Current Applied Physics 14 (2014) 1621–1624

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Electrical conductivity and optical transparency of bacterial cellulose based composite by static and agitated methods

Sera Jeon [a], Yeong-Min Yoo [a], Ji-Won Park [a], Hyun-Joong Kim [a, *], Jinho Hyun [b]

[a] Lab. of Adhesion & Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul 151-921, Republic of Korea
[b] Department of Biosystems and Biomaterials Science and Engineering, Seoul National University, Seoul 151-921, Republic of Korea

ARTICLE INFO

Article history:
Received 27 December 2013
Received in revised form
6 July 2014
Accepted 10 July 2014
Available online 16 September 2014

Keywords:
Bacterial cellulose
Ionic conducting polymer
Static culture
Agitated culture
Electrical conductivity
Optical transparency

ABSTRACT

Composites consisting of bacterial cellulose (BC) and ionic conducting polymer (ICP) were prepared. BC was biosynthesized in media at 0, 25, 50 and 100 rpm. ICP was chemically synthesized at different concentrations of ionic salt. The corresponding electrical conductivity of the composites was measured as a function of ionic salt concentration. ICP improved the optical transparency and electrical conductivity of the BC/ICP composites. Morphological images of BC/ICP composites showed that the pore size of the BC pellicle increased while the diameter and density of the BC fibers decreased. The cultivation method was critical in affecting the structure and electrical conductivity of the composites.

1. Introduction

Cellulose is the most abundant polymer and common natural resource in the earth. The crystalline structure of cellulose is critical in strength of materials. In the case of plant cellulose, it is very difficult to obtain pure cellulose with high crystallinity because it contains not only cellulose but also hemicellulose, lignin and other extractives. Therefore, cellulose from plant should be separated from other extractives such as hemicellulose and lignin through physical, mechanical and chemical treatment. Micro (or Nano) fibrillated cellulose (MFC, NFC) and nano whiskers are examples attained by previous treatment method before. Bacterial cellulose (BC), a nanostructured cellulose, is another type of nanocellulose [1].

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 (3-D) network structure, water holding capability, and biocompatibility. In contrast, fabricating nanocellulose through mechanical or chemo-mechanical processes, BC is produced by the biosynthesis of *Acetobacter xylinum* [2,3,4,5]. Static and agitated cultivation methods can also be used to produce BC, with very different. Appearance of static cultivation method produces a pellicle of BC at the surface of the culture medium as a gelatinous form. In contrast, agitated cultivation affords various sizes (10 μm–1 mm) and shapes (spherical, ellipsoidal, stellate or fibrous) of well-dispersed BC in the culture medium [6,7,8]. BC synthesized through static cultivation method exhibited higher Young's modulus, but lower water holding capacity compared to agitated cultivation [9].

Since Shirakawa et al. discoverd conducting polymers at the end of the 1970s, composites of conducting polymers have been developed for use in anti-static substances, smart windows, light-emitting diodes, solar cells and so on [2,10]. However, composites consist of conducting polymer are not fully environmentally friendly, biocompatible, and biodegradable. Ionic conducting polymer (ICP) using salt is fascinating in the eco-friendly electrical industry [11]. Conducting materials are carbon black, metal and

* Corresponding author.
E-mail address: hjokim@snu.ac.kr (H.-J. Kim).
URL: http://www.adhesion.org

http://dx.doi.org/10.1016/j.cap.2014.07.010
1567-1739/

conducting polymer like polyaniline, polythiophene and so on. The addition of metal powder or carbon particles caused the disadvantage of decreased transparency of the composite, but, ICP offers advantages such as non-pollution of substrate by ion migration and transparency by polymerization using acrylic monomer.

This study examines the effects of using different cultivation methods to structurally modify BC and of varing the ICP concentration to increase electrical and optical properties by taking advantage of the size effect of nanostructured BC. The composite consisting of BC impregnated with ICP, exhibited improced electrical conductivity due to the modified crystalline structure of BC compared with that of pure BC. It is expected that the BC/ICP composite reported herein will find application to chemical sensors and biomedical devices.

2. Experimental

2.1. Materials

The strain of *Gluconacetobacter xylinus* (ATCC 10245) was purchased from the Korean Culture Center of Microorganisms (KCCM) and used to produce the BC pellicles.

Ionic acrylic monomers and the initiator for polymerization, N-hydroxylethyl acrylamide (HEAA) and 3-sulfopropyl methacrylate potassium salt (3-SPMP) were all purchased from Sigma–Aldrich Co., LLC. USA and their chemical structures are shown in Fig. 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.

