the chemical pretreatment of the BC film could reduce tensile strength. The addition of chemical solutions (NaOH, H_2O_2, BmimCl) caused the dissolution on BC pellicles. The fiber of BC film dissolved and peeled. Therefore the binding capacity between fibers becomes brittle. The chemical pretreatment of BC film was able to increase porosity because the BC film was broken down, causing an increase of pore amount and water absorbability into the film.

Acknowledgments

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