Development of Bacterial Cellulose/Activated Carbon Composites Prepared by In Situ and Cast-drying Methods

Indriyati, R. Yudianti, and L. Indrarti

Abstract— **In order to investigate the potential use for bacterial cellulose (BC) as a novel backing layer for fuel cell, BC/Charcoal Activated (BC/CA) composites were prepared by in-situ and casting methods. The BC/CA composites were characterized by Scanning Electron Microscope (SEM) analysis, electrical conductivity measurement, and visual observation. Our results showed that the penetration of CA into BC network through in-situ method has occurred at concentration below 4 w/v %. It was proved by the changing of the color of culture medium from black (the solution of CA in coconut water) to clear after 2 weeks inoculation. In addition, this carbon still remained in the composites during neutralization. SEM analysis of the composites showed that BC matrix acted as a binder which supports mechanical properties of the composites. Addition of CA enhanced thermal degradation and electrical conductivity of the resultant composites. Electrical conductivity reaches 10^{-2} S/cm for the composites made by casting method containing 10% CA. Meanwhile, backing layer commercial has electrical conductivity of $5x10^{-2}$ S/cm obtained by the same measurement.**

Keywords— **Bacterial cellulose, activated carbon, casting, fuel cell**

I. Introduction

Known as an alternative energy source, fuel cell offers many benefits compared to conventional energy, for instance almost zero emission and high efficiency. Among many types of fuel cell, Proton Exchange Membrane Fuel Cell (PEMFC) is chosen due to its low operating temperature and quick start-up. One of essential components that contribute to water and gas reactant management in the PEMFC is backing layer, also called Gas Diffusion Backing (GDB) or Macro Porous Layer (MPL). Backing layer should have porosity to provide high rates of gas transport into the cell and should have high electrical conductivity to serve as a current collector [1][2]. Understanding the functionality of backing layer is very essential for its optimization to meet the service conditions. In general, the backing layer is made of carbon fiber-based porous media, either carbon cloth or carbon paper with thickness of 100-300 μm. Indonesian researchers have designed backing layer from different local sources in hope to not depend on imported product which is quite expensive.

One candidate material for backing layer is Bacterial Cellulose (BC). Several studies have investigated unique properties of BC attributed by the uniform ultrafine-fibre network structure and by the high planar orientation of the ribbon-like, namely porosity, crystallinity, and high mechanical properties [3]-[6]. Structure and properties of BC could be various, depend on its cultivation methods such as agitated or stationary culture in different kinds of reactors [7]. In addition, synthesis of BC is significantly influenced by numerous types of reagents that can be added to the medium [7]-[11]. For instance, agar [9] or sodium alginate [10] can be added to the medium to enhance the BC productivity. Moreover, addition of *hydroxypropylmethyl cellulose* (HPMC) and *carboxymethyl cellulose* (CMC) into the culture medium improves the hydration capacity of resulted BC [11]. In developing engineering materials, BC has been blended with thermoplastic polymers by various methods. BC sheet has been impregnated under specific pressure with poly(vinyl alcohol), PVA [12]. Interestingly, fragmented BC fibres could be formed into paper [13] with high mechanical properties up to one third of hot pressed BC gel-like sheet values [3,4,6].

In order to obtain more useful BC, composites from BC and activated carbon (AC) were prepared by in-situ (shaking incubation) and cast-drying methods. Both methods are simple and well-known technology, but it still remains the opportunity to study the effect of different materials on composites' properties, hence to provide cost-effective products. AC as the filler was added into BC to enhance electric conductivity of BC. It is expected that BC provides porosity and acts as the reinforcement in the composites. Penetration of AC into fibril structure of BC was observed visually. The effect of the addition of AC on thermal stability and electric conductivity of the composites will be evaluated in purpose to be a backing layer for PEMFC.