2.2. Cultivation of bacterial cellulose (BC)

Glucoacetobacter xylinus was cultured by static and agitated methods in Hestrin and Schramm (HS) medium at 0, 25, 50, and 100 rpm. The components of HS medium were 2 w/v % glucose, 0.5 w/v % yeast extract, 0.115 w/v % citric acid and 0.27 w/v % Na_2HPO_4, 0.05 w/v % $MgSO_4 \cdot 7H_2O$ [12]. The HS medium was sterilized by heating at 120 °C for 15 min in an autoclave. *Gluconacetobacter xylinus* was cultured in 200 ml of HS medium at 30 °C for 2 weeks. The BC pellicle was washed thoroughly with de-ionized water, and then with 0.25 M sodium hydroxide solution. After removing the cells remaining in the cellulose, it was kept in 20% ethanol solution below 15 °C.

2.3. Synthesis of ionic conducting polymer (ICP)

The solution polymerization was performed using HEAA 3-SPMP as the ionic acrylic monomer and de-ionized water as the solvent with initiator (V-70). Different weights (0, 1, 2, 5, 10 and 20 g) of 3-SPMP were dissolved in 10 g of HEAA as the acrylic monomer, 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 a magnetic stirrer.

2.4. Fabrication of composites

The same size of BC pellicle (diameter 4 cm) impregnated in 5 g of ICP was allowed to stand for a day at room temperature. Subsequently, BC impregnated with ICP was dried on polyethylene terephthalate (PET, SK Chemical, Republic of Korea) film at 22 ± 2 °C and 60 ± 5% relative humidity for 24 h. The composites were kept in a polyethylene bag after being dried.

2.5. Characterizations

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

X-ray diffraction analysis of BC was performed at different cultivation speed using a Bruker X-ray diffractometer (equipped with a 2-D detector) in reflection mode. XRD was carried out in the range between 5° and 40° by nickel-filtered CuKα radiation ($k = 0.15418$ nm) under a voltage of 40 kV and a current of 30 mA.

The surface resistivity of the composites was measured by the ring probe (URS) technique using an 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. The volume resistivity of composite was measured by URS using an MCP-HT 450 (22 °C, RCF(S): 0.273, 10 V).

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

3. Results and discussion

The surface morphology of BC with different agitation speeds during the cultivation is shown in Fig. 1. This images were in agreement with published work that showed a BC morphology consisting of an ultrafine network structure made of a random assembly of ribbon-shaped cellulose microfibrils less than 100 nm wide [13].

As shown in Table 1, the diameter of the fiber was decreased with increasing agitation speed due to lack of time while the bacteria made their pores compact.

X-ray diffraction was used to compare the structural changes in BC under different cultivation conditions and to determine if the agitated cultivation cuases any disturvance in the crystallization process. Fig. 2 presents the crystalline structural changes of BC. In BC, the two peaks located at $2\theta = 16.7°$ and 22.5° were assigned to (110) and (200) planes of cellulose I, respectively [14]. For BC with different cultivation speeds, these peaks representing smaller crystalline size of BC were produced in agitated cultivation than in static cultivation. On this basis, a hypothetical mechanism of formation and cell arrangement in the agitated culture was proposed. During agitated cultivation, cells are stacked together around the outer surface [15]. For BC with different cultivation speeds, CO_2 changes the crystallinity as well as the crystal system of BC.

It has a tendency to increase the electrical conductivity of the composite due to the increase in salt concentration the increased number of carrier ions dissociated and the decreased chain mobility [16]. In addition, the electrical conductivity with more agitation was higher than that of static cultivated BC because of the increase of the amorphous region by weakened crystallinity [17]. Figs. 3 and 4 showed that increasing rotation speed during the cultivation improved the electrical conductivity by polymer chain relaxation. The reduction in the fiber diameter and improvement of pores and surface area modified the BC structure, which affected to hopping mechanism in ICP by providing the pathway for ion transport. The addition of different salt concentrations affected the electrical conductivity, as shown in Fig. 3 [18]. However, the composite have a tendency that it affects more volume resistivity than surface resistivity with small amounts of ICP due to modified BC which have structural modification so that ion in ICP have energetic mobility while surface resistivity has only impacted by ion on the surface of composite has limited mobility.

