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A THESIS FOR THE DEGREE OF MASTER OF SCIENCE

**Electrical Conductivity and Optical Transparency of
Bacterial Cellulose based Composite
by static and agitated methods**

**정치배양법과 진탕배양법을 통한
박테리아 셀룰로오스 기반 복합재료의
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Sera Jeon

Advisor : Hyun-Joong Kim

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Abstract

Electrical Conductivity and Optical Transparency of structurally modified Bacterial Cellulose based Composite

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Bacterial cellulose (BC) is an environmental friendly material composed of pure cellulose, and many researchers have suggested its potentials to be extended to various applications in fields such as medical, beauty, clothes, diaphragm, food and so on.

The main purpose of this study was to investigate electrical conductivity and optical transparency of BC based composite through modification structure of BC by changing cultivation speed. BC by static and agitated cultivation methods evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM) and Brunauer–Emmett–Teller (BET). From these results indicated that bacteria synthesize cellulose with different diameter of fiber from 27.76 ± 4.05 at static cultivation to

20.62 ± 3.30 (nm) at agitated cultivation. And surface area increased about twice times due to centrifugal force.

The three-dimensional BC network served as a nanostructured substrate for ionic conducting polymer (ICP). ICP synthesized with varied contents of salt. The electrical conductivity of BC/ICP composite was verified by surface resistivity and volume resistivity. By enhancing ICP on BC led to the improvement in electrical conductivity than pure BC which is insulator. Moreover, the electrical conductivity of BC/ICP composite improved rapidly by BC with high agitated cultivation speed through filling more ICP due to surface area increased.

BC fibers are invisible due to its diameter was less than a visible light wavelength. However, a dried BC is opaque because the diameter of fibers is increased due to microfibrils of BC collapsed and piled on each other. Also, the pores inside BC lead to significant light scattering. To enhance the optical transparency of BC based composite, the transparent materials fill in these pores in BC nanostructures to prevent the fibers aggregation, which affect light scattering. BC/ICP composite has improvement about 6 times than pure BC in the optical transparency. These results indicated that pores within BC, occupied by ICP, prevented light scattering.

This electrically conductive and optical transparent nanocomposite can be useful in various applications requiring biocompatibility, electrical conductivity and optical transparency.

Keywords : bacterial cellulose, ionic conducting polymer, static cultivation, agitated cultivation, electrical property, optical property

Student Number : 2012-21121

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1. Introduction

1.1 Background of this study

Since Shirakawa *et al.* found conducting polymers at the end of the 1970s, composites of conducting polymers have been developed for use of anti-static substances, smart windows, light-emitting diodes, solar cells and so on (Shirakawa *et al.*, 1977, Chen *et al.*, 2010). However, composites consist of conducting polymer are not fully environmental friendly, biocompatible, and biodegradable. Ionic conducting polymer using salt is fascinating in eco-friendly electrical industry (Smela, 2003).

Cellulose is most abundant polymer and common natural resources in the earth. Bacterial cellulose (BC) has been considered a promising candidate material for biocomposite due to its acquisition through biosynthesis without chemical treatment among nanocellulose (Douglas *et al.*, 2008).

By incorporation conducting polymer and bacterial cellulose, filled pores in bacterial cellulose nanostructure with electrical conductive and optical transparent ionic conducting polymer (ICP). It can be implemented as high functional, flexible and lightweight composites and is environmentally friendly. Application of composite based on bacterial cellulose can be useful in various applications requiring biocompatibility and electrical conductivity such as biocompatible composite actuators, clothing sensor and so on.

This study is focused on effect of structurally modified BC in different cultivation methods and the varied concentration of ICP. The

composite consist of BC impregnated with ICP, which is expected to assign electrical conductivity and improve by modification crystalline structures of BC compared to pure BC. It is expected that the composite composed of biomaterial and ionic conducting polymer will have new possibilities for applications in industry as chemical sensors, biomedical devices, and so on.

1.2 Nanocellulose

Cellulose is an important natural material (Shi *et al.*, 2013). The crystallinity of cellulose is main issue because it directly relates to high strength performances. In case of plant cellulose, to obtain pure cellulose with high crystallinity is very tough because it contains not only cellulose but also hemicellulose, lignin and other extractives. Therefore, cellulose from plant should be separated from other extractives including hemicellulose and lignin through physical, mechanical and chemical treatment.

The production of nano-scaled cellulose and their application in composite material have gradually got increasing attention during the last decades because nanocellulose has many advantages (i.e. high crystallinity, high tensile strength, high melting temperature, 200 times more surface area, stiffness combined with low weight, and biodegradability). Recently, many researchers are attempting to find industry fields that commercialize nanocellulose (Eichhorn *et al.*, 2010).

Nanocellulose is classified four types in large as manufacturing method. The production of nano fibrillated cellulose is affected by the applied treatment to the fibers before homogenization. When fibers are subjected to high pressure by homogenizer, the cellulose is effectively fibrillated (Gilberto Siqueira, 2010, Chinga-Carrasco, 2011). There are also electro spinning nanocellulose via electro spinning, and the production through produce by bacterial cellulose cultures and bacteria, the BC which is nanostructured cellulose (Douglas *et al.*, 2008).

1.2.1 Bacterial cellulose

The fibers of cellulose are produced by certain bacteria such as the genera *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Rhizobium*, or *Sarcina*. *Acetobacter xylinum* (or *Gluconacetobacter xylinus*) is the most efficient producer among these bacteria, a gram-negative bacterium, which can produce cellulose and acetic acid in a culture medium containing carbon and nitrogen sources. BC presents unique properties such as high mechanical strength and an extremely fine and pure cellulose fiber network structure. This network structure is the form of a pellicle made up of random ribbon-shaped fibrils, less than 100 nm wide, which are composed of 2~4 nm in diameter. In addition, it has porosity, 3-dimensional network structure, water holding capability, and biocompatibility. In contrast to obtain nanocellulose through mechanical or chemo-mechanical processes, BC is produced by biosynthesis of *Acetobacter xylinum* (Chen *et al.*, 2010, Lee *et al.*, 2012, Ross *et al.*, 1991, Yamanaka *et al.*, 1989).

In polymer science, there are various methods and modifications of BC. Examples of fabrication method are as followings, fabrication BC with polymer matrix (Gea *et al.*, 2010), treatment of culture medium (Yoon *et al.*, 2006), and so on. Moreover, there is also lamination or deposition of transparent resins on the surface of BC (Nogi and Yano, 2008).

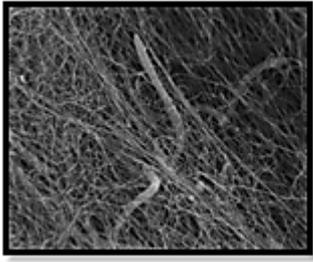
1.2.1.1 Cultivation methods of bacterial cellulose

BC cultivated pure cellulose by the bacteria of *Acetobacter xylinum*, culture methods are classified by static cultivation method and agitated cultivation method. Static and agitated cultivation methods are used to get BC as shown in figure 1. The appearance of the two types of BC by static and agitated cultivation is quite different. In the static cultivation method of BC, it is well known as pellicle at the surface of the culture medium as a gelatinous form. In contrast, various sizes (10 μm to 1 mm) and shapes (spherical, ellipsoidal, stellate or fibrous) of BC in well-dispersed in agitated culture medium as reported (Herstrin and Schramm, 1954, Dudman, 1960, Yoshinaga *et al.*, 1997).

BC synthesized through static cultivation method showed a high value of Young's modulus, while water holding capacity was lower than agitated cultivation method (Krystynowicz *et al.*, 2002).

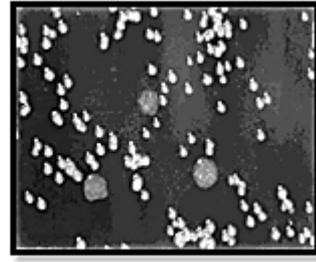
In this study, the cultured BC using the above two methods is to compare the impact on the electrical conductivity and transparency.

Static cultivation



Low water holding capacity
High Young's modulus
High yield production

Agitated cultivation



High water holding capacity
Low Young's modulus
Low yield production

Figure 1. Cultivation methods of bacterial cellulose
(Krystynowicz *et al.*, 2002)

1.3 Conducting polymer

When we fabricate nanocellulose composites with adding inorganic fillers, conjugated polymer, carbon-based materials, the composite have properties of transparency, flexibility, electric conductivity. And these characters are major factors to apply electric industry (Eichhorn *et al.*, 2010). Shirakawa *et al.* discovered that a polymer, polyacetylene, can be made conductive almost like a metal by doping with iodine (Shirakawa *et al.*, 1977). Conducting materials are carbon black, metal and conducting polymer like polyaniline, polythiophene and so on. The method of adding metal powder or carbon particle had a disadvantage that transparency of composite is decreased. However, ionic conducting polymer has advantages like non-pollution of substrate by ion migration and transparency by polymerization using acrylic monomer.

Electrical conductivity of composite is measured as followings. As measuring electrical resistance, electrical conductivity can be achieved due to their reciprocal. Resistance is classified into surface resistance and volume resistance. Surface resistance is measured the flow of current restricting surface. Volume resistance is the resistance on movement of electrons regardless of the thickness and conductive structure of the material.

2. Objectives

The purpose of this study is to prepare composite based on BC with electrical conductivity and optical transparency.

2.1 Modified structure of bacterial cellulose by different cultivation methods

In order to know how to perform electrical property in composite having difference structure, it is necessary to analyze the crystalline structure by cultivation methods. BC with different cultivation methods can be helpful to make a new structure like electron or charge path. As observed in BC crystalline structure, the electrical property of ICP can be associated preferentially with the mobility of ion.

2.2 Improvement in electrical conductivity and optical transparency of composite based on bacterial cellulose by incorporation conducting polymer with ionic monomer

With different concentration of potassium salts, the electrical conductivity can be controlled. Synthesized ICP with acrylic ionic monomers has electrical properties and optical transparency. It affects to composite that filling ICP into pores of BC, the composite performed electrical conductivity and optical transparency.

3. Literature reviews

3.1 Conductive cellulose nanocomposites

Due to wide range of morphological form of cellulose based composite provide opportunities to produce materials with high electrical conductivity. Cellulose and conducting materials can be combined by blending, doping and coating. And conducting polymers, carbon nanotubes, grapheme and ionic liquid are used as a conductor (Shi *et al.*, 2013).

Yoon *et al.* prepared electrically conducting polymeric membranes by incorporating multiwalled carbon nanotubes (MWCNTs) into BC pellicles produced by *Gluconacetobacter xylinum*. It was found that the incorporation process is a useful method not only for dispersing MWCNTs in an ultrafine fibrous network structure but also for enhancing the electrical conductivity of the polymeric membranes (Yoon *et al.*, 2006). Also, Feng *et al.* fabricated composite consist of BC and grapheme oxide (GO). By increasing contents from 0.1 wt% to 1 wt% GO after in situ reduction, the conductivity remarkably increased to 1.1×10^{-4} S/m. The nanocomposite has properties such as mechanically strong, flexible and conductive (Feng *et al.*, 2012). However, It has disadvantages in optical property to enhance electrical conductivity with carbon based material

Lee *et al.* described BC with conducting polymer which is polyaniline (PANI) by interfacial polymerization. With using two different phases between water and chloroform made composite with

PANi and BC. By the plain interfacial polymerization, the electrical conductivity of BC/PANi composite reached up to 3.8×10^{-1} S/m when 0.32 M of aniline was used (Lee *et al.*, 2012).

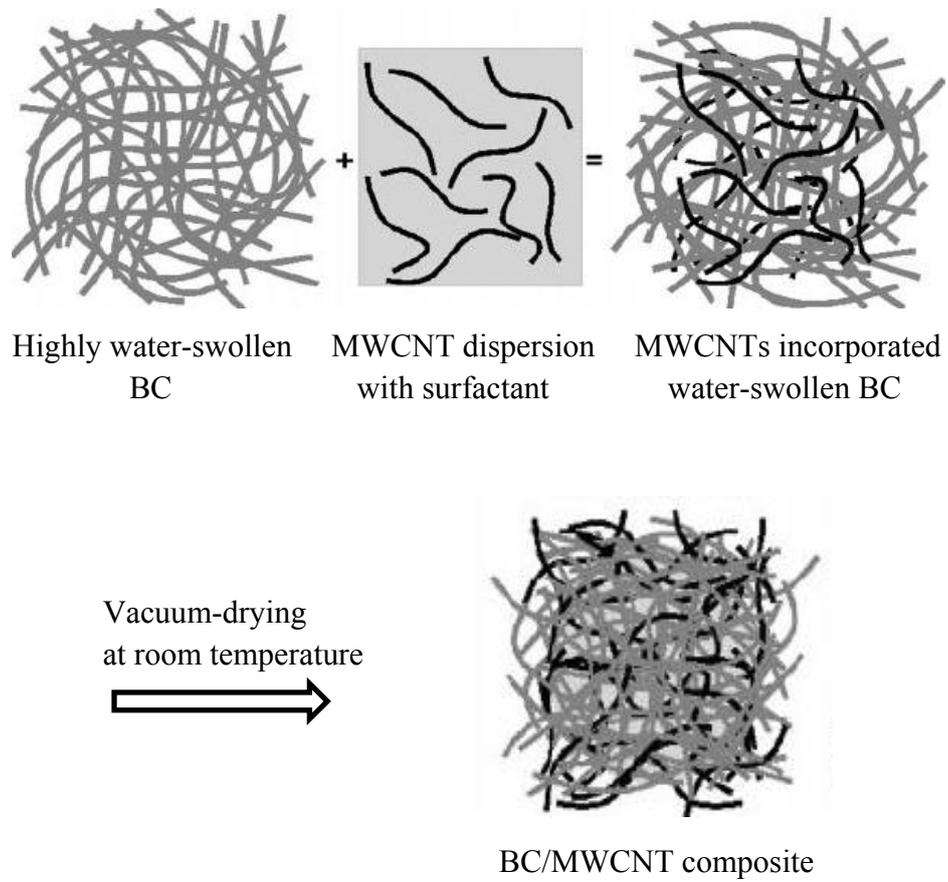


Figure 2. Schematic diagram of the process of incorporating the MWCNTs to BC (Yoon *et al.*, 2006)

3.2 Electrical property of ionic materials

Verdolotti *et al.* reported that the effect of the incorporation of several lithium salts on the electrical and mechanical properties of rigid polyurethane foam composite. Also the salts affected electrical conductivity. Different concentrations of salts were added and it affected electrical conductivity as shown in Figure 3 (Verdolotti *et al.*, 2011).

Jeon *et al.* founded that an electro-active biopolymer actuator based on the BC using lithium chloride (LiCl) for surface modification. With this modification, it affects to ionic conductivity LiCl treated BC were higher than pure BC due to increase of the amorphous region by weakened crystallinity (Jeon *et al.*, 2010).

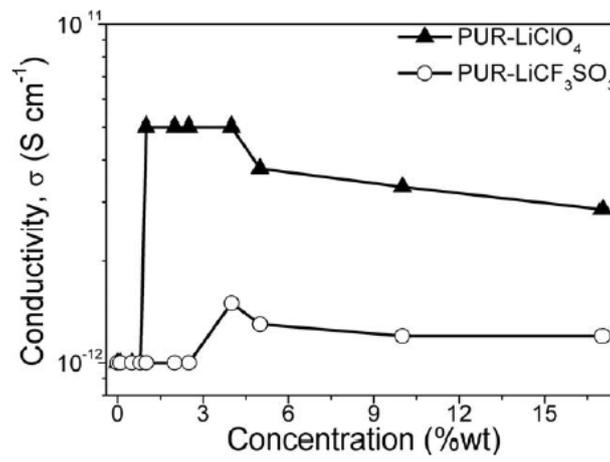
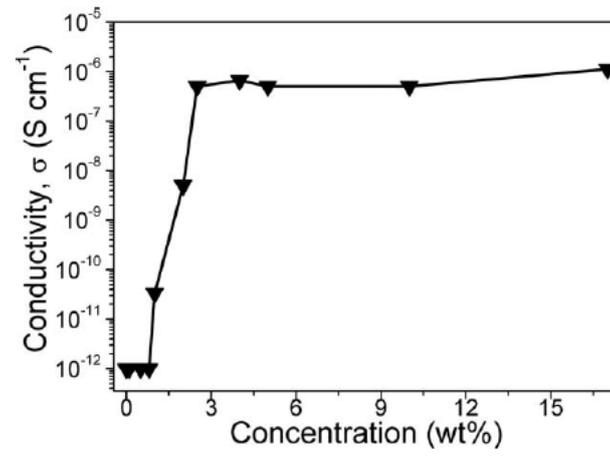


Figure 3. Electrical conductivity versus weight percentage of salt for the composites (Verdolotti *et al.*, 2011)

3.3 Structurally-modified cellulose by cultivation methods

Czaja *et al.* studied structural difference of BC produced in static and agitated cultivation. There is deduction in good correlation with smaller size of crystalline in agitated culture. During agitation, cells are stacked together in organized group around the outer surface of the cellulose sphere (Czaja *et al.*, 2004). The structural differences exist in the cellulose crystal and the molecular chain between the two types of BC from static and agitated cultivation. In the static culture, the crystallinity and cellulose Ia content of cellulose are higher than the agitated culture. Moreover, the degree of polymerization is higher for the cellulose molecules from the static culture. Watanabe *et al.* reported that the interference in the crystalline process of BC may lead to the formation of small sized crystalline in agitated culture (Watanabe *et al.*, 1998).