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II. METHODS

A. Preparation of Composites by In Situ Method

Coconut water (1.5 L), bought from local market, was filtered and then mixed with sugar under slow magnetic stirring. After all sugar dissolved, the solution pH was adjusted to 4.0 with addition of acetic acid (Merck). This solution is called culture medium. AC (Merck) with melting point of 3550°C, molar mass of 12.01 g/mol, and bulk density of 150-440 kg/m^3 was added into culture medium and then the composition was adjusted as listed in Table 1. The mixture was sterilized by boiling it for 10 min, followed by cooling it in room temperature. Then, 20 ml of inoculums was added into each mixture. The mixture was incubated at room temperature on a rotary shaker operating at rotational speed of 120 rpm. A control experiment without addition of activated carbon was also performed simultaneously. The pellicles grown in the culture medium after several days were harvested and washed until neutral using filtration method. Then, they were dried in an oven at 40 °C. After drying, the composites were hot pressed in order to obtain flat membrane.

TABLE I
FORMULA FOR COMPOSITES PREPARED BY IN SITU METHOD

Culture Medium	Inoculum	Activated Carbon	
(ml)	(ml)	(gr)	(%)
100	20	0	0
100	20	0,5	0,5
100	20	1	1
100	20	2	2
100	20	4	4
100	20	5	5

B. Preparation of Composites by Cast-drying Method

BC gels were purchased from local industry in Cianjur, West Java. The gels were rinsed thoroughly in running tap water until their pH was neutral. Subsequently, the gels were boiled in 2% w/w NaOH solution for 1 h, in order to remove non-cellulosic compounds. The gel-like pellicles were then washed again in running tap water to remove remain alkali solution on the BC gel. With the addition of 40% w/w water, BC gels were shredded using a home blender (Philips) for 5 min. AC with concentration of 1% (w/w) - 16% (w/w) was added into 20 gr of BC. The BC/AC mixture was then stirred for 3 min to form a homogeneous gel-like solution. The solution was subsequently cast on petri dish and kept in a gear oven at 40°C for 16-20 hrs. Then, the composites were collected and stored in a sealed-plastic container.

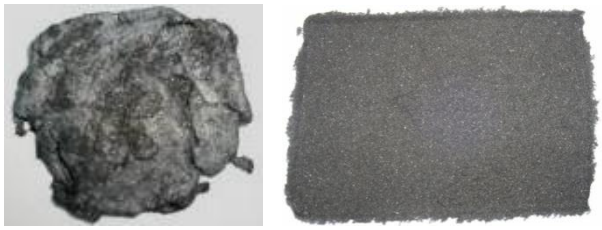
C. Characterizations

The appearance of composites made by both in-situ and cast-drying method will be analyzed visually. Thermal properties of the composites were investigated by Thermogravimetric Analysis (TG/DTA, Seiko Instruments Inc.), recording the composites weight variation with different temperatures. TGA measurement was carried out at a heating rate of 10°C/min with a temperature range of 30°C to 500°C, using sample mass around 5 mg and under atmosphere of N_2 (260 ml/min). A weight loss curve and its derivative curve were thus obtained. Morphological analysis on the surface of composite was performed using Scanning Electron Microscope (SEM, JEOL T330A). The specimen was cut and prepared under liquid nitrogen and mounted in an aluminum holder with double-sided carbon tape. It was then sputter coated with a thin gold layer using ion sputtering JFC 1100C and observed at an acceleration voltage of 20 kV. General radio *impedance bridge* type 1650-B was used for characterizing resistivity of the composites and electrical conductivity was calculated as the reciprocal of resistivity.

III. RESULT AND DISCUSSIONS

A. Visual Appearance

Visually, composite prepared by cast-drying method has a flat surface and a homogeneous thickness making it possible to take measurement of electrical conductivity (Fig. 1b), while composite prepared by in-situ method under agitated culture condition forms a fibrous suspension and irregular masses (Fig. 1a). Although hot press has been applied to composite after cultivation, uneven surface texture and un-homogeneous thickness were still obtained. Therefore, the electrical conductivity of in situ composites cannot be measured.



a b

Fig. 1. Visual appearance of biocellulose/activated carbon composite made by (a) in-situ method, (b) casting method

