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## Effect of Water Soluble Polymer on Structure and Mechanical Properties of Bacterial Cellulose Composites

Rike Yudianti and Lucia Indrarti

Division of New Material, Research Centre for Physics,  
Indonesian Institute of Sciences, Jalan Cisitua No. 21/154D, Bandung-40135, Indonesia

**Abstract:** Bacterial Cellulose (BC) sheet has a remarkably high elastic modulus and crystallinity inhibiting its processing. Short fibers of homogenized BC are utilized in Bacterial Cellulose Composites (BCC) formation. Water Soluble Polymers (WSP) (Carboxymethyl Cellulose (CMC) and glycerol) present in homogenized BC fiber have significant effects on mechanical properties and structure. Increasing CMC concentrations from 0 to 0.75% causes crystallinity index reduction from 81 to 61, 76 to 53 and 70 to 50% when treated glycerol concentrations of 0, 0.25 and 0.5%, respectively. Increasing CMC concentrations from 0 to 0.75% enhances elastic modulus from 2907.5 to 6245, 180.4 to 1581.3 and 30.5 to 212.5 Gpa greatly under glycerol concentrations of 0, 0.25 and 0.5%, respectively. Increasing tensile strengths from 64.8 to 167.7, 52.7 to 78.2 and 17.5 to 41.3 MPa and elongation reduction from 4.9 to 2.5, 14.5 to 9.2 and 29.6 to 23% occurs at glycerol concentrations of 0, 0.25 and 0.5%, respectively when CMC concentrations increased from 0 to 0.75%. Conversely, effects of glycerol treatment on tensile strength, elastic modulus and elongation are also presented in this study. Combination of CMC and glycerol treatment into homogenized BC is quite possible to modify BC characteristic as good processing BC.

**Key words:** Bacterial cellulose, water soluble polymer, CMC, glycerol, elastic modulus, tensile strength

### INTRODUCTION

Basically, native cellulose is mixture of two forms, I $\alpha$  and I $\beta$  celluloses. The I $\alpha$  cellulose form corresponds to a single chain triclinic crystal while I $\beta$  cellulose form corresponds to two parallel chain monoclinic crystal. The ratio of I $\alpha$  and I $\beta$  is vary depending on the cellulose source. The existence of 2 crystallographic phases for native cellulose, I $\alpha$  and I $\beta$  was demonstrated by Atalla and Vanderhart (1984) using <sup>13</sup>C Solid State NMR. The other methods in determination of two phases of cellulose were elucidated by using infrared spectroscopy (Sugiyama *et al.*, 1991a), electron microdiffraction (Sugiyama *et al.*, 1991b) and atomic force microscope (Baker *et al.*, 1998).

Bacterial Cellulose (BC) produced by *Acetobacter xylinum* at the top of growing pellicle where cellulose production takes place. Cellulose is produced at medium surface originated from growing the pellicle in downward direction. Any pellicle placed on the surface and grown around and embedded into the cellulose matrices. Cellulose markedly different from cellulose produced from trees and cotton, high purity which free of hemicellulose, lignin and other non-cellulosic compounds. Most attractive

characteristics of BC are extremely high crystallinity and ability to hold hundreds of times its weight in water. Cellulosic compound produced by *Acetobacter xylinum* has a linear  $\beta$ -1,4 glucose polymer. BC is composed of nanofibers determining properties of products. Nanofiber is constructed to sheet of cellulose chain, held together by hydrogen bonding within each sheet and by non-bonded interaction between sheet (Hirai *et al.*, 1998). The unique properties provided by the nanofiber structure have lead to a number of commercial products. Recently, material based on this type of cellulosic compound become increasingly important, including tires, headphone membrane, special papers and textiles, electrical application including conductive membrane (Yoon *et al.*, 2006).

In recent study, formation of Bacterial Cellulose Composites (BCC) prepared by Water Soluble Polymers (WSP) incorporation into short fiber matrix of homogenized BC. WSP including Carboxymethyl Cellulose (CMC) and glycerol solution were added to homogenized BC in which water contributes importantly for CMC and glycerol penetration. Balancing achievement of concentration of CMC and glycerol as important step inducing hardening and softening effects, respectively.