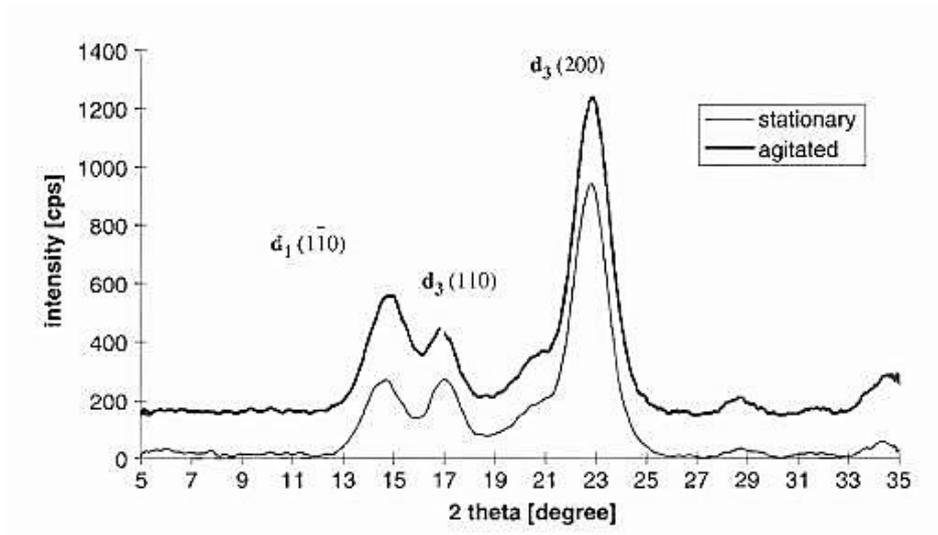


Figure 4. X-ray diffraction patterns obtained from BC samples synthesized in stationary and agitated culture conditions (Czaja *et al.*, 2004)

3.4 Optical transparency of nanocomposite based on bacterial cellulose

Yano *et al.* prepared transparent composites based on BC. The nanocomposites are optically clear with a fiber content as high as 70%, with a low thermal-expansion coefficient and a mechanical strength five times that of engineered plastics. These significant improvements in thermal and mechanical properties of the composite are due to web-like network of BC (Yano *et al.*, 2005).

Kwon reported that the composites made up 3-Glycidoxypropyltrimethoxysilane (GPTMS) and BC were fabricated with varied GPTMS concentration. The optical transparency of composites was improved by inducing GPTMS into BC. GPTMS formed in BC led to reduction of light scattering and prevented fiber from aggregating, so that the optical transparency of composites was improved (Kwon, 2013).

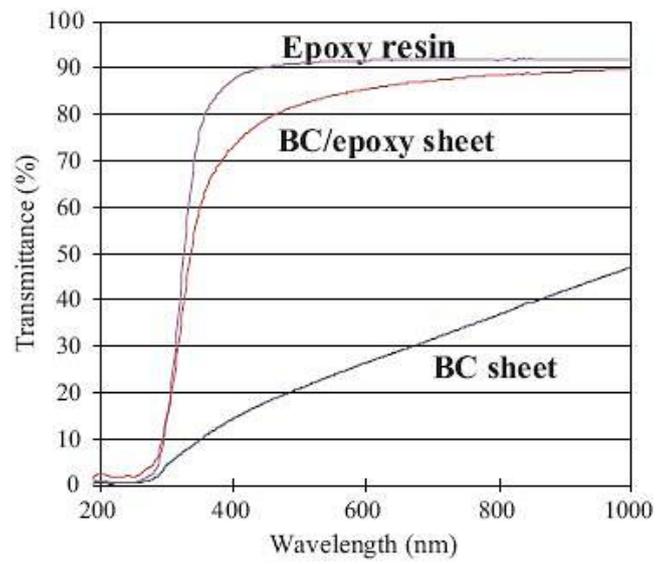


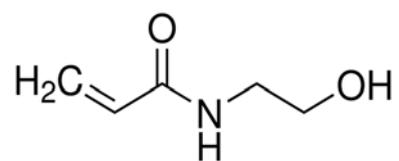
Figure 5. Light transmittance of a 65 μm thick BC/epoxy resin sheet, BC sheet, and epoxy resin sheet (Yano *et al.*, 2005)

4. Experimental

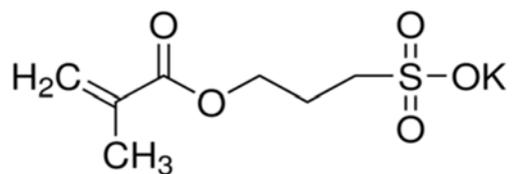
4.1 Materials

The strain of *Glucoacetobacter xylinus* (ATCC 10245) was purchased from Korean Culture Center of Microorganisms (KCCM) and used to produce the BC pellicles. BC cultivated using the cultivation method reported below.

Ionic acrylic monomers and the initiator for polymerization, N-hydroxyethyl acrylamide (HEAA) and 3-sulfopropyl methacrylate potassium salt (3-SPMP) were purchased from Sigma-Aldrich Co., LLC. USA and their chemical structures are shown in Figure 6. 2,2'-Azobis (4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Japan) was used as a thermal initiator. De-ionized water was used as solvent. All starting chemicals were used without further purification.



N-Hydroxyethyl acrylamide



3-Sulfopropyl methacrylate potassium salt

Figure 6. Structures of ionic acrylic monomers

4.2 Methods

4.2.1 Cultivation of bacterial cellulose

Glucoacetobacter xylinus was static and agitated cultured in Hestrin and Schramm (HS) medium at 0, 25, 50 and 100 rpm cultivation speed. Because the shape of BC changed sphere-like at over 100 rpm. The components of HS medium were 2 w/v % glucose, 0.5 w/v % yeast extract, 0.115 w/v % citric acid, 0.27 w/v % Na₂HPO₄, 0.05 w/v % MgSO₄•7H₂O (Reese *et al.*, 1950). The HS medium was sterilized by heating at 120 °C for 15 min in an autoclave. *Gluconacetobacter xylinus* was cultured in certain amount of HS medium at 30 °C for 2 weeks. The BC pellicle was washed thoroughly with de-ionized water, thereafter with 0.25 M sodium hydroxide solution. After removing the cells remaining cellulose, it was kept in 20 % ethanol solution below 15 °C.

4.2.2 Synthesis of ionic conducting polymer

The solution polymerization was performed using HEAA, 3-SPMP as ionic acrylic monomers and de-ionized water as solvent with initiator (V-70). Different weight (0, 1, 2, 5, 10 and 20 g) of 3-SPMP was dissolved in 10 g of HEAA, 70 g of de-ionized water as a solvent and 0.1 g of V-70 as a initiator. A mixture of monomers was heated to reaction temperature in a double boiler and stirred with magnetic stirrer.

Table 1. Composition of the ICP

Sample	3-SPMP (g)	HEAA (g)	DI water (g)	V-70 (g)
ICP-0	0	10	70	0.1
ICP-1	1	10	70	0.1
ICP-2	2	10	70	0.1
ICP-5	5	10	70	0.1
ICP-10	10	10	70	0.1
ICP-20	20	10	70	0.1

4.2.3 Fabrication of composite

The same size of BC pellicle (diameter 4 cm of circle) from 0, 25, 50 and 100 rpm impregnated in ICP was allowed to stand for a day at room temperature. Subsequently, BC impregnated with ICP was dried on polyethylene terephthalate (PET, SK Chemicals Co., Republic of Korea) film at 22 ± 2 °C for 24 h. These dried composites were kept in polyethylene bag before performing the other tests.

4.3 Characterization

4.3.1 Crystalline structure

4.3.1.1 Fourier transform infrared spectroscopy (FTIR)

The crystalline index was analyzed by Fourier transform infrared (FTIR) spectroscopy. The IR spectra were recorded using FTIR 6100 (JASCO, Japan) installed with a miracle accessory and an attenuated total reflectance (ATR). The FTIR spectra were collected over the range of 4000 - 600 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 30 scans.

4.3.1.2 X-ray diffraction (XRD)

X-ray diffraction analysis of bacterial cellulose with different cultivation speed performed using a Bruker X-ray diffractometer (equipped with a 2-D detector) in reflection mode. Tests were carried out with 2θ scanned between 5° and 40° nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) under a voltage of 40 kV and a current of 30 mA.

4.3.2 Morphology

4.3.2.1 Field emission-scanning electron microscopy (FE-SEM)

Field emission-scanning electron microscopy (FE-SEM, JSM-7600F, JEOL, Japan) at an accelerating voltage of 10 kV was conducted to observe the morphology of pure BC and BC/ICP composites. Prior to measurement, all samples were pre-coated with a homogeneous platinum layer (purity, 99.99 %) by ion sputtering to eliminate electron charging.

4.3.2.2 Brunauer–Emmett–Teller (BET)

Brunauer–Emmett–Teller (BET) nitrogen sorption experiments were conducted to calculate the surface area using an ASAP 2010 (Micromeritics, USA).

4.3.2.3 Energy dispersive spectroscopy (EDS)

Energy dispersive spectroscopy (EDS, SUPRA 55VP, Carl Zeiss, Germany) at an accelerating voltage of 15 kV was conducted to observe the morphology of pure BC and BC/ICP composites. Prior to measurement, all samples were pre-coated with a homogeneous platinum layer (purity, 99.99 %) by ion sputtering to eliminate electron charging.

4.3.3 Electrical conductivity

4.3.3.1 Surface resistivity

The surface resistivity of composite was measured by the ring probe (URS) technique using a MCP-HT 450 (Mitsubishi Co., Japan) on the basis of JIS-K6911. The temperature for the measurement was 23 °C and the value of RCF(S) was 10.09. The applied voltage was 10 V.

4.3.3.2 Volume resistivity

The volume resistivity of composite was measured using a MCP-HT 450 (Mitsubishi Co., Japan) by the ring probe (URS). The measuring temperature was 22 °C. The value of RCF(S) was 0.273. The applied voltage was 10 V.

4.3.4 Optical property

4.3.4.1 UV-vis spectrometer

The transparency of specimens was monitored at wavelengths from 200 - 700 nm using a UV-vis spectrometer, Lambda 20 (PerkinElemer, USA).

4.3.4.2 Refractive index

The ICP and composite were measured refractive index using Metricon (2010/M, USA). The composite detected at wavelengths of 404, 532, 632.8 and 829 (nm) in visible range using a prism coupler. And the incidence angle of the laser beam was varied so that the refractive index in both the thickness and planar directions could be determined.

5. Result and discussion

5.1 Crystalline structure

5.1.1 Fourier transform infrared spectroscopy (FTIR)

To confirm crystallinity index of BC, dried BC with different cultivation speed were analyzed by FTIR. IR spectra obtained as shown in Figures 7 and 8. The peaks near 3240, 750 (cm^{-1}) are specific to cellulose I α while the peaks near 3270, 710 (cm^{-1}) indicated the presence of cellulose I β (Yamamoto *et al.*, 1996). The I α peaks are clear in each spectrum as shown in Figure 7. The peaks near 3270, 710 (cm^{-1}) are hard to identify. From these result, it indicated that BC consist of almost cellulose I α

By cultivation speed, many characteristic bands are shifted at the peak absorbance is transformed. The bands at 1431, 1373, 1281, 1202, 1165, 1032, and 897 (cm^{-1}) are shifted to 1418, 1377, 1278, 1200, 1160, 1019, and 894 (cm^{-1}) as shown in Figure 8. Including the shift of O-H and C-H stretching vibrations (3353 to 3447, 2901 to 2883 cm^{-1}), all the bands are influenced by cultivation speed related to the change of intra- and intermolecular bonds (Oh *et al.*, 2005). The bands at 1431 cm^{-1} assigned as symmetric CH₂ bending (Cael *et al.*, 1975, Colom and Carrillo, 2002, Kondo and Sawatari, 1996, Nelson and O'Connor, 1964) and CH₂ wagging (Cao and Tan, 2004, Colom and Carrillo, 2002) are shifted to lower 1418 cm^{-1} . The bands at 1373, 1281 (cm^{-1}), all assigned as C-O-H bending, are decreased. The bands at 897 cm^{-1} assigned as C-O-C stretching moves toward 894 cm^{-1} by transformation. These

changes are consistent with a shift from order to disorder due to the change in hydrogen bonding patterns (Nelson and O'Connor, 1964).

The relative intensities of the peaks at 1429, 897 (cm^{-1}) were used for calculating the crystallinity index (Nelson and O'Connor, 1964). In fact, a weak and broad band at 897 cm^{-1} and a strong band at 1429 cm^{-1} (CH_2 scissoring) were present in the spectra of the two BC samples, defining them as cellulose I (Nelson and O'Connor, 1964). The intensity of the band at 1429 cm^{-1} has been also correlated with the degree of crystallinity and was often used as a standard band for its estimation. The crystallinity index was calculated absorbance at 1427/875 cm^{-1} (Czaja *et al.*, 2004, Oh *et al.*, 2005). The tendency of crystallinity index decreased rapidly as increasing cultivation speed as shown in Figure 10.

Because of centrifugal force, the bacteria has no efficient time to make crystalline structure during cultivation. Also, treatment of cultivation with different speed affect to connection with CO_2 , O_2 changes the crystal system of the cellulose due to the aerobic bacteria.

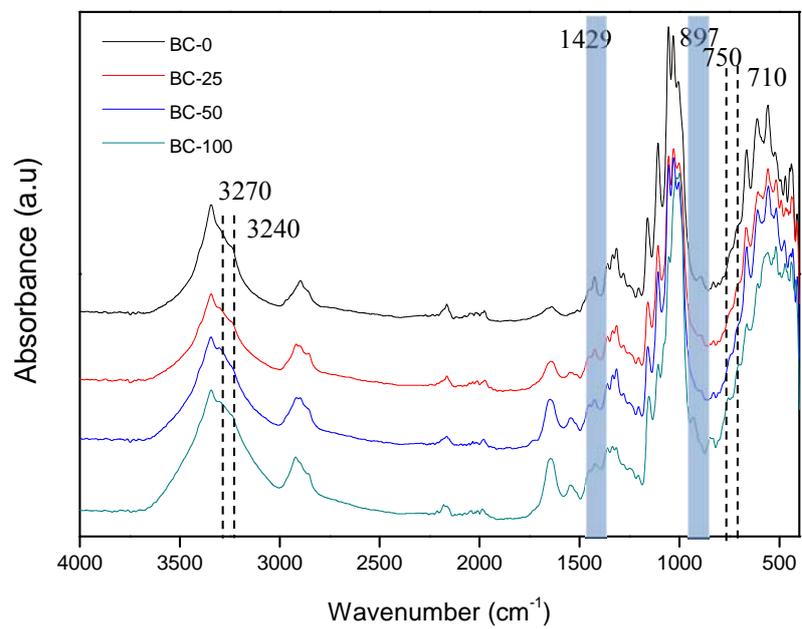


Figure 7. FTIR absorbance spectra of BC with different cultivation speed. The major bands are shaded.

