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Physical and Mechanical Properties of Modified Bacterial Cellulose Composite Films

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Abstract. To open wide range application opportunities of Bacterial Cellulose (BC) such as for agricultural purposes and edible film, BC slurries were blended with Glycerol (Gly), Sorbitol (Sor) and Carboxymethyl Cellulose (CMC). The physical and mechanical properties of BC composites were investigated to gain a better understanding of the relationship between BC and the additive types. Addition of glycerol, sorbitol and CMC influenced the water solubility of BC composite films. FTIR analysis showed the characteristic bands of cellulose. Addition of CMC, glycerol, and sorbitol slightly changed the FTIR spectrum of the composites. Tensile test showed that CMC not only acted as cross-linking agent where the tensile strength doubled up to 180 MPa, but also acted as plasticizer with the elongation at break increased more than 100% compared to that of BC film. On the other hand, glycerol and sorbitol acted as plasticizers that decreased the tensile strength and increased the elongation. Addition of CMC can improve film transparency, which is quite important in consumer acceptance of edible films in food industry.

INTRODUCTION

Bacterial cellulose (BC) is a natural biopolymer which is obtained from bacterial *Acetobacter xylinum* activity on a medium containing glucose as a carbon source [1]. It is very unique and interesting material, because it has both great mechanical strength and biodegradability in comparison with green plant cellulose or synthetic polymers [2,3]. BC film has a potential to replace synthetic polymers due to its high chemical purity and other excellent qualities such as high mechanical stability and strength. Today, BC was used commercially in a wide range application from foods to functional materials such as diaphragms in speakers and headphones, electronic devices, wound dressings, high-quality additive to paper, artificial skin, cellulose derivative, optic material, edible strips and membrane filter [3-8].

Much effort has been focused on developing bioplastics or edible films and coatings by blending renewable materials. When BC only was cast into film, the resulted film was relatively britlle [9]. BC is also known as an insoluble biopolymer due to its rigid crystalline structure owing to strong inter- and intramolecular hydrogen bonding [10]. Therefore, the addition of plasticizer agent to BC film was required to overcome film brittleness as well as to improve film solubility. Information about the effects of Carboxymethyl Cellulose (CMC), glycerol and sorbitol on physical and mechanical properties of composite films from BC is poorly available at present. The aim of this investigation was to make a comparative study of different types of additive and plasticizers incorporated into BC films.

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EXPERIMENTAL WORK

Washing, Purification and Preparation Slurry of BC

BC gels were purchased from local industry in Cianjur, province of West Java, Indonesia. BC gels were washed thoroughly in running tap water until its pH was neutral, then boiled with NaOH 1% w/v for 1 h to remove non cellulosic compound and to eliminate bacterial cell. Finally, they were washed again in running tap water to remove remain alkali solution on the BC until its pH was 7. Slurry of BC was prepared by cut of BC gels into cubes and blended for about 1 h using kitchenaid blender and stored in refrigerator. All pretreatment was conducted at room temperature.

Preparation of Bacterial Cellulose Composites

The blend films were composted of 30% w/w glycerol (gly), sorbitol (sor) and CMC over dried BC. Prior to mixing with BC slurry, CMC was solubilized in distilled water, while glycerol and sorbitol were used in the form of solution. Those additives were mixed with BC slurry in a beaker glass under magnetic stirring condition. Subsequently, the solutions were degassed under a vacuum bell jar to remove the bubbles, and then they were poured on the tray and cast. The trays were held overnight at 45 ^{o}C in gear oven, and then cooled to room temperature before peeling the films off the trays.

Characterization of BC Composite Films

The film solubility was determined according to the method of Ojagh et al. [11]. Film pieces 20 mm x 20 mm were dried at 110 ^{o}C in an oven and then weighted to the nearest 0.0001 g for the initial dry weight. Afterthat, films were immersed into 20 ml of distilled water at 60 ^{o}C for 3 h. The remaining solution and film pieces were poured onto nylon filter, rinsed with 10 ml distilled water, and dried at 110 ^{o}C in an oven for 24 h. The dried weights of the films were determined. Duplo measurements were conducted for each treatment. Film water solubility (WS) percentage calculated from the initial dry weight (Wo) and final dry weight of unsolved film (Wf) using the following equation:

$$WS(\%) = \frac{Wo - Wf}{Wo} x100\% \tag{1}$$

The color of BC composites have been measured using color difference meter (Murakami Color Research Lab) to get parameter in L*, a* and b* color space. L* is the lightness component, which ranges from 0 to 100, and parameters a* (from green to red) and b* (from blue to yellow) are the two chromatic components, which range from -120 to +120. Those parameters are often used in food research studies [12]. Prior to measurement, the equipment was calibrated using a white and a black standard. For measurement, films were placed on a white standard plate (L*=94.1, a*=-0.0 and b*= 1.6). Whiteness index was estimated using the following equation [13]:

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \tag{2}$$

The color was expressed as the difference of colour (ΔE*), accordingly to the equation [14]:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3}$$

where ΔL*, Δa* and Δb* correspond to the variation between the color parameter of film and that of white standard used as background. Opacity was measured by the Hunterlab method [15] using the same equipment of color measurement. Film opacity was calculated with reflectance measurements of each film (n=2) with standard black and white backing plates, using the following equation [16]:

$$Opacity = \frac{Y_{blackbacking}}{Y_{whitebacking}} x100 \quad (4)$$

where Y is the CIE tristimulus values of the film with the black ($Y_{blackbacking}$) or white ($Y_{whitebacking}$) backing plates.