Therefore, structure and mechanical properties of the composites should be evaluated by comparison with untreated BC as control. Structure of composites including crystallinity index and crystal size was evaluated from X-ray diffraction profiles. Crystallinity index determined from the ratio of crystalline scattering versus total scattering which the amorphous contributed. Presence of WSP within BC structure influences mechanical properties of BCC as well. The measurement of mechanical properties was conducted by using Tensile Tester. Monitoring of mechanical properties including elastic modulus, tensile strength and elongation significantly changed.

## MATERIALS AND METHODS

**Materials:** BC gel produced from fermentation of coconut water by *Acetobacter xylinum* under static condition and incubated at room temperature for several days to reach 5-6 mm in thickness. After incubation, the BC gel on the surface of media were harvested and extensively washed with water, boiled in 1% sodium hydroxide to remove protein and non-cellulosic compounds and neutralized by running tap water. BC gel was homogenized by blender operated at full speed for 5 min providing pseudoplastic behaviour which contains 0.6% w/v cellulosic fibers. The homogenized BC was stored at 5°C in distilled water.

Carboxymethylcellulose (CMC) used in this study soluble in water at room temperature with substitution degree (DS) of 0.7 producing viscosity 500-900 cps at concentration of 1% (Brookfield LV 30 rpm). Homogenized BC poured to CMC solution slowly under heating 50°C. The concentrations of CMC in homogenized BC are 0% (BC), 0.25% (BCC C1), 0.5% (BCC C2), 0.75% (BCC C3) and kept on temperature of 50°C to get a homogenous solution. Subsequently, 0.25 and 0.5% glycerol concentrations were added to BC, BCC C1, BCC C2, BCC C3 solutions as BCC G, BCC C1G, BCC C2G, BCC C3G and BCC G1, BCC C1G1, BCC C2G1, BCC C3G1, respectively. Air removal of the solution was conducted by ultrasonic vibration. The solution was casted onto teflon tray and dried in gear oven at temperature of 40°C.

### Methods

**X-ray diffraction:** X-ray diffraction profiles of Bacterial Cellulose (BC) and Bacterial Cellulose Composites (BCC) were recorded by using X-Ray diffraction Rigaku RINT 2500, using Ni filtered Cu-K $\alpha$  radiation ( $\lambda = 0.1542$  nm). The operating voltage and current were 35 kV and 40 mA, respectively. The scanning of  $2\theta$  (10-40°) was employed with speed of 5° min<sup>-1</sup>. The relative crystallinity index was estimated by Segal's method using the following equation:

$$Cr = \frac{100 \times [I_{(002)} - I_{am}]}{I_{(002)}}$$

Where,  $I_{(002)}$  is the peak intensity corresponding to the (110) plane at  $2\theta = 22.7^\circ$  for the overall intensity and  $I_{am}$  is the peak intensity of amorphous fraction at  $2\theta = 18^\circ$ .

The apparent lateral width of the crystals was calculated for most intense peak at  $2\theta = 22.7^\circ$ , using the Scherrer formula:

$$t = \frac{K\lambda}{B \cos \theta}$$

Where:

t = Crystal width

$\lambda$  = Wavelength

B = Diffraction line-width at half peak size

$\theta$  = Bragg angle

K = Constant usually taken as 0.9 for cellulose (Klug and Alexander, 1954)

**Tensile testing:** Specimens were mounted into 5 N load cell of Universal Tensile Machine, Tensilon, Orientec, type UCT-5T. Dumbell type used for specimen cutting is ISO 527 type 5B. One load cell statically fixed with the tensile machine frame and the second one fixed with the moveable part of the machine. Specimens were strained at displacement rate of 1 mm min<sup>-1</sup>. All specimens were deformed under controlled room condition at temperature of 23±1°C and humidity of 50±5%.

## RESULTS AND DISCUSSION

The X-ray diffraction profiles of Bacterial Cellulose (BC) and Bacterial Cellulose Composites (BCC) are shown in Fig. 1. BC established as I $\alpha$  cellulose, indicated in presence of d spacing 6.17, 5.235 and 3.91 nm as calculated by Sugiyama *et al.* (1991b). Addition of CMC (0, 0.25, 0.5, 0.75%) and glycerol (0, 0.25, 0.5%) to BC forms a slight different structure compared with BC structure as control. Basically, BC and BCC have similar profiles arranged in three peaks at  $2\theta = 15^\circ$ ,  $17^\circ$  and  $22.7^\circ$  as assigned to (100), (010), (110), respectively. Apart from a slight shoulder at scattering angle of (100) ( $2\theta = 15^\circ$ ) and (110) ( $2\theta = 22.7^\circ$ ) indicates the presence of high crystalline portion of I $\alpha$  cellulose in BC structure. Most composites pointed out conversion d spacing of (100) at 0.617 to 0.607 nm. According to Sugiyama *et al.* (1991b), the presence of d spacing of 0.607 nm assigned as I $\beta$  cellulose contribution. Scattering plane of (100) is most closely occupied by hydroxyl group as studied by Takai *et al.* (1975). Hence the scattering plane is most sensitive if any disturbance within structure. In the