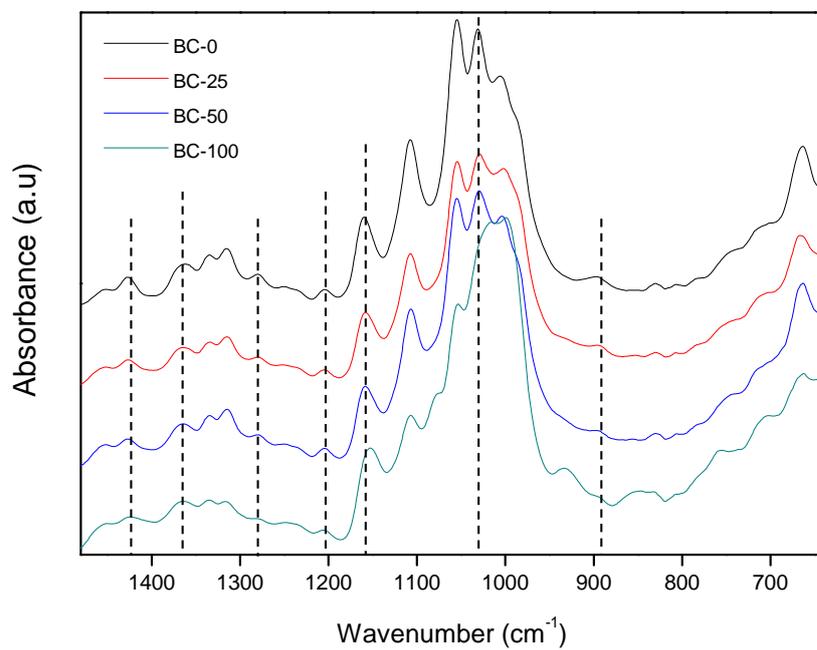
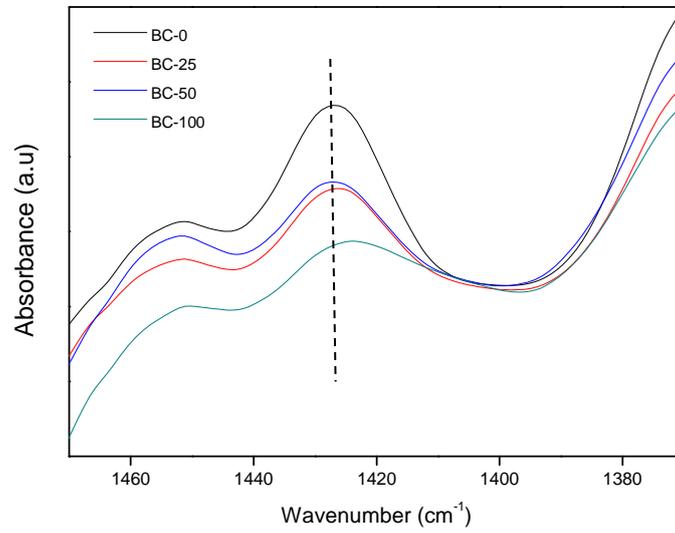


Figure 8. FTIR absorbance spectra of BC with different cultivation speed. The bands at 1431, 1373, 1281, 1202, 1165, 1032, and 897 (cm⁻¹).

(A)



(B)

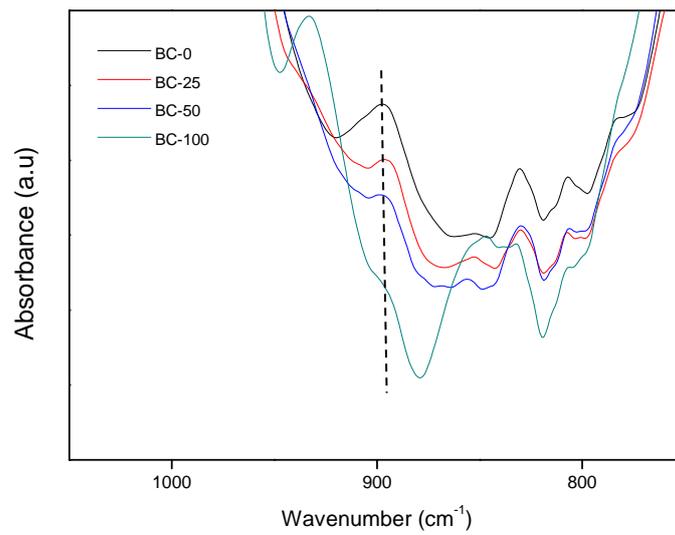


Figure 9. IR bands of BC with different cultivation speed
(A) band at 1429 cm⁻¹, (B) band at 897 cm⁻¹

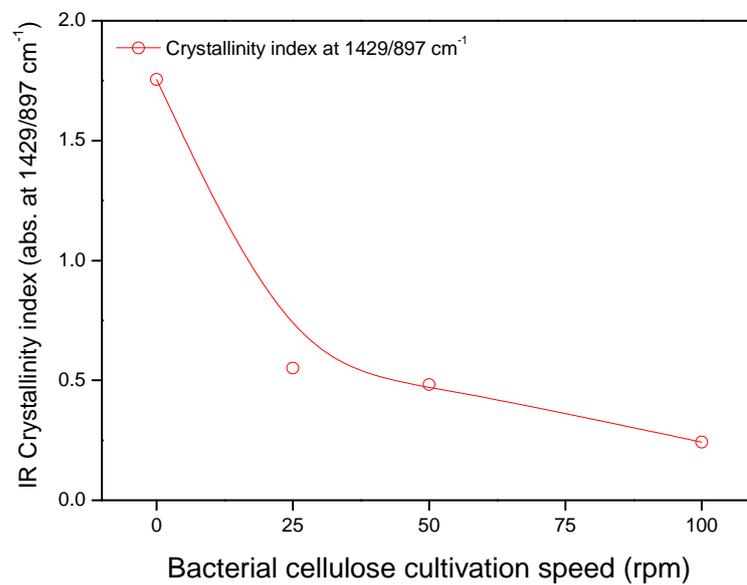


Figure 10. IR crystallinity index (abs. at 1429/897 cm⁻¹) of BC

5.1.2 X-ray diffraction (XRD)

In order to compare the structural changes in BC from different cultivation conditions and estimate if the agitated cultivation causes any disturbance in the crystallization process, X-ray diffraction was used. The XRD of BC corroborates the results obtained by FTIR. In fact diffraction gives rise to reflections corresponding to those for native cellulose and indicates the very high value of crystallinity. Estimation of crystallinity percentage from these diagrams was determined by comparing the integrated intensities of the crystalline peaks. These results were in very good agreement with the analysis carried out on the basis of the FTIR data.

Figure 11 presents the crystalline structural changes of BC. In BC, the two peaks located at $2\theta = 16.7^\circ$, 22.5° which assigned with (110) (200) planes of cellulose I (Gea *et al.*, 2010). For BC with different cultivation speed, these peaks were indicated smaller crystalline index of BC produced in agitated cultivation than static cultivation. It calculated as the ratio of the area of the crystalline peaks to the total area (Jeon *et al.*, 2010). On this basis, a hypothetical mechanism of formation and cell arrangement in the agitated culture has been proposed. During agitated cultivation, cells are stacked together around the outer surface (Czaja *et al.*, 2004). As BC with different cultivation speed, CO₂ changes the crystallinity as well as the crystal system of BC.

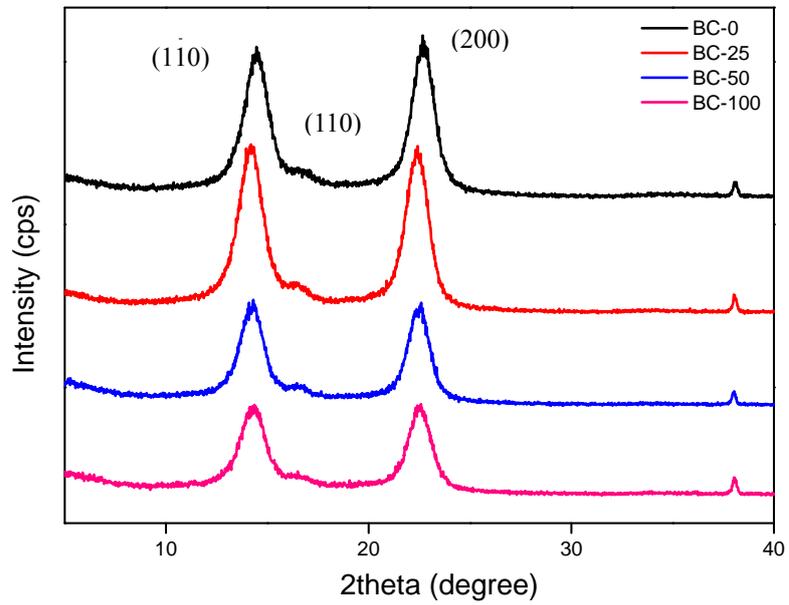


Figure 11. X-ray diffraction patterns obtained from BC synthesized in static and agitated cultivation conditions

5.2 Morphology

The surface morphology of BC with different agitation speed during the cultivation is shown in Figures 12 and 13. This images were confirmed with published work that showed morphology of BC revealed the ultrafine network structure made of a random assembly of ribbon-shaped cellulose microfibrils less than 100 nm wide (Barud *et al.*, 2008).

As shown in Table 2, the diameter of fibers was decreased by following increasing of their agitated cultivation speed while the bacteria make their pores compact. It means the density of BC become lower. Moreover, the surface area increased by increasing cultivation speed due to deduction of the diameter of fibers as shown in Table 3.

The composite were measured by EDS to confirm the qualification and quantification of ionic salt. By this tool, potassium salt peak was confirmed as shown in Figure14 and Table 4. And this result can explain the synthesized ICP and fabrication of composite by composition each element contents.

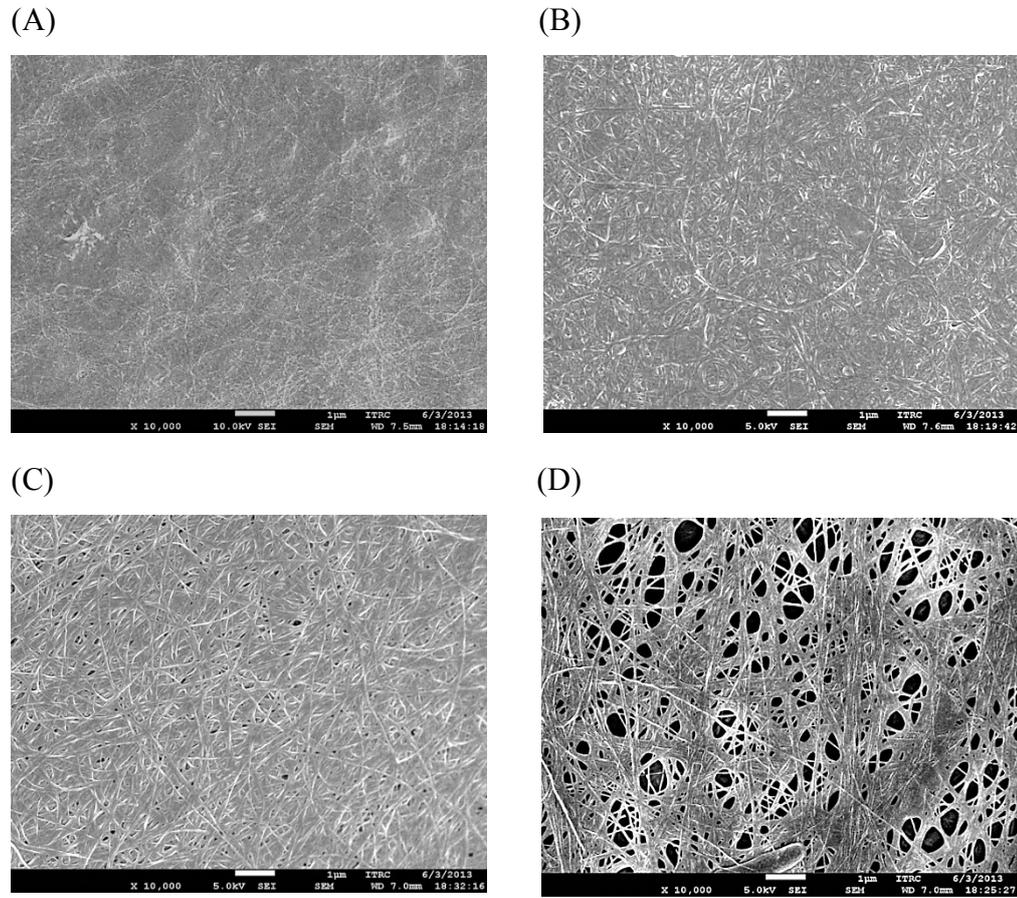


Figure 12. FE-SEM images of (A) BC-0, (B) BC-25, (C) BC-50, (D) BC-100. The samples were freeze dried. The images were magnified 10,000 times real sized and scale bar represents 1 μm .

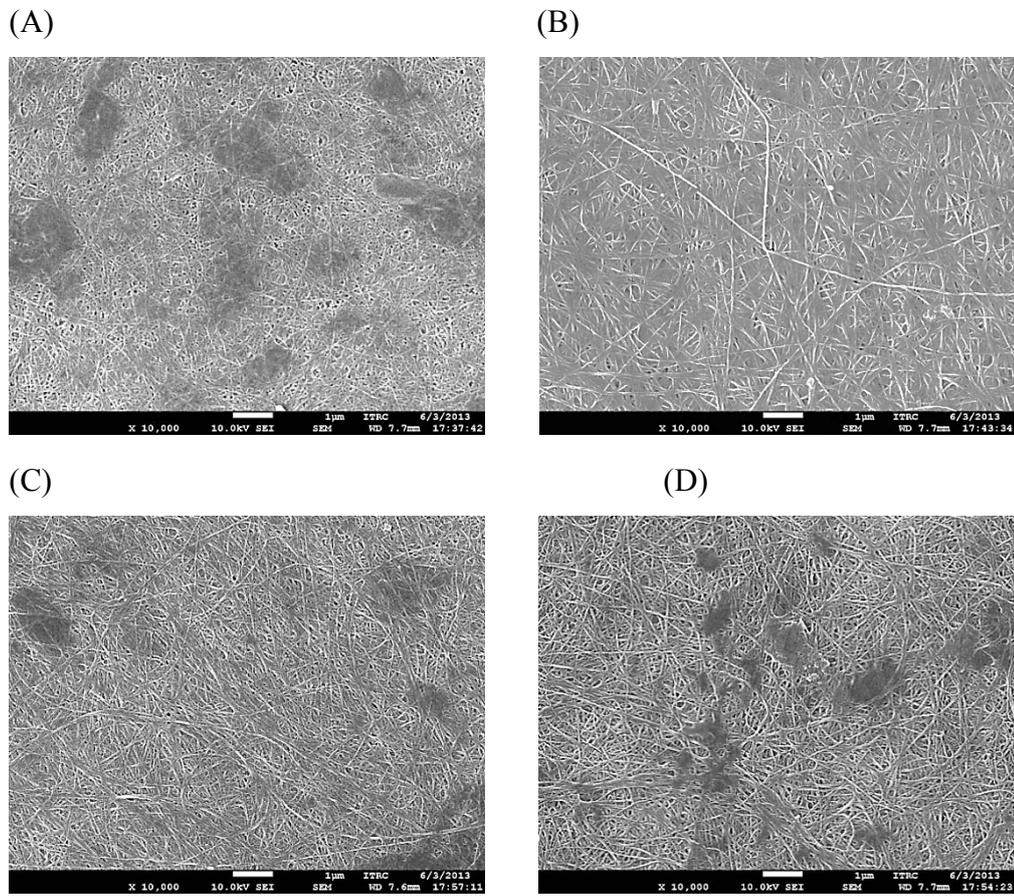


Figure 13. FE-SEM images of (A) BC-0, (B) BC-25, (C) BC-50, (D) BC-100. The samples were oven dried. The images were magnified 10,000 times real sized and scale bar represents 1 μm .