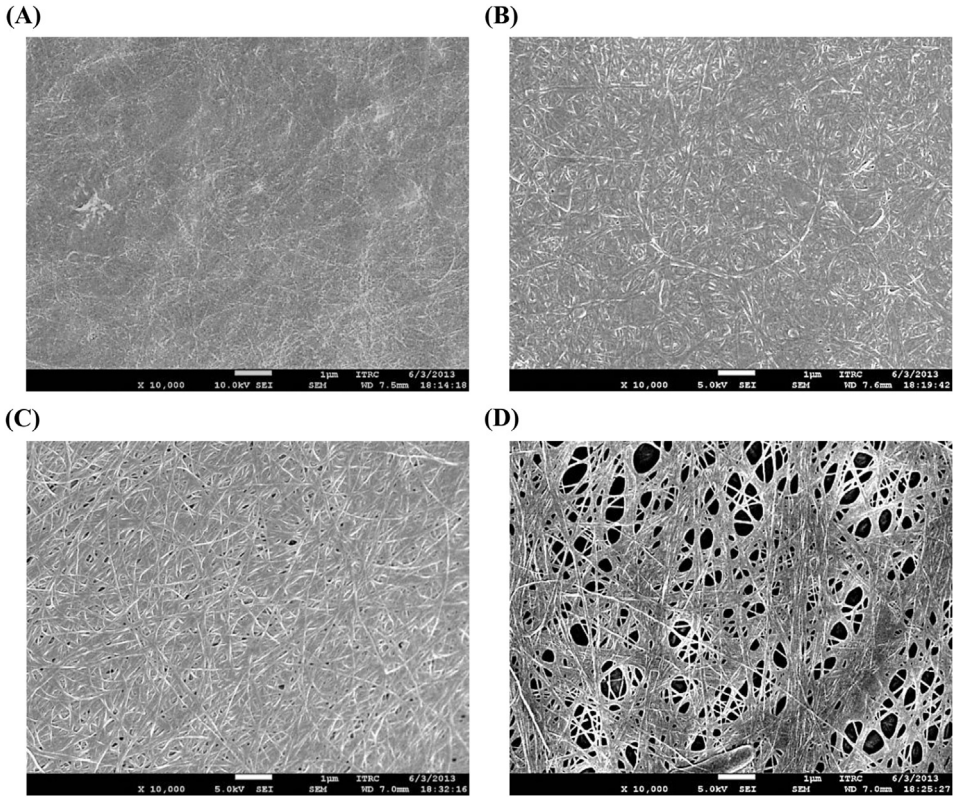

Fig. 1. FE-SEM images of (A) BC-0 (B) BC-25 (C) BC-50 (D) BC-100. The samples were freeze dried. The images were magnified 10,000 times real sized and scale bar represents 1 μm.

Table 1
Specifications of BC circle sized with the diameter 4 cm by following rpm.

	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.

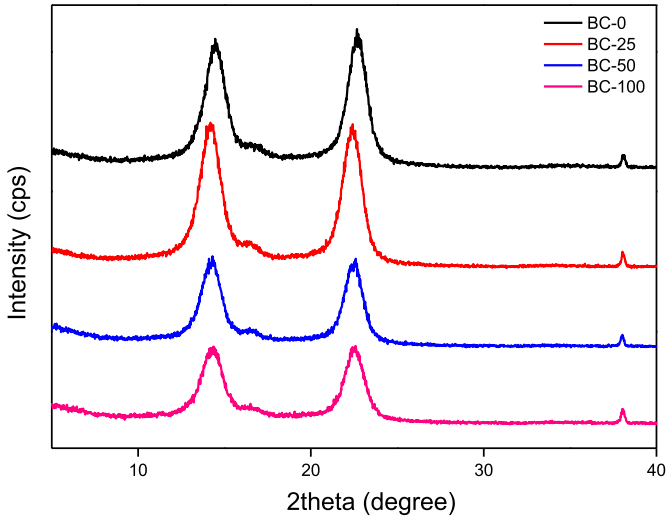

Fig. 2. X-ray diffraction patterns obtained from bacterial cellulose synthesized in static and agitated cultivation conditions.

The surface resistivity and volume resistivity results show from insulator to the composite have almost conductor as the value of resistivity 1.09 × 10^6 ohms/square and 2.05 × 10^6 ohms·square, respectively. The structural modification of BC dramatically increased the electrical conductivity, which was attributed to the nanostructural pore networks and the effect of the fiber diameter on ion mobility.