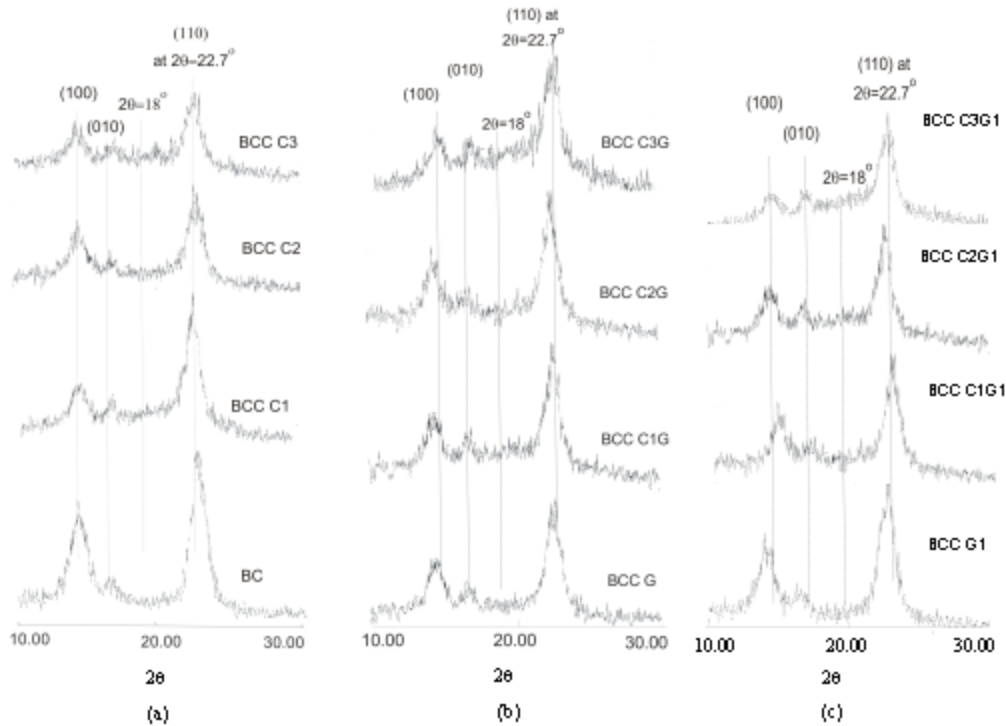


Fig 1: X-Ray diffraction profiles of BC (control) and BCC (a) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0%, (b) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0.25% and (c) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0.5%

crystal structure of cellulose, the scattering plane has the largest number of hydroxyl cellulose since the hydroxyl groups are largely responsible for the sorption of water. Low concentrations of Water Soluble Polymers (WSP), CMC and glycerol were able to make a broadening of scattering planes (110) and (100). Broadening peaks indicate a change of crystalline portion. Low concentrations of CMC (0-0.75%) interpenetrating to BC network are unable to change structure conformation by shift in scattering plane (010) at  $2\theta = 17^\circ$  to  $2\theta = 20.4^\circ$  as scattering plane of cellulose II.

Change of the composite profiles after incorporation indicates a slight shoulder at scattering planes of (100) and (110). The evaluation of crystallinity index was estimated by Segal's method leading to crystalline portion of Ix cellulose in the composite decreased from the highest crystallinity index of 81.0% to the lowest crystallinity index of 51.2%, as shown in Fig. 2. Increasing CMC concentrations from 0 to 0.75% gives considerably crystallinity index reduction from 81% (control) to 61% (BCC C3), 76% (BCC G) to 53% (BCC C3G), 70% (BCC G1) to 50% (BCC C3G1) corresponding to glycerol concentrations of 0, 0.25 and 0.5%, respectively.