Table 2. Specifications of BC circle sized with the diameter 4 cm by following cultivation speed

	BC-0	BC-25	BC-50	BC-100
Average diameter of fibers (nm)	27.76 ± 4.05	26.23 ± 4.68	25.24 ± 1.81	20.62 ± 3.30
Observed by FE-SEM				

Table 3. BET surface area of BC circle sized with the diameter 4 cm

	BC-0	BC-25	BC-50	BC-100
BET surface area (m ² /g)	18.6	19.7	27.7	37.5

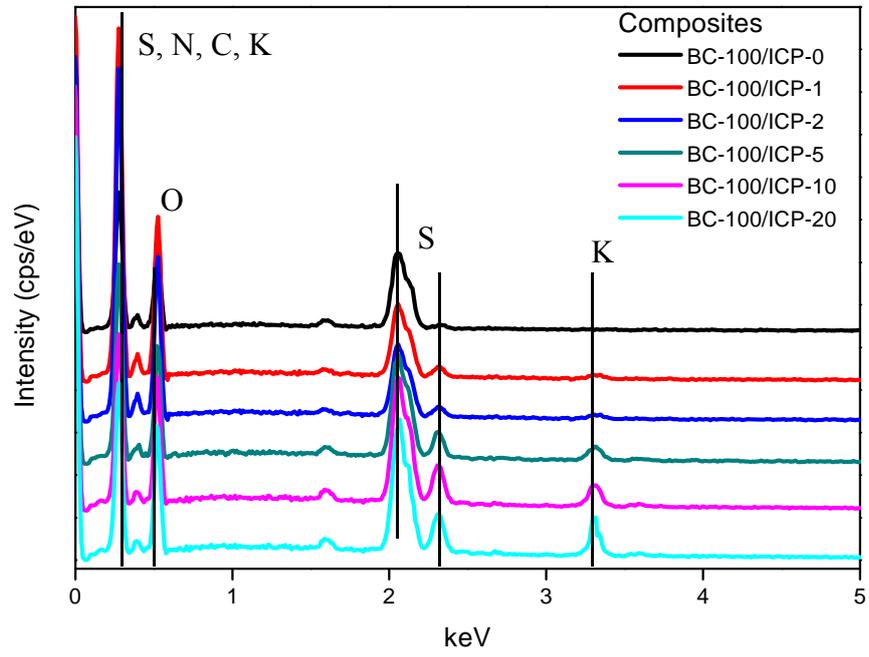


Figure 14. EDS analysis of BC-100/ICP composite with different salt contents

Table 4. Elements consist of BC-100/ICP composites with different salt contents

Elements	BC-100 /ICP 0 (wt. %)	BC-100 /ICP 1 (wt. %)	BC-100 /ICP 2 (wt. %)	BC-100 /ICP 5 (wt. %)	BC-100 /ICP 10 (wt. %)	BC-100 /ICP 20 (wt. %)
Carbon	47.35	53.87	49.86	48.52	43.35	36.55
Oxygen	39.17	32.30	34.06	31.84	32.65	35.88
Nitrogen	13.48	11.59	11.35	10.44	10.45	10.54
Potassium		1.19	2.40	4.88	7.59	8.94
Sulfur		1.04	2.33	4.31	5.95	8.09
Total				100		

5.3 Electrical conductivity

It has a tendency of increasing electrical conductivity of composite effects caused by the increase in salt concentration. The increased number of carrier ions dissociated and decreased chain mobility (Huh *et al.*, 2004). Also, the electrical conductivity of BC in more agitation was higher than static cultivated that owing to the increase of the amorphous region by weakened crystallinity (Ifuku *et al.*, 2009).

The crystalline regions do not allow easy passage of charge carriers, and hinder the conduction process. If ions are trapped in the intracrystalline regions or in the bulk crystalline regions, they contribute very little to ion conductivity. A reduction in the size of such crystalline traps would, therefore, help in conduction, while increase in size of voids (free volume) in amorphous phase also helps ion conduction, assuming that they provide a continuous path for ion motion (Tarafdar *et al.*, 2002)

From this Figures 15 and 16, the electrical behavior cannot be related to percolation effects of the salt concentration but rather to structurally difference in BC. By following increasing rotation speed during the cultivation, it affects improvement of electrical conductivity by polymer chain relaxation. With reduction in the diameter of fibers, and improvement of pores and surface area, it leads to structure modification of BC, it affect to hopping mechanism in ICP by providing the path to carry ions.

The results of surface resistivity and volume resistivity shows electrical conductivity from insulator to the composite has almost conductor as the value of resistivity 1.09×10^6 ohms/squares and 2.05×10^6 ohms-square respectively. With structural modification of BC using ICP, it has dramatically increased in electrical conductivity. It can be explained the nanostructure networks and the diameter of fibers affect to ion mobility.

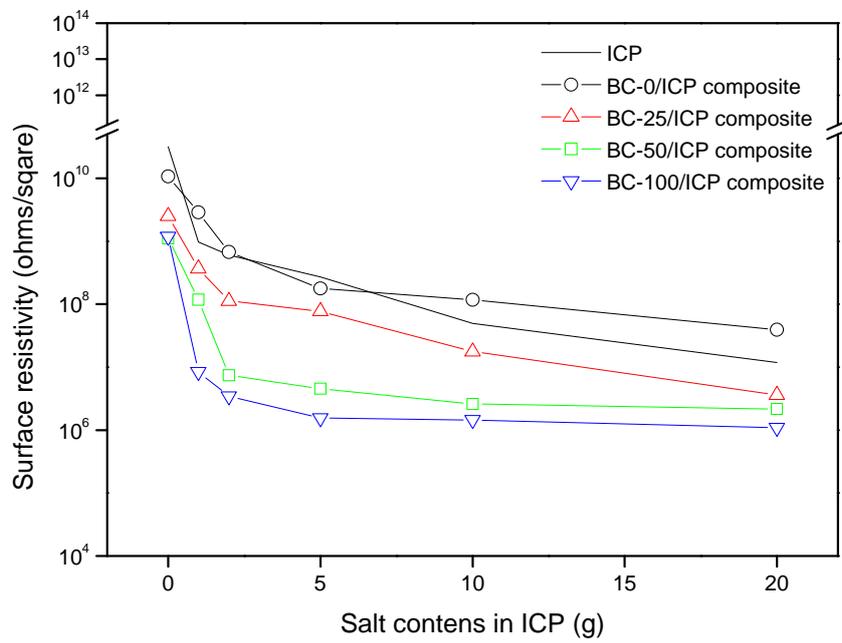


Figure 15. Surface resistivity of ICP, BC/ICP composites by following BC cultivation speed

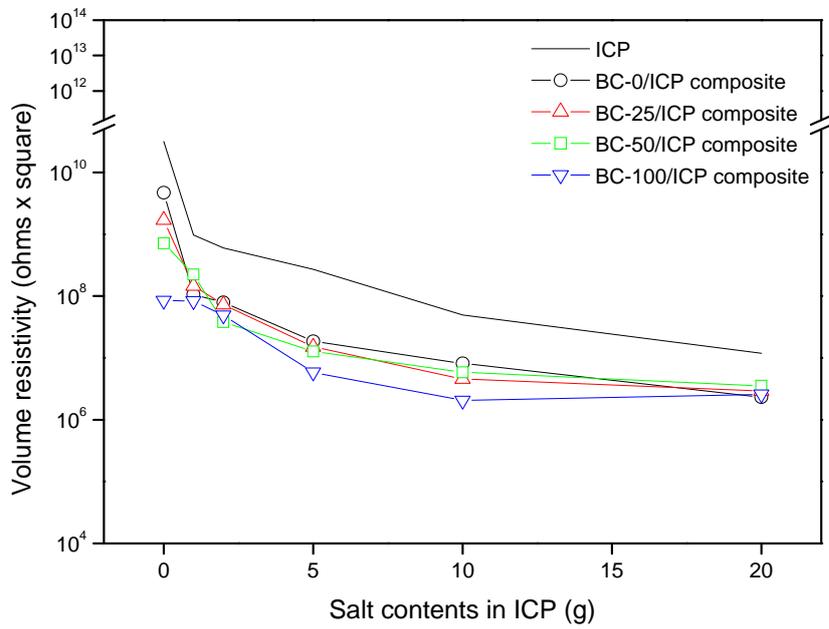


Figure 16. Volume resistivity of ICP, BC/ICP composites by following BC cultivation speed

5.4 Optical property

BC/ICP composite was optically transparent as shown in Figure 17 by filling into BC network structure with transparent material. The transmittance of the composite at 550 nm, which is middle of the visible light range are presented. The diameters of fibers making up BC are smaller than the wavelength of visible light, so that they cannot visible by naked eye. As mentioned before, BC composed of the ultrafine network structure made of a random assembly of ribbon-shaped cellulose has many pores inside BC. It caused a light scattering. After drying, BC became opaque due to many aggregations of fibers. To improve transparency of BC, impregnation method is used in this study. In case of BC/ICP composite, their results showed from many analyzers indicated that the ICP were certainly introduced into the network structure of BC. It plays a role of improvement of transparency by filling pores between fibers in network structure of BC.

Transparency of composite was improved due to incorporation of ICP. By inducing ICP into BC was light scattering and fiber aggregation reduced. The transmittance of BC/ICP composite improved about 6 times than original BC. In addition to, the composite showed a limitation of increasing transmittance that the highest improvement in optical transparency at 5 g of salt contents in ICP. Because the pores of BC have limited area can be filled with transparence polymer. By increasing agitation speed, the limitation of pores increased as shown in the range of transmittance.

Bacterial cellulose sheet can be considered as a three-dimensional network structure of nanosized fibers with air interstices in between. The opacity of the bacterial cellulose can be ascribed to the light diffraction at the interface between the cellulose fiber and the air interstices. The matching refractive index (RI) of the ICP and BC means that the light diffraction at the interface between the two components will be restricted and that the transparent film can be achieved. The RI of the composite and ICP were measured as shown in Table 5. In comparison, the RI of cellulose has been reported as 1.618 along the fiber axis and 1.544 in the transverse direction (Nogi and Yano, 2008). ICP helped to encapsulate the bacterial cellulose fibers and protect it from moisture and the surrounding atmosphere (Ummartyotin *et al.*, 2012).

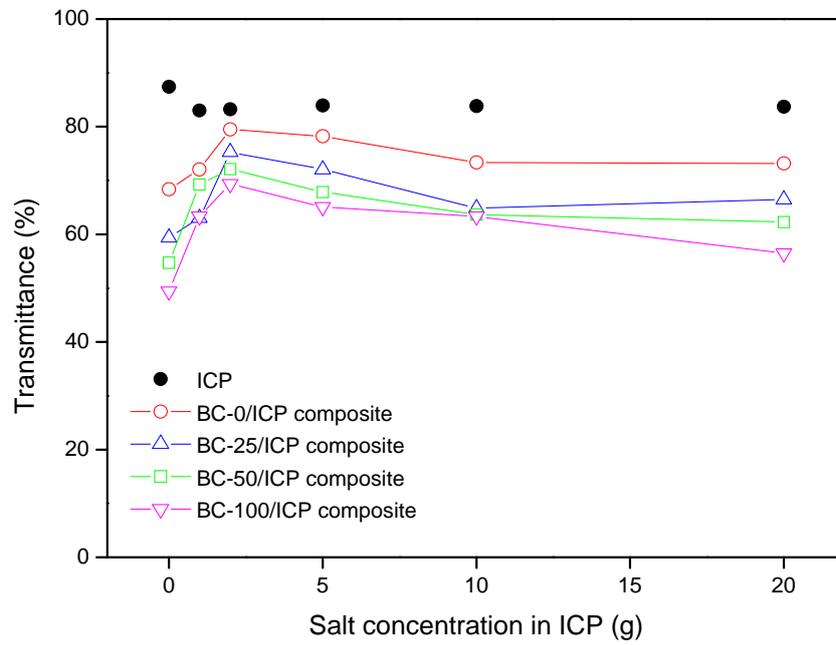


Figure 17. The transmittance of ICP, BC/ICP composites at 550 nm

Table 5. Refractive index of ICP and BC/ICP composites

sample	RI	sample	RI
ICP-0	1.52	BC-0/ICP-0	1.52
ICP-1	1.52	BC-0/ICP-1	1.52
ICP-2	1.52	BC-0/ICP-2	1.52
ICP-5	1.52	BC-0/ICP-5	1.51
ICP-10	1.51	BC-0/ICP-10	1.50
ICP-20	1.51	BC-0/ICP-20	1.50

6. Conclusion

Electrical conductive and optically transparent composite were successfully prepared by incorporation of ICP to BC. The crystalline structures were modified by cultivation speed. The crystalline structure of BC was changed nano network structures of BC, decrease the diameter of BC nanofibers and increase surface area of BC.

The crystalline regions do not allow easy passage of charge carriers, and hinder the conduction process. If ions are trapped in the intracrystalline regions or in the bulk crystalline regions, they contribute very little to ion conductivity. With different cultivation methods, the bacterial cellulose was modified in structurally. By increasing cultivation speed, the crystallinity index changed to decrease. In size of amorphous phase which helps ion conduction. It affects to increase of electrical conductivity.

Also, BC filled with ICP which avoid aggregation fibers of BC so that light scattering decreased.

Present results show the potential of the BC as biopolymers for electrical devices and electrolyte that with incorporation ICP by controlling salt concentration and with different cultivation by controlling crystallinity of pristine BC.

Nano-composite based BC was able to get the effect such as flexible and foldable. Also, the composite could be obtained properties like transparency by filling transparency polymers and electrical conductivity by ICP. The nanocomposite have applicable major factors such as conductivity, transparency, flexibility in the field of electrical

and electronics industry. It is to be expected that significant of BC composite would have a major material in electrical and electronics industry applications.

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초 록

박테리아 셀룰로오스는 리그닌과 헤미셀룰로오스 및 기타 추출물의 제거가 필요없는 순수 셀룰로오스이며, 나노셀룰로오스 중 박테리아의 생합성에 의해 생산되는 친환경 재료이다. 박테리아 셀룰로오스에 금속, 전도성 고분자, 탄소나노튜브 등을 이용하여 전도성을 부여하거나 고분자를 사용하여 투명성을 부여하는 등 다양한 목적을 부여하는 연구가 주목받고 있다. 높은 기계적 물성, 결정화도, 3D 나노구조를 가지는 박테리아 셀룰로오스 기반 복합재료는 의료용, 미용, 식용, 전기·전자 분야 등 다양하게 적용되고 있다.

본 연구에서는 박테리아 셀룰로오스 배양 시 교반 속도를 달리하여 그 구조적 성질을 달리하고, 박테리아 셀룰로오스의 특징인 나노사이즈의 피브릴이 얽혀진 3차원적 망상 구조의 변화를 통해 전기전도성 및 투명성에 미치는 영향을 살펴보고자 하였다. 전도성 고분자 합성 시 염의 함량을 달리하여 이온 전도성 고분자를 합성하였다. 이 고분자를 박테리아 셀룰로오스 나노구조에 함침하여 제조한 박테리아 셀룰로오스/이온 전도성 고분자로 이루어진 복합재료의 성능을 평가하였다.

박테리아 셀룰로오스의 구조적 변화는 FTIR, XRD 측정을 통하여 결정화도의 정도를 평가하였다. 배양 시 교반 속도가 증가할수록 결정성이 현저히 감소함을 확인할 수 있었다. 또한, FE-SEM 으로 표면 관찰 시, 박테리아 셀룰로오스 섬유의 직경은 정지배양 시에는 27.76 ± 4.05 nm 에서 진탕배양 속도가 최대 100 rpm 으로 증가했을 때에는 20.62 ± 3.30 nm 로 줄어들었으며,

나노구조를 이루는 섬유와 치밀성의 정도가 떨어지는 것을 알 수 있었다. 이에 따라 BET 로 측정된 표면적이 정치배양 18.6 m²/g 에서 진탕배양 속도가 최대인 조건에서 37.5 m²/g 로 박테리아 셀룰로오스 섬유의 직경이 감소함에 따라 표면적이 두 배 가까이 증가했음을 확인할 수 있었다.

부도체인 박테리아 셀룰로오스와 달리 박테리아 셀룰로오스와 이온 전도성 고분자로 이루어진 복합재료의 전도성의 경우, 염의 함량이 증가함에 따라 향상되는 것은 물론이며, 박테리아의 배양 속도가 증가할수록 전도성 고분자가 채워질 수 있는 공간이 넓어지고 비결정구조가 증가되어 전기전도도가 향상되었다. 정치배양 시에는 4.73 x 10¹⁰ ohms/square 의 표면저항을 갖는 반면, 진탕배양 시 최대 1.09 x 10⁶ ohms/square 을 가져 전기전도도가 상당히 향상되었음을 알 수 있었다. 이로써 박테리아 셀룰로오스의 구조적 변화를 통해 고분자의 함침량이 증가되어 복합재료의 전도도 향상에 기여한다는 것을 형태학적 관찰과 전기전도도 측정을 통해 구명하였다.

또한, 복합재료의 광투과도의 경우, 제조된 박테리아 셀룰로오스/이온 전도성 고분자 복합재료는 박테리아 셀룰로오스의 나노구조 안의 공극에 투명한 물질이 채워짐에 따라 광산란이 줄어들어 광투과도가 향상됨을 알 수 있었다.

이상과 같이 본 연구는 박테리아 셀룰로오스와 이온 전도성 고분자를 이용하여 전기전도성 및 광투과도가 개선된 복합재료를 제작하였으며, 이는 향후 전기전도성 및 투명성이 동시에 요구되는 전기·전자 산업분야에 있어 적용 가능성이 있는 것으로 판단된다.