The BC/ICP composite was optically transparent as shown in Fig. 5, due to the filling of the BC network structure with transparent material. The diameters of the BC fibers are smaller than the

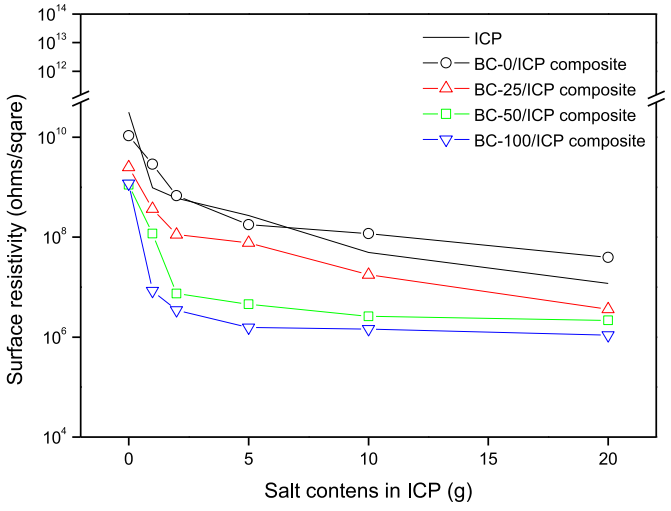

Fig. 3. Surface resistivity of ICP, BC/ICP composite by following BC cultivation speed.

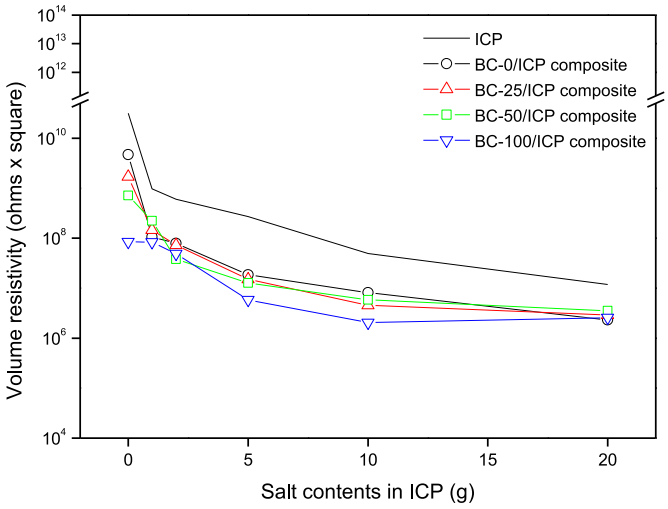

Fig. 4. Volume resistivity of ICP, BC/ICP composite by following BC cultivation speed.

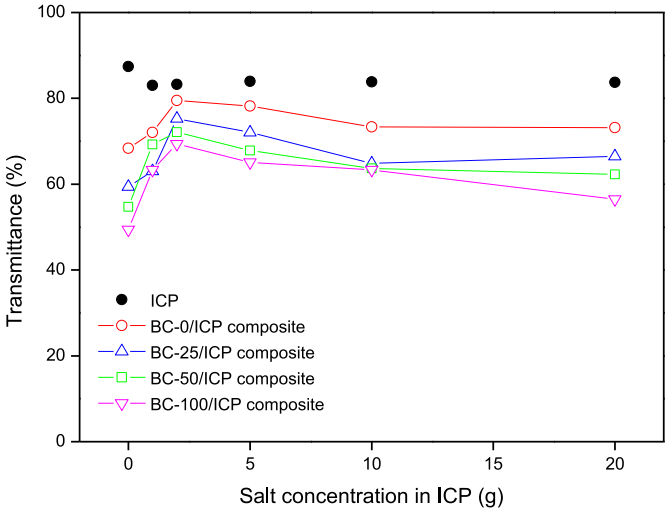

Fig. 5. The transmittance of ICP, BC/ICP composite at 550 nm.

wavelength of visible light, so that they are not visible by naked eye. As mentioned before, the ultrafine BC network structure consisting of a random assembly of ribbon-shaped cellulose resulted in many pores inside BC, which caused a light scattering effect. After drying, BC became opaque due to the many aggregations of the fibers. To improve the transparency of BC, impregnation method was used in this study. Many analysis of the BC/ICP composite indicated that the ICP was certainly introduced into the network structure of BC, where it improved the transparency by filling pores between fibers in the BC network structure [19]. In addition, the composite exhibited only a limited transmittance increase with the greatest improvement in optical transparency occurring at an ICP salt content of 2 g. The limited area of the pores in BC allowed them to be filled with transparent polymer. The limitation of the pores increased with increasing agitation speed, as shown in the range of transmittance.

4. Conclusions

For incorporating ICP into BC, BC/ICP composites were fabricated by filling the pores in BC nanostructures. The nanostructure was modified with different cultivation speeds. The modified nanostructured BC provided a good substrate to improve the electrical conductivity and optical transparency with ICP. The salt content and electrical conductivity of the BC/ICP composites were investigated according to the ionic salt concentration. Beyond the limit point of an impregnated ICP salt content of 2 g, the optical transparency showed no further significant increase. The BC/ICP composite is environmentally friendly and can be implemented as high functional, flexible and lightweight composites. These composites based on BC can be useful in various applications requiring biocompatibility and electrical conductivity such as biocompatible composite actuator, and clothing sensor.