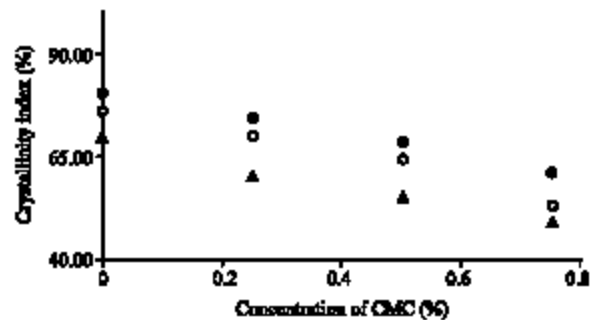


Fig 2: Crystallinity index of BC (control) and BCC, (●) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0%; (○) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0.25%; (▲) Variation of CMC concentrations (0-0.75%) at glycerol concentration of 0.5%

Contribution of CMC and glycerol in BCC formation is also monitored by conversion of 5-37.5% crystalline to amorphous portion which affinity of CMC and glycerol have important role in amorphous structure formation of BCC.

Table 1: Mechanical properties of BC (control) and BCC

Materials	Elastic modulus (Gpa)	Tensile strength (MPa)	Elongation (%)
BC	2907.5	64.8	4.9
BCC C1	3710.2	130.1	4.7
BCC C2	5058.5	148.6	2.9
BCC C3	6245.0	167.7	2.5
BCC G	180.4	50.4	14.5
BCC C1G	299.2	52.7	13.8
BCC C2G	1047.8	58.3	13.3
BCC C3G	1581.3	78.1	9.2
BCC G1	30.5	17.5	29.6
BCC C1G1	34.3	22.6	25.8
BCC C2G1	74.1	31.5	24.3
BCC C3G1	212.5	41.3	23.4

Based on the X-ray diffraction profiles is determined crystal size of the composites using Sherer formula. Evaluation in crystal size of (110) as the most intense scattering plane corresponded to sheet of hydrogen bonded chains, approximated from a half peak width of (110) at  $2\theta = \sim 22.7^\circ$ . Addition of CMC and glycerol shows a little effect on alteration crystal size from 1.4 nm for BC to 1.1 nm for the composites. Hydrogen bonding present in homogenized BC forms weak inter and intramolecular force due to short fibers formation. CMC act as deflocculating agents causing cellulose fibers disperse in suspension and establish a network of solution. Consequently, less aggregation of a crystallized cellulose is probable to arise during drying. Weak hydrogen bonding between cellulose and CMC predicted to emerge as crystalline prevention. Solubilization of glycerol in water could easily penetrate cellulose fiber to prevent crystalline.

Addition of CMC and glycerol to homogenized BC formed composite structures with a change of mechanical properties compared with BC as control. The increasing CMC concentrations to the composites of BCC to BCC C3, BCC G to BCC C3G, BCC G1 to BCC C3G1 exhibit increasing tensile strength from 64.8 to 167.7, 52.7 to 78.1, 17.5 to 41.3 MPa and Elastic modulus from 2907 to 6245, 180.4 to 1581 and 30.5 to 212.5 MPa, respectively. Treatment of glycerol (0 to 0.5%) has a trend toward reducing tensile strength from 167.7 to 17.5 MPa and Elastic modulus from 6245.0 to 30.5 MPa (Table 1). Otherwise, glycerol treatment gradually increased elongation from 2.5 to 29.6%. The probable cause of high elongation caused by presence of hydrophilic alcohol hydroxyl group. In any case, CMC builds-up cellulose backbond inducing line in order of structure to be more crystalline. CMC reduces elongation of composites to be more breakable. Dispersion of cellulose fiber in colloidal solution interact between themselves in order to build up a network which provides a gelling structure. CMC within

homogenized BC ensure easier dispersion providing good bonded BC fibers. CMC as deflocculating agent can be useful in employing homogenized BC in uniform distribution inducing enhancement fiber to fiber bonding to make stronger sheet and durable.

Referred to mechanical properties and structure evaluation, CMC and glycerol play important role in modification of BC characteristic. Balancing CMC and glycerol concentrations within homogenized BC open the opportunity to improve BC characteristic to be friendly water soluble plastic. The importance of water contribution is emphasized in composite formation. Therefore, further study relating to improvement of BC characteristic should be conducted.

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