키워드 : 박테리아 셀룰로오스, 이온 전도성고분자, 정치배양,
진탕배양, 전기전도도, 광투과도

학번 : 2012-21121



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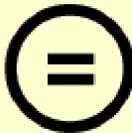
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**Electrical Conductivity and Optical Transparency of
Bacterial Cellulose based Composite
by static and agitated methods**

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산림과학부 환경재료과학전공
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2013 년 12 월

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Abstract

Electrical Conductivity and Optical Transparency of structurally modified Bacterial Cellulose based Composite

Sera Jeon

Program in Environmental Materials Science

Graduate School

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Bacterial cellulose (BC) is an environmental friendly material composed of pure cellulose, and many researchers have suggested its potentials to be extended to various applications in fields such as medical, beauty, clothes, diaphragm, food and so on.

The main purpose of this study was to investigate electrical conductivity and optical transparency of BC based composite through modification structure of BC by changing cultivation speed. BC by static and agitated cultivation methods evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM) and Brunauer–Emmett–Teller (BET). From these results indicated that bacteria synthesize cellulose with different diameter of fiber from 27.76 ± 4.05 at static cultivation to

20.62 ± 3.30 (nm) at agitated cultivation. And surface area increased about twice times due to centrifugal force.

The three-dimensional BC network served as a nanostructured substrate for ionic conducting polymer (ICP). ICP synthesized with varied contents of salt. The electrical conductivity of BC/ICP composite was verified by surface resistivity and volume resistivity. By enhancing ICP on BC led to the improvement in electrical conductivity than pure BC which is insulator. Moreover, the electrical conductivity of BC/ICP composite improved rapidly by BC with high agitated cultivation speed through filling more ICP due to surface area increased.

BC fibers are invisible due to its diameter was less than a visible light wavelength. However, a dried BC is opaque because the diameter of fibers is increased due to microfibrils of BC collapsed and piled on each other. Also, the pores inside BC lead to significant light scattering. To enhance the optical transparency of BC based composite, the transparent materials fill in these pores in BC nanostructures to prevent the fibers aggregation, which affect light scattering. BC/ICP composite has improvement about 6 times than pure BC in the optical transparency. These results indicated that pores within BC, occupied by ICP, prevented light scattering.

This electrically conductive and optical transparent nanocomposite can be useful in various applications requiring biocompatibility, electrical conductivity and optical transparency.

Keywords : bacterial cellulose, ionic conducting polymer, static cultivation, agitated cultivation, electrical property, optical property

Student Number : 2012-21121

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1. Introduction

1.1 Background of this study

Since Shirakawa *et al.* found conducting polymers at the end of the 1970s, composites of conducting polymers have been developed for use of anti-static substances, smart windows, light-emitting diodes, solar cells and so on (Shirakawa *et al.*, 1977, Chen *et al.*, 2010). However, composites consist of conducting polymer are not fully environmental friendly, biocompatible, and biodegradable. Ionic conducting polymer using salt is fascinating in eco-friendly electrical industry (Smela, 2003).

Cellulose is most abundant polymer and common natural resources in the earth. Bacterial cellulose (BC) has been considered a promising candidate material for biocomposite due to its acquisition through biosynthesis without chemical treatment among nanocellulose (Douglas *et al.*, 2008).

By incorporation conducting polymer and bacterial cellulose, filled pores in bacterial cellulose nanostructure with electrical conductive and optical transparent ionic conducting polymer (ICP). It can be implemented as high functional, flexible and lightweight composites and is environmentally friendly. Application of composite based on bacterial cellulose can be useful in various applications requiring biocompatibility and electrical conductivity such as biocompatible composite actuators, clothing sensor and so on.

This study is focused on effect of structurally modified BC in different cultivation methods and the varied concentration of ICP. The

composite consist of BC impregnated with ICP, which is expected to assign electrical conductivity and improve by modification crystalline structures of BC compared to pure BC. It is expected that the composite composed of biomaterial and ionic conducting polymer will have new possibilities for applications in industry as chemical sensors, biomedical devices, and so on.

1.2 Nanocellulose

Cellulose is an important natural material (Shi *et al.*, 2013). The crystallinity of cellulose is main issue because it directly relates to high strength performances. In case of plant cellulose, to obtain pure cellulose with high crystallinity is very tough because it contains not only cellulose but also hemicellulose, lignin and other extractives. Therefore, cellulose from plant should be separated from other extractives including hemicellulose and lignin through physical, mechanical and chemical treatment.

The production of nano-scaled cellulose and their application in composite material have gradually got increasing attention during the last decades because nanocellulose has many advantages (i.e. high crystallinity, high tensile strength, high melting temperature, 200 times more surface area, stiffness combined with low weight, and biodegradability). Recently, many researchers are attempting to find industry fields that commercialize nanocellulose (Eichhorn *et al.*, 2010).

Nanocellulose is classified four types in large as manufacturing method. The production of nano fibrillated cellulose is affected by the applied treatment to the fibers before homogenization. When fibers are subjected to high pressure by homogenizer, the cellulose is effectively fibrillated (Gilberto Siqueira, 2010, Chinga-Carrasco, 2011). There are also electro spinning nanocellulose via electro spinning, and the production through produce by bacterial cellulose cultures and bacteria, the BC which is nanostructured cellulose (Douglas *et al.*, 2008).

1.2.1 Bacterial cellulose

The fibers of cellulose are produced by certain bacteria such as the genera *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Rhizobium*, or *Sarcina*. *Acetobacter xylinum* (or *Gluconacetobacter xylinus*) is the most efficient producer among these bacteria, a gram-negative bacterium, which can produce cellulose and acetic acid in a culture medium containing carbon and nitrogen sources. BC presents unique properties such as high mechanical strength and an extremely fine and pure cellulose fiber network structure. This network structure is the form of a pellicle made up of random ribbon-shaped fibrils, less than 100 nm wide, which are composed of 2~4 nm in diameter. In addition, it has porosity, 3-dimensional network structure, water holding capability, and biocompatibility. In contrast to obtain nanocellulose through mechanical or chemo-mechanical processes, BC is produced by biosynthesis of *Acetobacter xylinum* (Chen *et al.*, 2010, Lee *et al.*, 2012, Ross *et al.*, 1991, Yamanaka *et al.*, 1989).

In polymer science, there are various methods and modifications of BC. Examples of fabrication method are as followings, fabrication BC with polymer matrix (Gea *et al.*, 2010), treatment of culture medium (Yoon *et al.*, 2006), and so on. Moreover, there is also lamination or deposition of transparent resins on the surface of BC (Nogi and Yano, 2008).

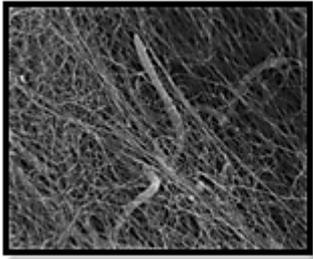
1.2.1.1 Cultivation methods of bacterial cellulose

BC cultivated pure cellulose by the bacteria of *Acetobacter xylinum*, culture methods are classified by static cultivation method and agitated cultivation method. Static and agitated cultivation methods are used to get BC as shown in figure 1. The appearance of the two types of BC by static and agitated cultivation is quite different. In the static cultivation method of BC, it is well known as pellicle at the surface of the culture medium as a gelatinous form. In contrast, various sizes (10 μm to 1 mm) and shapes (spherical, ellipsoidal, stellate or fibrous) of BC in well-dispersed in agitated culture medium as reported (Herstrin and Schramm, 1954, Dudman, 1960, Yoshinaga *et al.*, 1997).

BC synthesized through static cultivation method showed a high value of Young's modulus, while water holding capacity was lower than agitated cultivation method (Krystynowicz *et al.*, 2002).

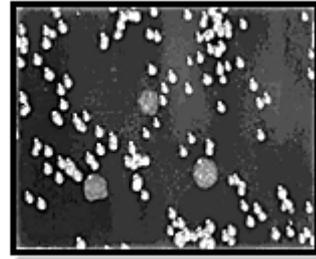
In this study, the cultured BC using the above two methods is to compare the impact on the electrical conductivity and transparency.

Static cultivation



Low water holding capacity
High Young's modulus
High yield production

Agitated cultivation



High water holding capacity
Low Young's modulus
Low yield production

Figure 1. Cultivation methods of bacterial cellulose
(Krystynowicz *et al.*, 2002)

1.3 Conducting polymer

When we fabricate nanocellulose composites with adding inorganic fillers, conjugated polymer, carbon-based materials, the composite have properties of transparency, flexibility, electric conductivity. And these characters are major factors to apply electric industry (Eichhorn *et al.*, 2010). Shirakawa *et al.* discovered that a polymer, polyacetylene, can be made conductive almost like a metal by doping with iodine (Shirakawa *et al.*, 1977). Conducting materials are carbon black, metal and conducting polymer like polyaniline, polythiophene and so on. The method of adding metal powder or carbon particle had a disadvantage that transparency of composite is decreased. However, ionic conducting polymer has advantages like non-pollution of substrate by ion migration and transparency by polymerization using acrylic monomer.

Electrical conductivity of composite is measured as followings. As measuring electrical resistance, electrical conductivity can be achieved due to their reciprocal. Resistance is classified into surface resistance and volume resistance. Surface resistance is measured the flow of current restricting surface. Volume resistance is the resistance on movement of electrons regardless of the thickness and conductive structure of the material.

2. Objectives

The purpose of this study is to prepare composite based on BC with electrical conductivity and optical transparency.

2.1 Modified structure of bacterial cellulose by different cultivation methods

In order to know how to perform electrical property in composite having difference structure, it is necessary to analyze the crystalline structure by cultivation methods. BC with different cultivation methods can be helpful to make a new structure like electron or charge path. As observed in BC crystalline structure, the electrical property of ICP can be associated preferentially with the mobility of ion.

2.2 Improvement in electrical conductivity and optical transparency of composite based on bacterial cellulose by incorporation conducting polymer with ionic monomer

With different concentration of potassium salts, the electrical conductivity can be controlled. Synthesized ICP with acrylic ionic monomers has electrical properties and optical transparency. It affects to composite that filling ICP into pores of BC, the composite performed electrical conductivity and optical transparency.

3. Literature reviews

3.1 Conductive cellulose nanocomposites

Due to wide range of morphological form of cellulose based composite provide opportunities to produce materials with high electrical conductivity. Cellulose and conducting materials can be combined by blending, doping and coating. And conducting polymers, carbon nanotubes, grapheme and ionic liquid are used as a conductor (Shi *et al.*, 2013).

Yoon *et al.* prepared electrically conducting polymeric membranes by incorporating multiwalled carbon nanotubes (MWCNTs) into BC pellicles produced by *Gluconacetobacter xylinum*. It was found that the incorporation process is a useful method not only for dispersing MWCNTs in an ultrafine fibrous network structure but also for enhancing the electrical conductivity of the polymeric membranes (Yoon *et al.*, 2006). Also, Feng *et al.* fabricated composite consist of BC and grapheme oxide (GO). By increasing contents from 0.1 wt% to 1 wt% GO after in situ reduction, the conductivity remarkably increased to 1.1×10^{-4} S/m. The nanocomposite has properties such as mechanically strong, flexible and conductive (Feng *et al.*, 2012). However, It has disadvantages in optical property to enhance electrical conductivity with carbon based material

Lee *et al.* described BC with conducting polymer which is polyaniline (PANI) by interfacial polymerization. With using two different phases between water and chloroform made composite with

PANi and BC. By the plain interfacial polymerization, the electrical conductivity of BC/PANi composite reached up to 3.8×10^{-1} S/m when 0.32 M of aniline was used (Lee *et al.*, 2012).

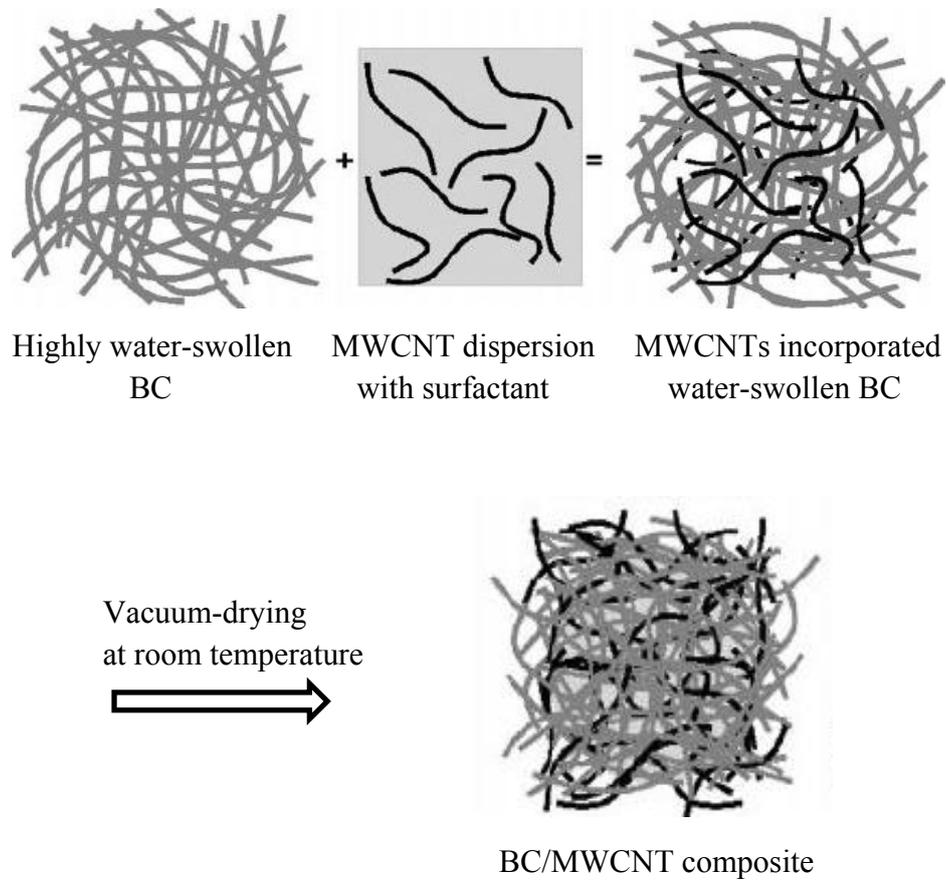


Figure 2. Schematic diagram of the process of incorporating the MWCNTs to BC (Yoon *et al.*, 2006)

3.2 Electrical property of ionic materials

Verdolotti *et al.* reported that the effect of the incorporation of several lithium salts on the electrical and mechanical properties of rigid polyurethane foam composite. Also the salts affected electrical conductivity. Different concentrations of salts were added and it affected electrical conductivity as shown in Figure 3 (Verdolotti *et al.*, 2011).

Jeon *et al.* founded that an electro-active biopolymer actuator based on the BC using lithium chloride (LiCl) for surface modification. With this modification, it affects to ionic conductivity LiCl treated BC were higher than pure BC due to increase of the amorphous region by weakened crystallinity (Jeon *et al.*, 2010).

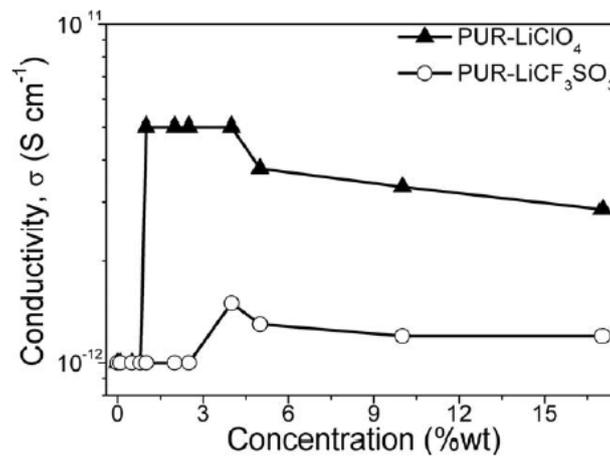
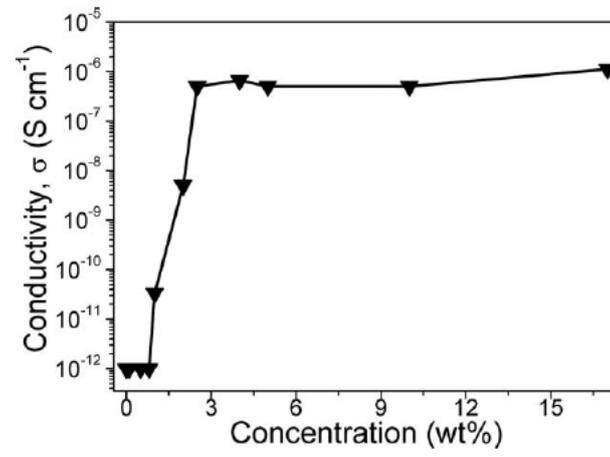


Figure 3. Electrical conductivity versus weight percentage of salt for the composites (Verdolotti *et al.*, 2011)

3.3 Structurally-modified cellulose by cultivation methods

Czaja *et al.* studied structural difference of BC produced in static and agitated cultivation. There is deduction in good correlation with smaller size of crystalline in agitated culture. During agitation, cells are stacked together in organized group around the outer surface of the cellulose sphere (Czaja *et al.*, 2004). The structural differences exist in the cellulose crystal and the molecular chain between the two types of BC from static and agitated cultivation. In the static culture, the crystallinity and cellulose Ia content of cellulose are higher than the agitated culture. Moreover, the degree of polymerization is higher for the cellulose molecules from the static culture. Watanabe *et al.* reported that the interference in the crystalline process of BC may lead to the formation of small sized crystalline in agitated culture (Watanabe *et al.*, 1998).