In stationary cultivation, a thick, gelatinous membrane of BC is accumulated on the surface of a culture medium. Hence, flat and homogeneous thickness of membrane could be obtained by hot pressing. However, AC will be sediment to the bottom of flask during static cultivation. Therefore, agitated culture was chosen with very low shaking rate in order to disperse carbon particle inside the culture medium. Besides, it was reported that agitated cultivation might be the most suitable technique for economical scale production because higher production rate can be achieved [14]. In agitated culture, the BC shapes are not uniformly regular. Cellulose is synthesized in deep media and the production rate and yield of BC are proportional to the oxygen transfer rate and oxygen transfer coefficient [14]. The strong stress forces in agitated culture change the aggregation of sub-elementary fibrils and form the irregular shape assemblies [8]. The irregular shape of the composites resulted unhomogeneous

thickness of membrane even though they had been hot pressed.

However, penetration of AC through agitated incubation had occurred for composites with AC concentration below 4% (w/v). It is proved by a change in color in the medium from black (culture medium containing AC) to clear after 2 weeks incubation. In addition, AC trapped in the tangled of BC fibers and still remain between fibers of cellulose even during the process of neutralization. There is no chemical bond between AC and BC because AC carbon is an inert substance.

BC/AC composites can be harvested at day 5, day 8, and day 12 for the concentration of AC 0,5% (w/v), 1% (w/v), and 2% (w/v), respectively. While for the culture medium containing AC 4% (w/v), the new composite can be harvested after 15 days. Cellulose fibers did not occur in a culture medium containing AC 5% (w/v). This suggests that there is a slowing growth influenced by addition of AC. The addition of AC into the culture medium changed the bacterial growth medium, thus inhibiting the bacteria in the production of cellulose. Therefore, the higher the carbon concentration in the medium will take longer for bacteria for adaptation to produce cellulose.

B. Thermal Analysis

Thermal analysis (TGA) is important parameter to know the temperature where the substances start to degrade. TG and DTG curve of composites prepared by cast-drying and in-situ method show enhancing thermal stability as a function of AC concentration (Fig. 2 and Fig. 3). The weight loss at the beginning of process (under 100°C) was due to evaporation of free moisture content. As the temperature was increased further, the water bound in the BC also evaporated. A major weight loss occurs in the temperature range of 220°C to 340°C for both composites prepared by in-situ and cast-drying method containing 0-2% AC, whereas it occurs in the temperature range of 340°C to 400°C for the composites made by casting method containing 8% and 16% AC. These results indicate that the presence of AC in the composites increases the degradation temperature and decreases the weight loss of BC. The TGA curves showed that the initial temperature of degradation for composites prepared by casting and in-situ methods were 310°C and 275°C, respectively. Concentration variation of AC from 0.5% to 2% for in-situ method did not significantly affect degradation temperature of the composites. They resulted in almost similar TGA curves with weight loss less than 20%. Based on thermal analysis result, all composites samples are suitable material for backing layer of fuel cells because they have degradation temperature higher than 150°C, the temperature for hot pressing membrane and electrode of fuel cells.