Acknowledgments

This research was supported by the Basic Research Program of National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2011-0009390).

References

[1] J.G. Douglas, S.O. Gloria, M. Ryan, M.A.S.A. Samir, Adhesion and surface Issues in cellulose and nanocellulose, J. Adhesion Sci. Technol. 22 (2008) 545–567.
[2] P. Chen, S.Y. Cho, H.-J. Jin, Modification and applications of bacterial celluloses in polymer science, Macromol. Res. 18 (2010) 309–320.
[3] B.-H. Lee, H.-J. Kim, H.-S. Yang, Polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films, Curr. Appl. Phys. 12 (2012) 75–80.
[4] P. Ross, R. Mayer, M. Benziman, Cellulose biosynthesis and function in bacteria, Microbiological 55 (1991) 35–58.
[5] S. Yamanaka, K. Watanabe, N. Kitamura, M. Iguchi, S. Mitsuhasi, Y. Nishi, M. Uryu, The structure and mechanical properties of sheets prepared from bacterial cellulose, J. Mater. Sci. 24 (1989) 3141–3145.
[6] S. Herstrin, M. Schramm, Synthesis of cellulose by Acetobacter xylinum, Biochem. J. 58 (1954) 345–352.
[7] W.F. Dudman, Cellulose production by acetobacter strains in submerged culture, J. Gen. Microbiol. 22 (1960) 25–39.
[8] F. Yoshinaga, N. Tonouchi, K. Watanabe, Research progress in production of bacterial cellulose by aeration and agitation culture and its application as a new industrial material, Biosci. Biotechnol. Biochem. 61 (1997) 219–224.
[9] A. Krystynowicz, W. Czaja, A. Wiktorowska Jezierska, M. Gonçalves Miśkiewicz, M. Turkiewicz, S. Bielecki, Factors affecting the yield and properties of bacterial cellulose, J. Ind. Microbiol. Biotechnol. 29 (2002) 189–195.
[10] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH), J. Chem. Soc. Chem. Commun. 0 (1977) 578–580.
[11] E. Smela, Conjugated polymer actuators for biomedical applications, Adv. Mater. 15 (2003) 481–494.
[12] E.T. Reese, R.G.H. Siu, H.S. Levinson, The biological degradation of soluble cellulose derivatives and its relationship to the mechanism of cellulose hydrolysis, J. Bacteriol. 59 (1950) 485.
[13] H.S. Barud, C. Barrios, T. Regiani, R.F.C. Marques, M. Verelst, J. Dexpert-Ghys, Y. Messaddeq, S.J.L. Ribeiro, Self-supported silver nanoparticles containing bacterial cellulose membranes, Mater. Sci. Eng. C 28 (2008) 515–518.
[14] S. Gea, E. Bilotti, C.T. Reynolds, N. Soykeabkeaw, T. Peijs, Bacterial cellulose–poly(vinyl alcohol) nanocomposites prepared by an in-situ process, Mater. Lett. 64 (2010) 901–904.
[15] W. Czaja, D. Romanovicz, R. Malcolm Brown, Jr, Structural investigations of microbial cellulose produced in stationary and agitated culture, Cellulose 11 (2004) 403–411.
[16] P.-H. Huh, M.-G. Choi, N. Jo, J.-K. Lee, J.-O. Lee, W. Yang, Effect of salt concentration on the glass transition temperature and ionic conductivity of poly(ethylene glycol)-polyurethane/LiClO4 complexes, Macromol. Res. 12 (2004) 422–426.
[17] S. Ifuku, M. Tsuji, M. Morimoto, H. Saimoto, H. Yano, Synthesis of silver nanoparticles templated by TEMPO-mediated oxidized bacterial cellulose nanofibers, Biomacromolecules 10 (2009) 2714–2717.
[18] L. Verdolotti, S. Colini, G. Porta, S. Iannace, Effects of the addition of LiCl, $LiClO_4$, and LiCF3SO3 salts on the chemical structure, density, electrical, and mechanical properties of rigid polyurethane foam composite, Polym. Eng. Sci. 51 (2011) 1137–1144.
[19] H.J. Kwon, Improvement of Thermal Stability and Optical Transparency Properties of Bacterial Cellulose – Epoxysilane Composite, A Thesis for the Degree of Master of Science, Seoul National University, 2013.