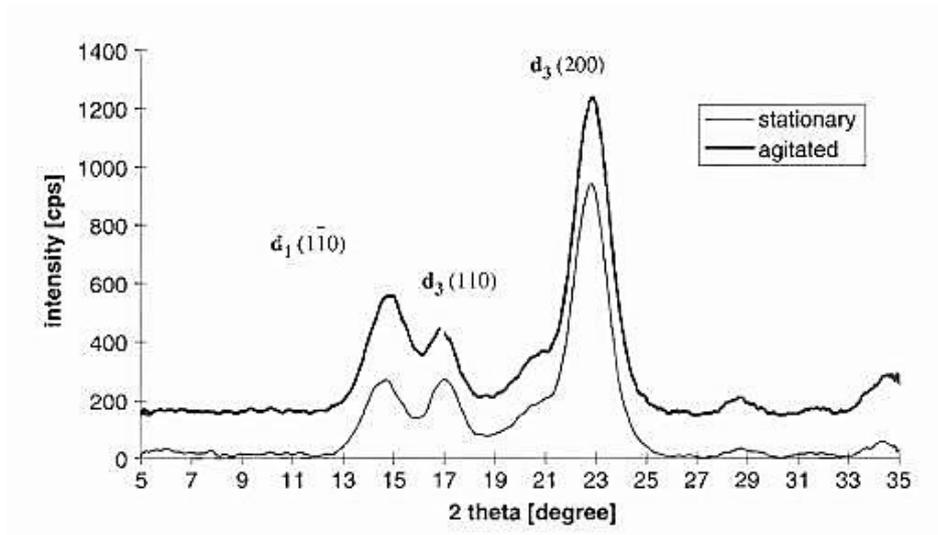


Figure 4. X-ray diffraction patterns obtained from BC samples synthesized in stationary and agitated culture conditions (Czaja *et al.*, 2004)

3.4 Optical transparency of nanocomposite based on bacterial cellulose

Yano *et al.* prepared transparent composites based on BC. The nanocomposites are optically clear with a fiber content as high as 70%, with a low thermal-expansion coefficient and a mechanical strength five times that of engineered plastics. These significant improvements in thermal and mechanical properties of the composite are due to web-like network of BC (Yano *et al.*, 2005).

Kwon reported that the composites made up 3-Glycidoxypropyltrimethoxysilane (GPTMS) and BC were fabricated with varied GPTMS concentration. The optical transparency of composites was improved by inducing GPTMS into BC. GPTMS formed in BC led to reduction of light scattering and prevented fiber from aggregating, so that the optical transparency of composites was improved (Kwon, 2013).

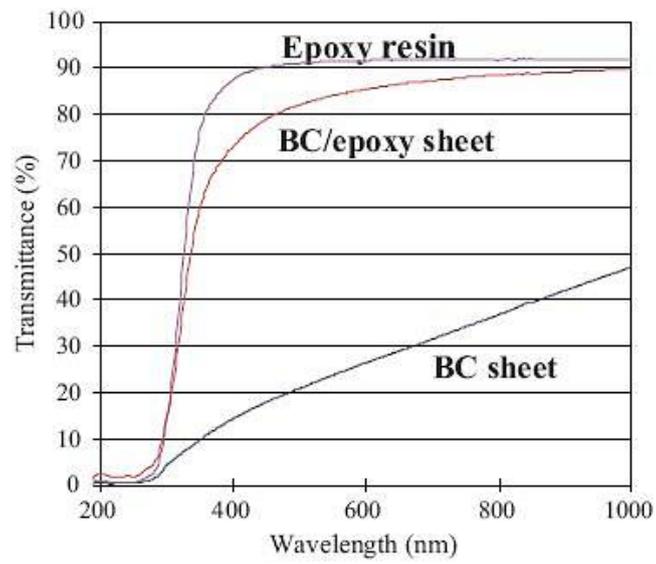


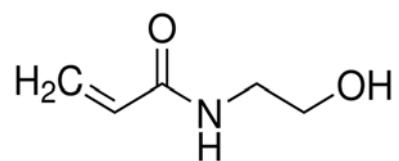
Figure 5. Light transmittance of a 65 μm thick BC/epoxy resin sheet, BC sheet, and epoxy resin sheet (Yano *et al.*, 2005)

4. Experimental

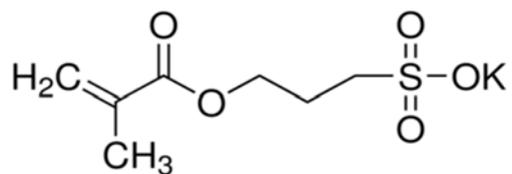
4.1 Materials

The strain of *Glucoacetobacter xylinus* (ATCC 10245) was purchased from Korean Culture Center of Microorganisms (KCCM) and used to produce the BC pellicles. BC cultivated using the cultivation method reported below.

Ionic acrylic monomers and the initiator for polymerization, N-hydroxyethyl acrylamide (HEAA) and 3-sulfopropyl methacrylate potassium salt (3-SPMP) were purchased from Sigma-Aldrich Co., LLC. USA and their chemical structures are shown in Figure 6. 2,2'-Azobis (4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Japan) was used as a thermal initiator. De-ionized water was used as solvent. All starting chemicals were used without further purification.



N-Hydroxyethyl acrylamide



3-Sulfopropyl methacrylate potassium salt

Figure 6. Structures of ionic acrylic monomers

4.2 Methods

4.2.1 Cultivation of bacterial cellulose

Glucoacetobacter xylinus was static and agitated cultured in Hestrin and Schramm (HS) medium at 0, 25, 50 and 100 rpm cultivation speed. Because the shape of BC changed sphere-like at over 100 rpm. The components of HS medium were 2 w/v % glucose, 0.5 w/v % yeast extract, 0.115 w/v % citric acid, 0.27 w/v % Na₂HPO₄, 0.05 w/v % MgSO₄•7H₂O (Reese *et al.*, 1950). The HS medium was sterilized by heating at 120 °C for 15 min in an autoclave. *Gluconacetobacter xylinus* was cultured in certain amount of HS medium at 30 °C for 2 weeks. The BC pellicle was washed thoroughly with de-ionized water, thereafter with 0.25 M sodium hydroxide solution. After removing the cells remaining cellulose, it was kept in 20 % ethanol solution below 15 °C.

4.2.2 Synthesis of ionic conducting polymer

The solution polymerization was performed using HEAA, 3-SPMP as ionic acrylic monomers and de-ionized water as solvent with initiator (V-70). Different weight (0, 1, 2, 5, 10 and 20 g) of 3-SPMP was dissolved in 10 g of HEAA, 70 g of de-ionized water as a solvent and 0.1 g of V-70 as a initiator. A mixture of monomers was heated to reaction temperature in a double boiler and stirred with magnetic stirrer.

Table 1. Composition of the ICP

Sample	3-SPMP (g)	HEAA (g)	DI water (g)	V-70 (g)
ICP-0	0	10	70	0.1
ICP-1	1	10	70	0.1
ICP-2	2	10	70	0.1
ICP-5	5	10	70	0.1
ICP-10	10	10	70	0.1
ICP-20	20	10	70	0.1

4.2.3 Fabrication of composite

The same size of BC pellicle (diameter 4 cm of circle) from 0, 25, 50 and 100 rpm impregnated in ICP was allowed to stand for a day at room temperature. Subsequently, BC impregnated with ICP was dried on polyethylene terephthalate (PET, SK Chemicals Co., Republic of Korea) film at 22 ± 2 °C for 24 h. These dried composites were kept in polyethylene bag before performing the other tests.

4.3 Characterization

4.3.1 Crystalline structure

4.3.1.1 Fourier transform infrared spectroscopy (FTIR)

The crystalline index was analyzed by Fourier transform infrared (FTIR) spectroscopy. The IR spectra were recorded using FTIR 6100 (JASCO, Japan) installed with a miracle accessory and an attenuated total reflectance (ATR). The FTIR spectra were collected over the range of 4000 - 600 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 30 scans.

4.3.1.2 X-ray diffraction (XRD)

X-ray diffraction analysis of bacterial cellulose with different cultivation speed performed using a Bruker X-ray diffractometer (equipped with a 2-D detector) in reflection mode. Tests were carried out with 2θ scanned between 5° and 40° nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) under a voltage of 40 kV and a current of 30 mA.

4.3.2 Morphology

4.3.2.1 Field emission-scanning electron microscopy (FE-SEM)

Field emission-scanning electron microscopy (FE-SEM, JSM-7600F, JEOL, Japan) at an accelerating voltage of 10 kV was conducted to observe the morphology of pure BC and BC/ICP composites. Prior to measurement, all samples were pre-coated with a homogeneous platinum layer (purity, 99.99 %) by ion sputtering to eliminate electron charging.

4.3.2.2 Brunauer–Emmett–Teller (BET)

Brunauer–Emmett–Teller (BET) nitrogen sorption experiments were conducted to calculate the surface area using an ASAP 2010 (Micromeritics, USA).

4.3.2.3 Energy dispersive spectroscopy (EDS)

Energy dispersive spectroscopy (EDS, SUPRA 55VP, Carl Zeiss, Germany) at an accelerating voltage of 15 kV was conducted to observe the morphology of pure BC and BC/ICP composites. Prior to measurement, all samples were pre-coated with a homogeneous platinum layer (purity, 99.99 %) by ion sputtering to eliminate electron charging.

4.3.3 Electrical conductivity

4.3.3.1 Surface resistivity

The surface resistivity of composite was measured by the ring probe (URS) technique using a MCP-HT 450 (Mitsubishi Co., Japan) on the basis of JIS-K6911. The temperature for the measurement was 23 °C and the value of RCF(S) was 10.09. The applied voltage was 10 V.

4.3.3.2 Volume resistivity

The volume resistivity of composite was measured using a MCP-HT 450 (Mitsubishi Co., Japan) by the ring probe (URS). The measuring temperature was 22 °C. The value of RCF(S) was 0.273. The applied voltage was 10 V.

4.3.4 Optical property

4.3.4.1 UV-vis spectrometer

The transparency of specimens was monitored at wavelengths from 200 - 700 nm using a UV-vis spectrometer, Lambda 20 (PerkinElemer, USA).

4.3.4.2 Refractive index

The ICP and composite were measured refractive index using Metricon (2010/M, USA). The composite detected at wavelengths of 404, 532, 632.8 and 829 (nm) in visible range using a prism coupler. And the incidence angle of the laser beam was varied so that the refractive index in both the thickness and planar directions could be determined.

5. Result and discussion

5.1 Crystalline structure

5.1.1 Fourier transform infrared spectroscopy (FTIR)

To confirm crystallinity index of BC, dried BC with different cultivation speed were analyzed by FTIR. IR spectra obtained as shown in Figures 7 and 8. The peaks near 3240, 750 (cm^{-1}) are specific to cellulose I α while the peaks near 3270, 710 (cm^{-1}) indicated the presence of cellulose I β (Yamamoto *et al.*, 1996). The I α peaks are clear in each spectrum as shown in Figure 7. The peaks near 3270, 710 (cm^{-1}) are hard to identify. From these result, it indicated that BC consist of almost cellulose I α

By cultivation speed, many characteristic bands are shifted at the peak absorbance is transformed. The bands at 1431, 1373, 1281, 1202, 1165, 1032, and 897 (cm^{-1}) are shifted to 1418, 1377, 1278, 1200, 1160, 1019, and 894 (cm^{-1}) as shown in Figure 8. Including the shift of O-H and C-H stretching vibrations (3353 to 3447, 2901 to 2883 cm^{-1}), all the bands are influenced by cultivation speed related to the change of intra- and intermolecular bonds (Oh *et al.*, 2005). The bands at 1431 cm^{-1} assigned as symmetric CH₂ bending (Cael *et al.*, 1975, Colom and Carrillo, 2002, Kondo and Sawatari, 1996, Nelson and O'Connor, 1964) and CH₂ wagging (Cao and Tan, 2004, Colom and Carrillo, 2002) are shifted to lower 1418 cm^{-1} . The bands at 1373, 1281 (cm^{-1}), all assigned as C-O-H bending, are decreased. The bands at 897 cm^{-1} assigned as C-O-C stretching moves toward 894 cm^{-1} by transformation. These

changes are consistent with a shift from order to disorder due to the change in hydrogen bonding patterns (Nelson and O'Connor, 1964).

The relative intensities of the peaks at 1429, 897 (cm^{-1}) were used for calculating the crystallinity index (Nelson and O'Connor, 1964). In fact, a weak and broad band at 897 cm^{-1} and a strong band at 1429 cm^{-1} (CH_2 scissoring) were present in the spectra of the two BC samples, defining them as cellulose I (Nelson and O'Connor, 1964). The intensity of the band at 1429 cm^{-1} has been also correlated with the degree of crystallinity and was often used as a standard band for its estimation. The crystallinity index was calculated absorbance at 1427/875 cm^{-1} (Czaja *et al.*, 2004, Oh *et al.*, 2005). The tendency of crystallinity index decreased rapidly as increasing cultivation speed as shown in Figure 10.

Because of centrifugal force, the bacteria has no efficient time to make crystalline structure during cultivation. Also, treatment of cultivation with different speed affect to connection with CO_2 , O_2 changes the crystal system of the cellulose due to the aerobic bacteria.

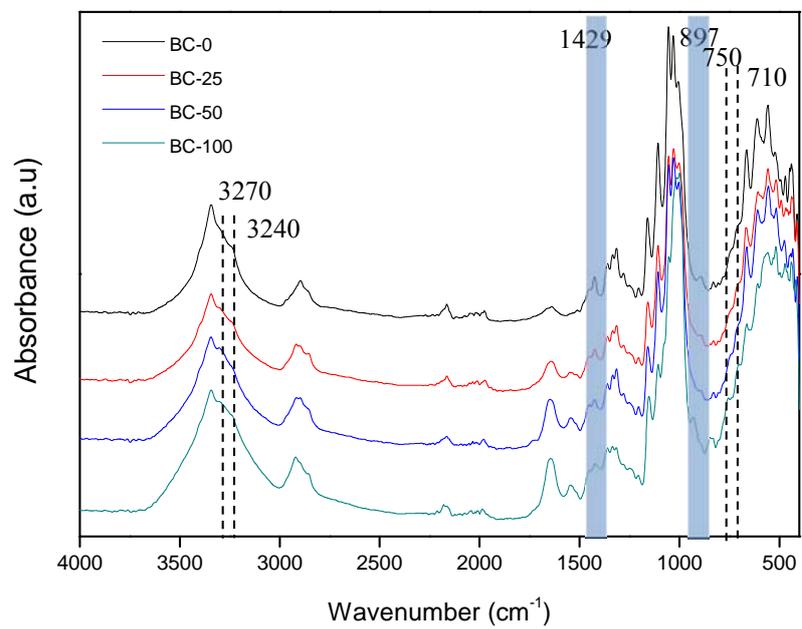


Figure 7. FTIR absorbance spectra of BC with different cultivation speed. The major bands are shaded.