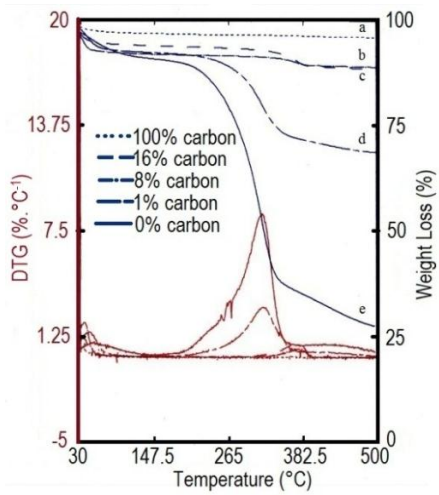


Fig. 2. TG and DTG curves of composites prepared casting method

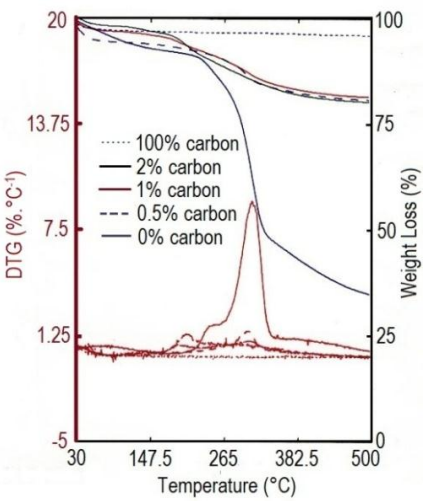


Fig. 3. TG and DTG curves of composites prepared in situ method

C. Morphological Analysis

Surface morphological analysis was performed on the cast-drying composites in order to observe the fibril of BC and its ability as a binder (Fig. 4-6). For AC concentration of 1%, AC trapped between the webs of cellulose fibers. The more AC concentration in the composite, the less BC network binds them as seen in Fig. 5 and Fig. 6. This result will cause a decrease in mechanical properties of the composite.

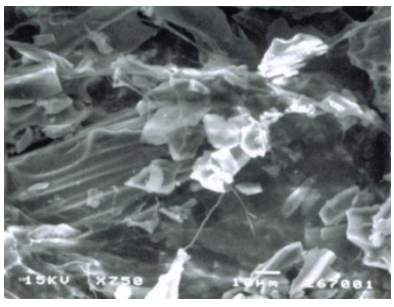


Fig. 4. Morphological surface of BC/AC (1% AC) composite prepared by cast-drying method

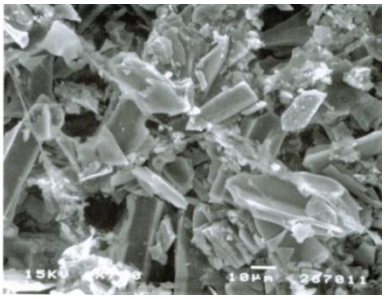


Fig. 5. Morphological surface of BC/AC (8% AC) composite prepared by cast-drying method

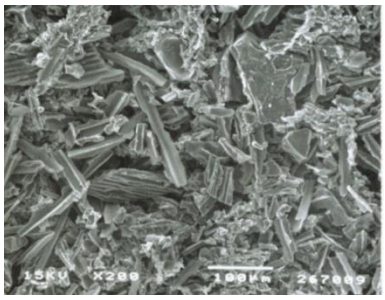


Fig. 6. Morphological surface of BC/AC (16% AC) composite prepared by cast-drying method

D. Electrical Conductivity

Measurement of electrical conductivity was conducted to BC/AC composites prepared by casting method with the range of AC concentration from 2% (w/w) to 11% (w/w) (Fig. 7). The thicknesses are range from 0.3 mm to 1.4 mm as a function of AC concentration. Electrical conductivity reached 10^{-2} S/cm at concentration of AC of 10% (w/w). This value is almost similar to conductivity of commercial backing layer, 5 x 10^{-2} S/cm, measured using the same equipment. This indicates that AC is a good conductor and effectively produces electrical conductivity required for a backing layer at a concentration of 10% (w/w).

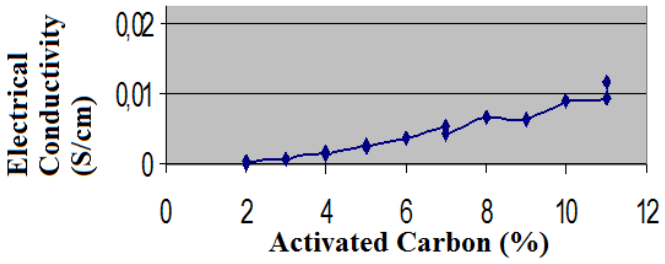


Fig. 7. Electrical conductivity of cast-drying composites

IV. CONCLUSION

Cast-drying method is a better technique to produce thin layer with flat surface texture and homogeneous thickness than in situ method. Electrical conductivity of the composites prepared by casting method reached 10^{-2} S/cm with carbon concentration of 10% (w/w). This value is closed to electrical conductivity of commercial backing layer measured by the same equipment. Therefore, the composite prepared by casting method could be proposed as an alternative material to a backing layer of PEMFC. Addition of activated carbon increase thermal decomposition and electrical conductivity of the composites. Mechanical properties of the composites could be improved by incorporating nanoparticle AC as the filler.

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