FTIR analysis was recorded on a Shimadzu 4300 FTIR Spectrophotometer, using the potassium bromide disk technique, in the range of 4200–400 cm^{-1}. The disk was prepared from grinded samples (1 mg) and KBr (100 mg) using 400 kg/cm^2 pressure for 10 min.

The mechanical properties of BC composite films were characterized by Orientec UCT-5T universal testing with 100 kgf load cell according to ISO 527- 1993E standard method. Dumbbell-shaped specimens were obtained from each film according to ISO 527-2 type 5A. The measurement was conducted at temperature of 23 °C and relative humidity of 50%. At least five specimens of each sample were measured and computerized calculated to obtain the average value.

RESULTS AND DISCUSSION

The film solubility of the BC, BC/Gly, BC/Sor and BC/CMC film are shown in Table 1. Addition of glycerol and sorbitol increased the water solubility of BC composites film, whereas addition of CMC decreased the water solubility of BC composite films compared to the control (BC).

TABLE 1. Composites solubility

Samples	Film Solubility (%)
BC (control)	17.61
BC/Gly	23.31
BC/Sor	23.25
BC/CMC	8.75

Film color can be an important factor in terms of consumer acceptance of both edible and inedible films [12]. All color parameters of films are presented in Table 2. The addition of CMC, glycerol and sorbitol slightly changed some color parameters. However, addition of sorbitol and glycerol gave almost similar effect on the color parameter, while CMC affected in opposite trend.

TABLE 2. Color parameters of BC, BC/Gly, BC/Sor and BC/CMC composite films

Samples	Plasticizer concentration (%)	L*	a*	b*	Color difference (ΔE)	Whiteness index (WI)	Opacity (%)
BC (control)	0	91.4	0.8	8.1	7	88.16	34.05
BC/Gly	30	91.6	0.8	8.8	7.6	87.81	29.07
BC/Sor	30	91.6	1.2	8.6	7.5	88.27	28.54
BC/CMC	30	93.5	0.5	4.7	4.7	91.96	16.88

In order to analyze the effect of additives in bacterial cellulose chemical structure, FTIR spectrum was analyzed in the range of 4200-400 cm^{-1}. All spectrums of BC composite films clearly show the presence of the characteristic bands of BC. The FTIR spectra of bacterial cellulose (Fig. 1-BC) showed distinguish peaks of 3440 cm^{-1}, 2926 cm^{-1}, 1650 and 1300 cm^{-1}, and 1440 cm^{-1}, which correspond to O-H stretching, C-H stretching of alkane and asymmetric of CH_2 stretching, O-H deformation, and CH_2 deformation [17]. Hydroxyl groups in cellulose contribute to the formation of various kinds of inter- and intra-molecular hydrogen bonds. The formation of inter- and intra-molecular hydrogen bonds in the cellulose plays an important role in the physical properties of the cellulose. In Fig. 1-BC/CMC, BC/CMC film shows the presence of strong absorption band at 1602 cm^{-1}. It confirms the presence of COO− group of CMC. The absorbance peak at wave numbers 3458 cm^{-1} became slightly broad due to the -OH group its support the increasing of mechanical properties of BC/CMC composite films.