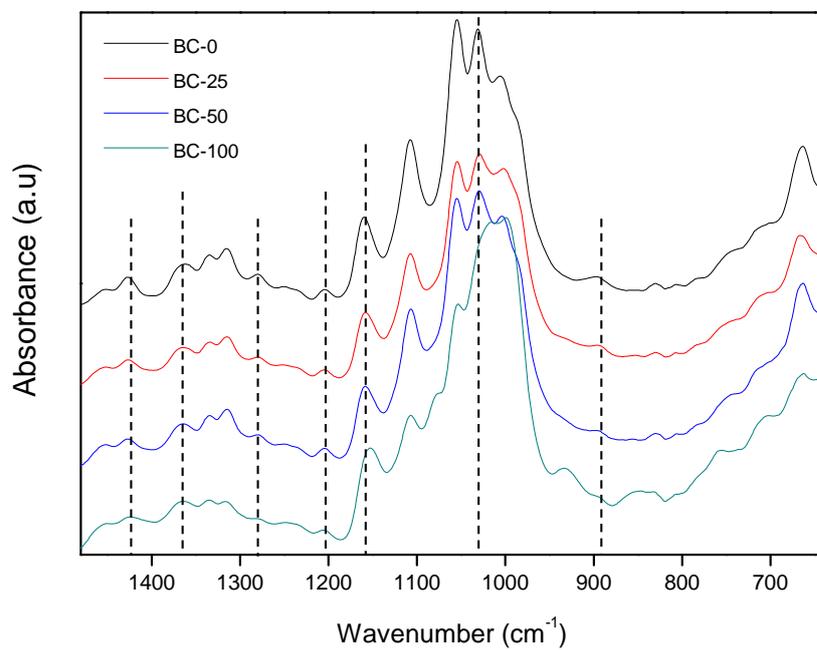
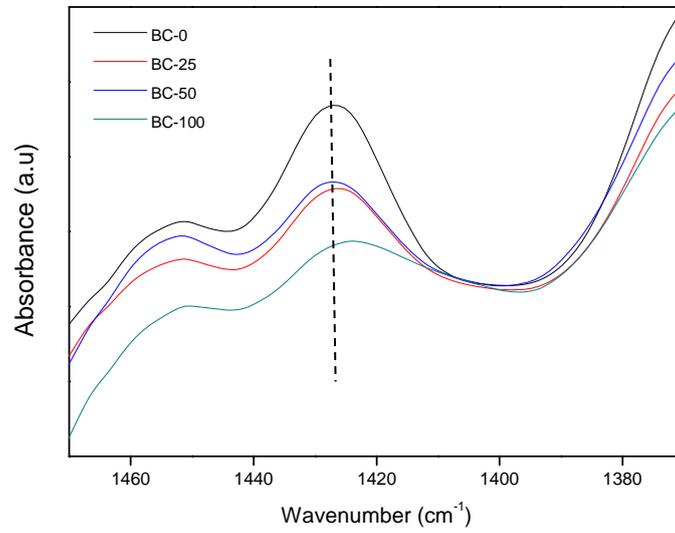


Figure 8. FTIR absorbance spectra of BC with different cultivation speed. The bands at 1431, 1373, 1281, 1202, 1165, 1032, and 897 (cm⁻¹).

(A)



(B)

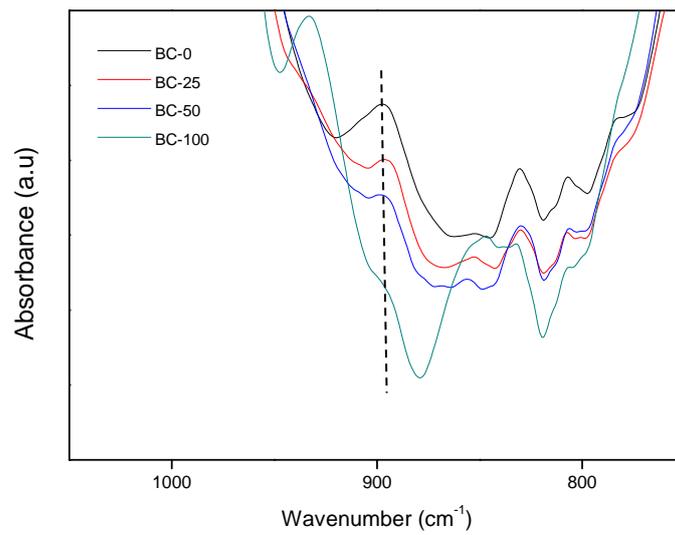


Figure 9. IR bands of BC with different cultivation speed
(A) band at 1429 cm^{-1} , (B) band at 897 cm^{-1}

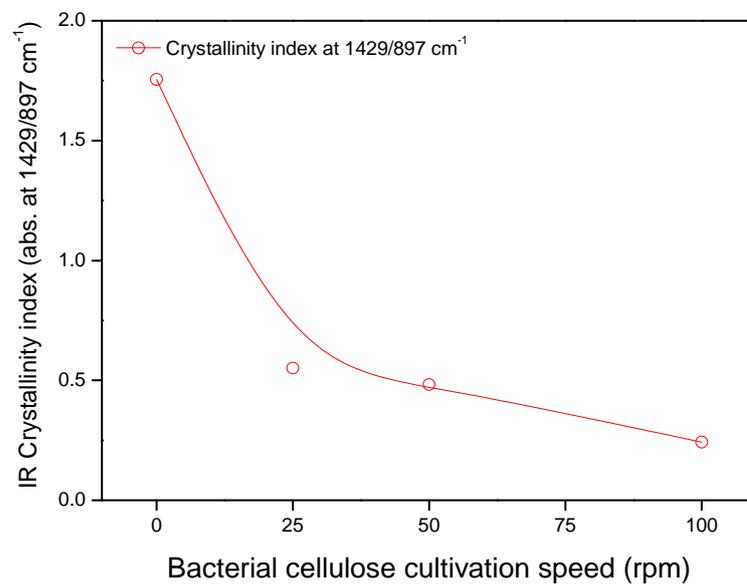


Figure 10. IR crystallinity index (abs. at 1429/897 cm⁻¹) of BC

5.1.2 X-ray diffraction (XRD)

In order to compare the structural changes in BC from different cultivation conditions and estimate if the agitated cultivation causes any disturbance in the crystallization process, X-ray diffraction was used. The XRD of BC corroborates the results obtained by FTIR. In fact diffraction gives rise to reflections corresponding to those for native cellulose and indicates the very high value of crystallinity. Estimation of crystallinity percentage from these diagrams was determined by comparing the integrated intensities of the crystalline peaks. These results were in very good agreement with the analysis carried out on the basis of the FTIR data.

Figure 11 presents the crystalline structural changes of BC. In BC, the two peaks located at $2\theta = 16.7^\circ$, 22.5° which assigned with (110) (200) planes of cellulose I (Gea *et al.*, 2010). For BC with different cultivation speed, these peaks were indicated smaller crystalline index of BC produced in agitated cultivation than static cultivation. It calculated as the ratio of the area of the crystalline peaks to the total area (Jeon *et al.*, 2010). On this basis, a hypothetical mechanism of formation and cell arrangement in the agitated culture has been proposed. During agitated cultivation, cells are stacked together around the outer surface (Czaja *et al.*, 2004). As BC with different cultivation speed, CO₂ changes the crystallinity as well as the crystal system of BC.

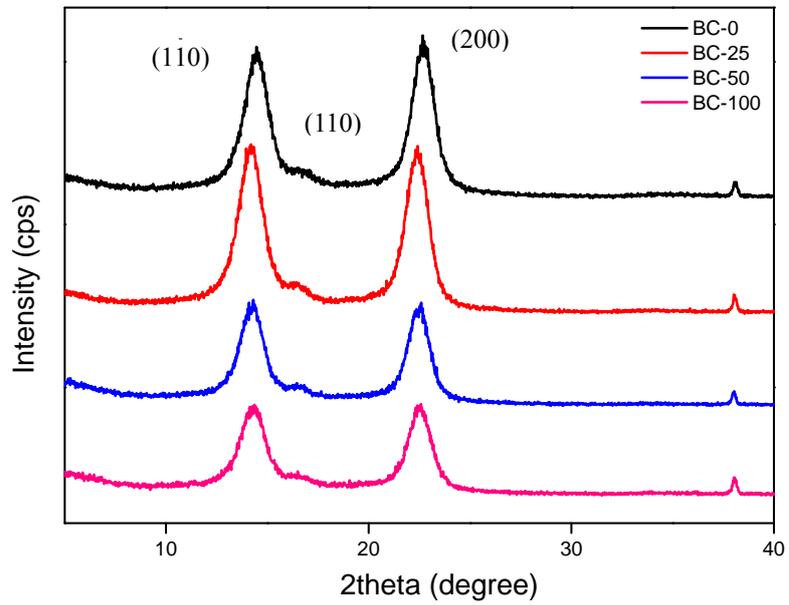


Figure 11. X-ray diffraction patterns obtained from BC synthesized in static and agitated cultivation conditions

5.2 Morphology

The surface morphology of BC with different agitation speed during the cultivation is shown in Figures 12 and 13. This images were confirmed with published work that showed morphology of BC revealed the ultrafine network structure made of a random assembly of ribbon-shaped cellulose microfibrils less than 100 nm wide (Barud *et al.*, 2008).

As shown in Table 2, the diameter of fibers was decreased by following increasing of their agitated cultivation speed while the bacteria make their pores compact. It means the density of BC become lower. Moreover, the surface area increased by increasing cultivation speed due to deduction of the diameter of fibers as shown in Table 3.

The composite were measured by EDS to confirm the qualification and quantification of ionic salt. By this tool, potassium salt peak was confirmed as shown in Figure14 and Table 4. And this result can explain the synthesized ICP and fabrication of composite by composition each element contents.

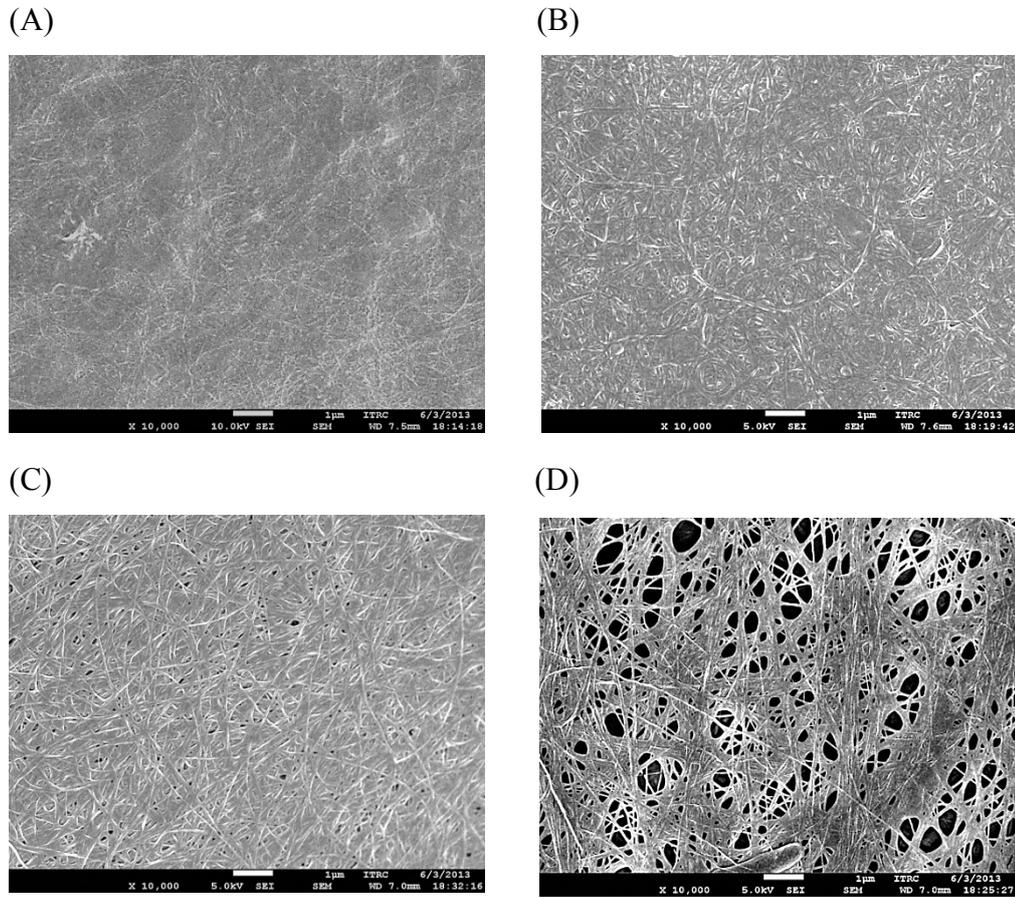


Figure 12. FE-SEM images of (A) BC-0, (B) BC-25, (C) BC-50, (D) BC-100. The samples were freeze dried. The images were magnified 10,000 times real sized and scale bar represents 1 μm .

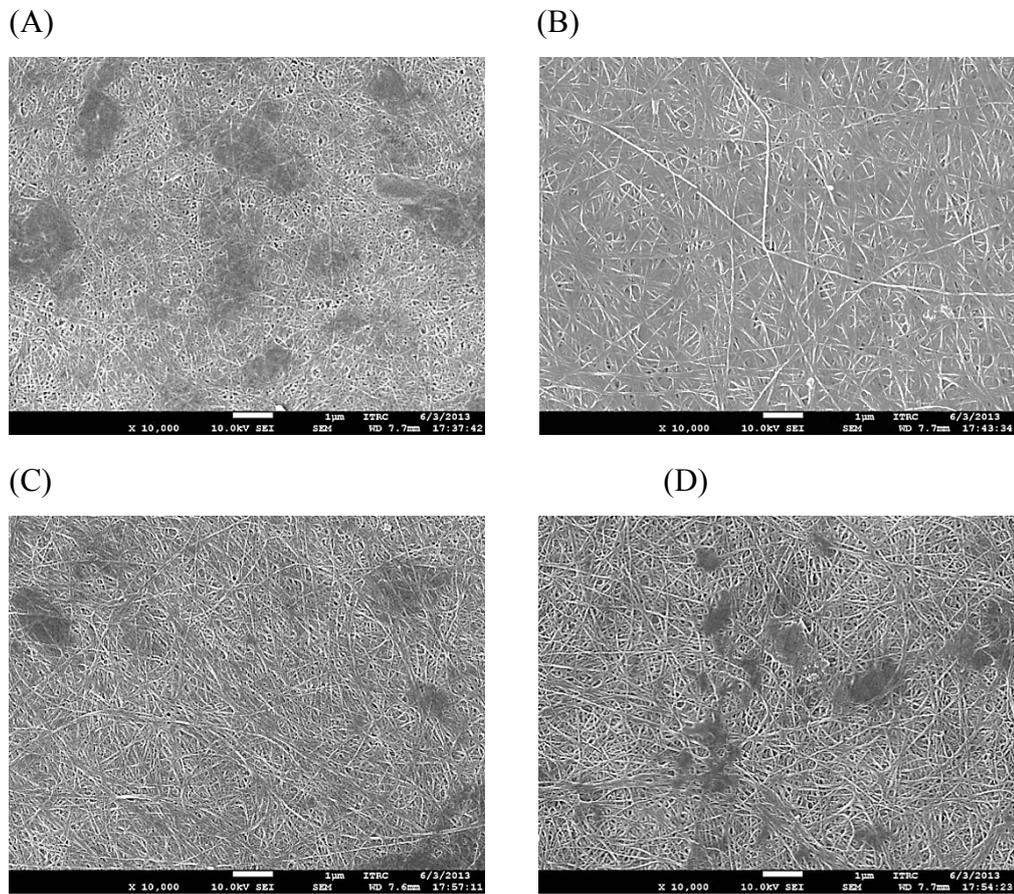


Figure 13. FE-SEM images of (A) BC-0, (B) BC-25, (C) BC-50, (D) BC-100. The samples were oven dried. The images were magnified 10,000 times real sized and scale bar represents 1 μm .