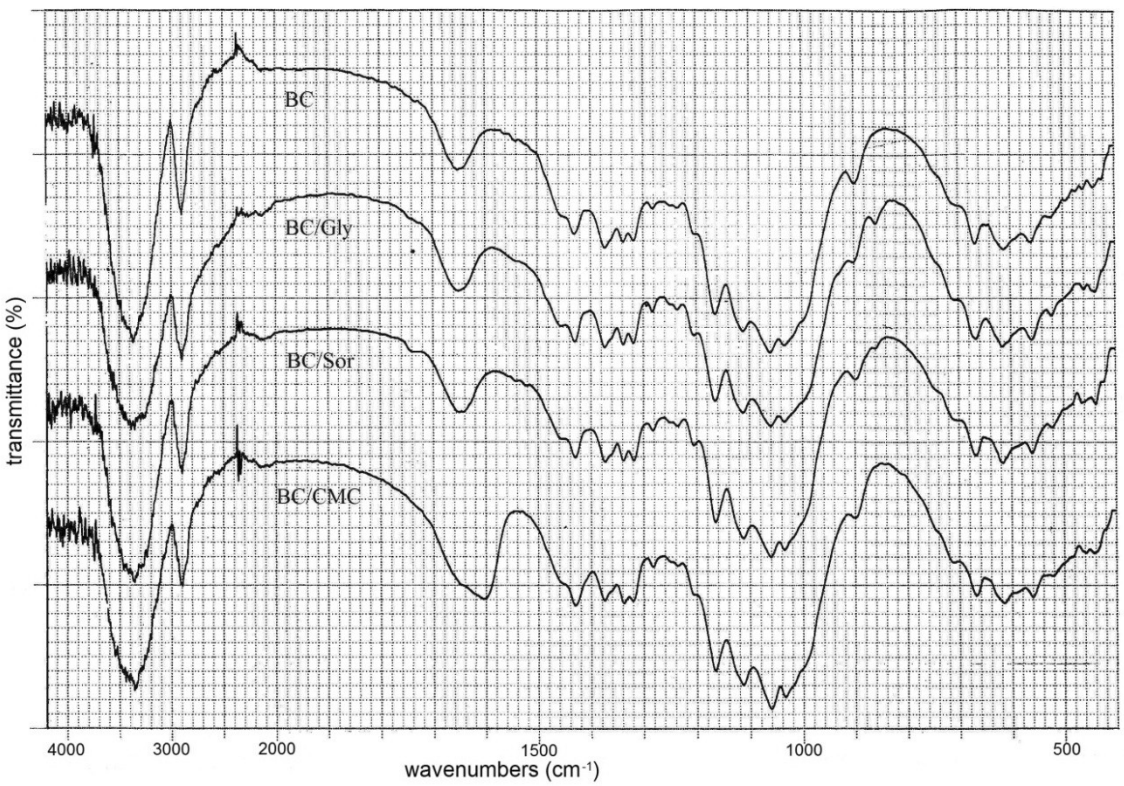

FIGURE 1. The FTIR spectra of BC films, BC/Gly BC/Sor and BC/CMC composite films

Tensile strength (TS) is the maximum tensile stress sustained by the sample during the tension test, while elongation at break is the extendibility of film length from initial length to the point of break. This parameter (E%) helps to determine the flexibility and stretchability of films. The desired flexibility of biopackaging films depends on their intended application and subsequent transportation, handling and storage of packaged foods [18]. Effect of glycerol, sorbitol, and CMC at an equal concentration on mechanical properties of BC-based films was compared (Table 3). The cross-linking agents and the plasticizers often have the contrary effects on the tensile properties [19]. Generally, the tensile strength increased and the elongation at break decreased as cross-linking agent added. The results are often opposite when the plasticizers are added [20]. Interestingly, CMC acted both as cross-linking agent and as plasticizer, while glycerol and sorbitol acted as plasticizers. As shown in Table 3, the TS and EM of the BC-based films were significantly improved by incorporating CMC into the composites. This is in agreement with previous report who described that a significant improvement of mechanical properties of cellulose-based films was achieved by adding CMC [19]. It was observed an important increase of more than twice when 30% (w/w) of CMC was added to the BC slurry. This was due to chemical similarity (cellulose structure) of BC and CMC resulted in good interfacial interaction. The increases of tensile stress for BC-CMC films are probably caused by the formations of new hydrogen bonds networks and stacking interactions between cellulose and CMC.

On the other hand, addition of glycerol and sorbitol resulted in the decreased of the TS and increase of the elongation. The observed increase in film elongation is because plasticizers decrease the intermolecular bonds and thus, substitute them with hydrogen bonds formed between plasticizer and BC molecules. Such disruption and reconstruction of BC molecular chains reduce the rigidity and promotes flexibility of films by allowing more chain mobility. Sorbitol and glycerol are low molecular weight hydrophilic. However, among these two plasticizers, glycerol has higher efficiency in plasticizing BC-based films than sorbitol as shown in higher reduction in tensile strength for BC/Gly films than that of BC/Sor films. This tendency can be ascribed to the smaller molar mass of glycerol (92.0928 g/mol) and sorbitol (182 g/mol) which facilitate easy interaction between glycerol–starch molecular chains [18].

TABLE 3. Mechanical properties of BC, BC/Gly, BC/Sor and BC/CMC composite films

Samples	TS (MPa)	Elongation (%)	Elastic Modulus (GPa)
BC (control)	84.1	5.0	3.81
BC/Gly	66.7	6.4	2.70
BC/Sor	79.4	6.7	3.15
BC/CMC	180	11.8	5.21

CONCLUSIONS

Composite films have been prepared by casting technique using bacterial cellulose as the main material. CMC, glycerol and sorbitol were added in order to improve physical and mechanical properties of BC-based films. Those additives influenced the water solubility of BC composite films compared to the control (BC film). FTIR analysis showed the characteristic bands of cellulose. Addition of CMC, glycerol, and sorbitol slightly changed the FTIR spectrum of the composites. Tensile test shows that CMC not only acted as cross-linking agent with the tensile strength significantly increased more than 100 %, but also acted as a plasticizer with the elongation at break rose up to 136 % compared to that of BC film. On the other hand, glycerol and sorbitol acted as plasticizers that showed decrease in the TS and increase in the elongation. Additon of CMC can improve film transparency, which is quite important in food industry.

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