Table 2. Specifications of BC circle sized with the diameter 4 cm by following cultivation speed

	BC-0	BC-25	BC-50	BC-100
Average diameter of fibers (nm)	27.76 ± 4.05	26.23 ± 4.68	25.24 ± 1.81	20.62 ± 3.30
Observed by FE-SEM				

Table 3. BET surface area of BC circle sized with the diameter 4 cm

	BC-0	BC-25	BC-50	BC-100
BET surface area (m ² /g)	18.6	19.7	27.7	37.5

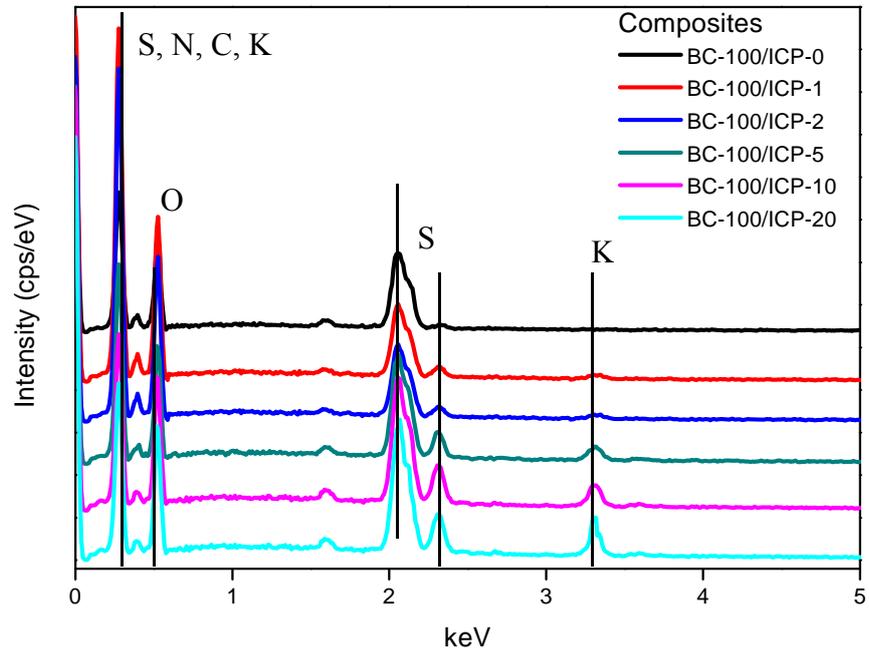


Figure 14. EDS analysis of BC-100/ICP composite with different salt contents

Table 4. Elements consist of BC-100/ICP composites with different salt contents

Elements	BC-100 /ICP 0 (wt. %)	BC-100 /ICP 1 (wt. %)	BC-100 /ICP 2 (wt. %)	BC-100 /ICP 5 (wt. %)	BC-100 /ICP 10 (wt. %)	BC-100 /ICP 20 (wt. %)
Carbon	47.35	53.87	49.86	48.52	43.35	36.55
Oxygen	39.17	32.30	34.06	31.84	32.65	35.88
Nitrogen	13.48	11.59	11.35	10.44	10.45	10.54
Potassium		1.19	2.40	4.88	7.59	8.94
Sulfur		1.04	2.33	4.31	5.95	8.09
Total				100		

5.3 Electrical conductivity

It has a tendency of increasing electrical conductivity of composite effects caused by the increase in salt concentration. The increased number of carrier ions dissociated and decreased chain mobility (Huh *et al.*, 2004). Also, the electrical conductivity of BC in more agitation was higher than static cultivated that owing to the increase of the amorphous region by weakened crystallinity (Ifuku *et al.*, 2009).

The crystalline regions do not allow easy passage of charge carriers, and hinder the conduction process. If ions are trapped in the intracrystalline regions or in the bulk crystalline regions, they contribute very little to ion conductivity. A reduction in the size of such crystalline traps would, therefore, help in conduction, while increase in size of voids (free volume) in amorphous phase also helps ion conduction, assuming that they provide a continuous path for ion motion (Tarafdar *et al.*, 2002)

From this Figures 15 and 16, the electrical behavior cannot be related to percolation effects of the salt concentration but rather to structurally difference in BC. By following increasing rotation speed during the cultivation, it affects improvement of electrical conductivity by polymer chain relaxation. With reduction in the diameter of fibers, and improvement of pores and surface area, it leads to structure modification of BC, it affect to hopping mechanism in ICP by providing the path to carry ions.

The results of surface resistivity and volume resistivity shows electrical conductivity from insulator to the composite has almost conductor as the value of resistivity 1.09×10^6 ohms/squares and 2.05×10^6 ohms-square respectively. With structural modification of BC using ICP, it has dramatically increased in electrical conductivity. It can be explained the nanostructure networks and the diameter of fibers affect to ion mobility.

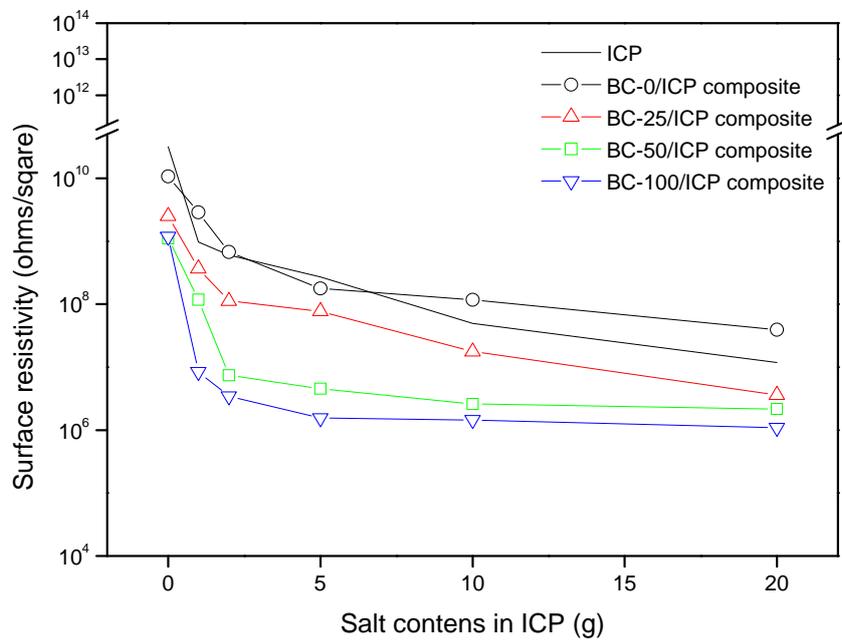


Figure 15. Surface resistivity of ICP, BC/ICP composites by following BC cultivation speed

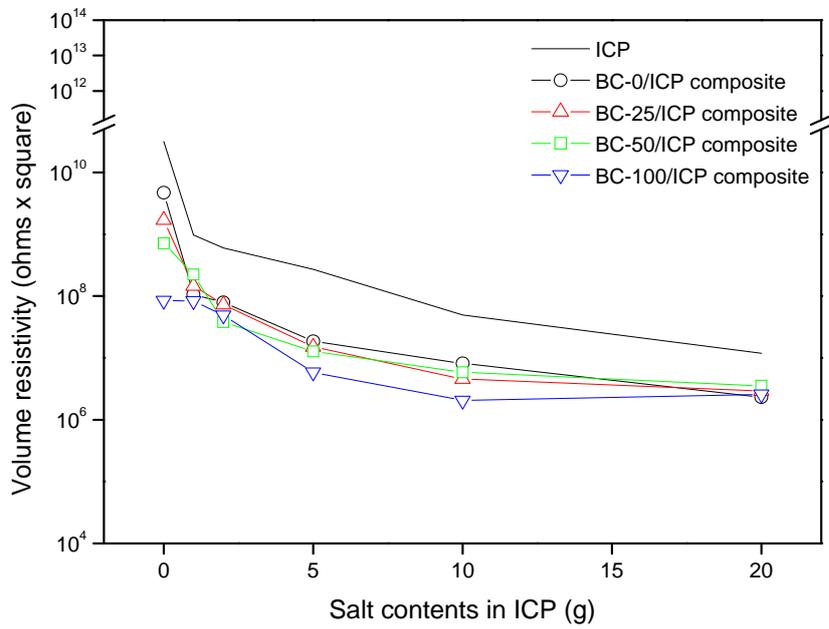


Figure 16. Volume resistivity of ICP, BC/ICP composites by following BC cultivation speed

5.4 Optical property

BC/ICP composite was optically transparent as shown in Figure 17 by filling into BC network structure with transparent material. The transmittance of the composite at 550 nm, which is middle of the visible light range are presented. The diameters of fibers making up BC are smaller than the wavelength of visible light, so that they cannot visible by naked eye. As mentioned before, BC composed of the ultrafine network structure made of a random assembly of ribbon-shaped cellulose has many pores inside BC. It caused a light scattering. After drying, BC became opaque due to many aggregations of fibers. To improve transparency of BC, impregnation method is used in this study. In case of BC/ICP composite, their results showed from many analyzers indicated that the ICP were certainly introduced into the network structure of BC. It plays a role of improvement of transparency by filling pores between fibers in network structure of BC.

Transparency of composite was improved due to incorporation of ICP. By inducing ICP into BC was light scattering and fiber aggregation reduced. The transmittance of BC/ICP composite improved about 6 times than original BC. In addition to, the composite showed a limitation of increasing transmittance that the highest improvement in optical transparency at 5 g of salt contents in ICP. Because the pores of BC have limited area can be filled with transparence polymer. By increasing agitation speed, the limitation of pores increased as shown in the range of transmittance.

Bacterial cellulose sheet can be considered as a three-dimensional network structure of nanosized fibers with air interstices in between. The opacity of the bacterial cellulose can be ascribed to the light diffraction at the interface between the cellulose fiber and the air interstices. The matching refractive index (RI) of the ICP and BC means that the light diffraction at the interface between the two components will be restricted and that the transparent film can be achieved. The RI of the composite and ICP were measured as shown in Table 5. In comparison, the RI of cellulose has been reported as 1.618 along the fiber axis and 1.544 in the transverse direction (Nogi and Yano, 2008). ICP helped to encapsulate the bacterial cellulose fibers and protect it from moisture and the surrounding atmosphere (Ummartyotin *et al.*, 2012).

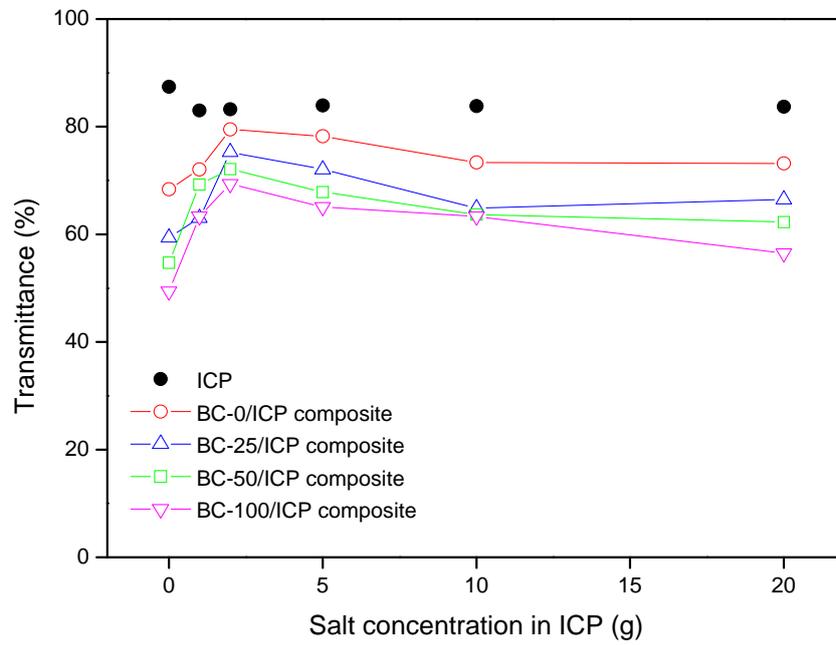


Figure 17. The transmittance of ICP, BC/ICP composites at 550 nm

Table 5. Refractive index of ICP and BC/ICP composites

sample	RI	sample	RI
ICP-0	1.52	BC-0/ICP-0	1.52
ICP-1	1.52	BC-0/ICP-1	1.52
ICP-2	1.52	BC-0/ICP-2	1.52
ICP-5	1.52	BC-0/ICP-5	1.51
ICP-10	1.51	BC-0/ICP-10	1.50
ICP-20	1.51	BC-0/ICP-20	1.50

6. Conclusion

Electrical conductive and optically transparent composite were successfully prepared by incorporation of ICP to BC. The crystalline structures were modified by cultivation speed. The crystalline structure of BC was changed nano network structures of BC, decrease the diameter of BC nanofibers and increase surface area of BC.

The crystalline regions do not allow easy passage of charge carriers, and hinder the conduction process. If ions are trapped in the intracrystalline regions or in the bulk crystalline regions, they contribute very little to ion conductivity. With different cultivation methods, the bacterial cellulose was modified in structurally. By increasing cultivation speed, the crystallinity index changed to decrease. In size of amorphous phase which helps ion conduction. It affects to increase of electrical conductivity.

Also, BC filled with ICP which avoid aggregation fibers of BC so that light scattering decreased.

Present results show the potential of the BC as biopolymers for electrical devices and electrolyte that with incorporation ICP by controlling salt concentration and with different cultivation by controlling crystallinity of pristine BC.

Nano-composite based BC was able to get the effect such as flexible and foldable. Also, the composite could be obtained properties like transparency by filling transparency polymers and electrical conductivity by ICP. The nanocomposite have applicable major factors such as conductivity, transparency, flexibility in the field of electrical

and electronics industry. It is to be expected that significant of BC composite would have a major material in electrical and electronics industry applications.

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초 록

박테리아 셀룰로오스는 리그닌과 헤미셀룰로오스 및 기타 추출물의 제거가 필요없는 순수 셀룰로오스이며, 나노셀룰로오스 중 박테리아의 생합성에 의해 생산되는 친환경 재료이다. 박테리아 셀룰로오스에 금속, 전도성 고분자, 탄소나노튜브 등을 이용하여 전도성을 부여하거나 고분자를 사용하여 투명성을 부여하는 등 다양한 목적을 부여하는 연구가 주목받고 있다. 높은 기계적 물성, 결정화도, 3D 나노구조를 가지는 박테리아 셀룰로오스 기반 복합재료는 의료용, 미용, 식용, 전기·전자 분야 등 다양하게 적용되고 있다.

본 연구에서는 박테리아 셀룰로오스 배양 시 교반 속도를 달리하여 그 구조적 성질을 달리하고, 박테리아 셀룰로오스의 특징인 나노사이즈의 피브릴이 얽혀진 3차원적 망상 구조의 변화를 통해 전기전도성 및 투명성에 미치는 영향을 살펴보고자 하였다. 전도성 고분자 합성 시 염의 함량을 달리하여 이온 전도성 고분자를 합성하였다. 이 고분자를 박테리아 셀룰로오스 나노구조에 함침하여 제조한 박테리아 셀룰로오스/이온 전도성 고분자로 이루어진 복합재료의 성능을 평가하였다.

박테리아 셀룰로오스의 구조적 변화는 FTIR, XRD 측정을 통하여 결정화도의 정도를 평가하였다. 배양 시 교반 속도가 증가할수록 결정성이 현저히 감소함을 확인할 수 있었다. 또한, FE-SEM 으로 표면 관찰 시, 박테리아 셀룰로오스 섬유의 직경은 정지배양 시에는 27.76 ± 4.05 nm 에서 진탕배양 속도가 최대 100 rpm 으로 증가했을 때에는 20.62 ± 3.30 nm 로 줄어들었으며,

나노구조를 이루는 섬유와 치밀성의 정도가 떨어지는 것을 알 수 있었다. 이에 따라 BET 로 측정된 표면적이 정치배양 18.6 m²/g 에서 진탕배양 속도가 최대인 조건에서 37.5 m²/g 로 박테리아 셀룰로오스 섬유의 직경이 감소함에 따라 표면적이 두 배 가까이 증가했음을 확인할 수 있었다.

부도체인 박테리아 셀룰로오스와 달리 박테리아 셀룰로오스와 이온 전도성 고분자로 이루어진 복합재료의 전도성의 경우, 염의 함량이 증가함에 따라 향상되는 것은 물론이며, 박테리아의 배양 속도가 증가할수록 전도성 고분자가 채워질 수 있는 공간이 넓어지고 비결정구조가 증가되어 전기전도도가 향상되었다. 정치배양 시에는 4.73×10^{10} ohms/square 의 표면저항을 갖는 반면, 진탕배양 시 최대 1.09×10^6 ohms/square 을 가져 전기전도도가 상당히 향상되었음을 알 수 있었다. 이로써 박테리아 셀룰로오스의 구조적 변화를 통해 고분자의 함침량이 증가되어 복합재료의 전도도 향상에 기여한다는 것을 형태학적 관찰과 전기전도도 측정을 통해 구명하였다.

또한, 복합재료의 광투과도의 경우, 제조된 박테리아 셀룰로오스/이온 전도성 고분자 복합재료는 박테리아 셀룰로오스의 나노구조 안의 공극에 투명한 물질이 채워짐에 따라 광산란이 줄어들어 광투과도가 향상됨을 알 수 있었다.

이상과 같이 본 연구는 박테리아 셀룰로오스와 이온 전도성 고분자를 이용하여 전기전도성 및 광투과도가 개선된 복합재료를 제작하였으며, 이는 향후 전기전도성 및 투명성이 동시에 요구되는 전기·전자 산업분야에 있어 적용 가능성이 있는 것으로 판단된다.

키워드 : 박테리아 셀룰로오스, 이온 전도성고분자, 정치배양,
진탕배양, 전기전도도, 광투과도

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