박테리아 셀룰로오스를 이용한 이온교환막의 제조와 특성분석

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Preparation and Characterization of Acrylic Acid-Treated Bacterial Cellulose Cation-Exchange Membrane

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1. Introduction

Biomaterials have recently drawn interest as renewable chemical feedstock [1]. Of the biomaterials, cellulose produced by microorganisms may be more useful for the preparation of multi-functionalized materials and the improvement of mechanical properties. Bacterial cellulose (BC) is known to have high tensile strength due to its high degree of crystallinity and high water-holding capacity resulting from its hydrophilic chemical nature.

Its unique structural features and properties facilitate diverse applications, from wound-dressing, cover-membrane for glucose biosensor, and culture substrate for mammalian cells to membrane separation and fuel cells [2]. Moreover, BC has the potential as adsorbent and ion-exchange membrane (IEM) to recover heavy metals from industrial wastewater. It has been reported that a cellulose-type adsorbent, having similar structure as that of BC, exhibited excellent adsorbability for metal ions. Even though BC has high potential as ion-exchanger, the preparation of an IEM has not been previously studied.

In this study the feasibility of using BC as a source for environmentally compatible IEM was studied. BC was modified with

cation-exchangeable acrylic acid (AAc) using ultraviolet (UV)-graft polymerization to prepare membranes having ion-exchange capacity and greater structural density. The chemical and physical structure of AAc-modified BCs were investigated using Fourier transform infrared (FTIR) spectroscopy and field emission-scanning electron microscopy (FE-SEM). Also, the prepared membranes were characterized in terms of the mechanical and electrochemical properties.

2. Experimental

The AAc was used as a monomer to introduce ion-exchangeable group to BC. Benzophenone (BP) was purified by recrystallizing in a methanol/water mixture at -5 °C, and 5 wt% BP in methanol was used as photo-initiator. BC was supplied by Laboratory of Fermentation and Physiology of Pusan National University and Environmental Biotechnology Laboratory of Chunnam National University.

BC was immersed in BP methanol solution for 3 h. After being dried in air for 30 min, the BC was then irradiated with UV light (400 W, 110 nm-400 nm mercury lamp) for 3 min under a N_2 atmosphere in order to activate BC membrane. Ten (10) g of AAc solution was added into the resulting BC, which was then irradiated with UV light for 5-20 min. The resulting AAc-treated BC membrane was thoroughly cleaned with methanol/acetone using an ultrasonic cleaner to remove any remaining homopolymers.

3. Results and Discussion

3.1. Morphological evaluation through FE-SEM photograph

Fig.1 shows the SEM images of the surfaces of AAc-treated BC membranes prepared at different UV-radiation time. As UV-irradiation time increased, the membranes developed denser structure. As shown in Fig.1, many pores in the untreated BC membrane were found, leading to lower permselectivity due to the leak of co-ions (Cl⁻) through the membrane. Pores in the membrane prepared at 20 min of UV-irradiation time (AAc-20-BC membrane) could be hardly observed. Accordingly, the membrane rejected co-ions, resulting in the increasing

permselectivity.

3.2. Mechanical properties

The AAc-20-BC membrane exhibited excellent tensile strength (~68.5 MPa) compared to that of CMX membrane (~28.5 MPa) which contains reinforcing material. Both tensile strength and elongation of AAc-treated BC membranes increased with UV-irradiation. Margutti et al. reported that grafting reactions with UV-irradiation improved the mechanical properties of cellulosic materials [3].

3.3. Electrochemical properties

Fig.2 presents relationships of membrane electrical resistance (MER) and ion-exchange capacity (IEC) of the membranes as a function of UV-irradiation time. As UV-radiation time increased, IEC increased as a consequence of increased AAc binding to the BC. With the pores of the AAc-20-BC membrane blocked, MER of the membrane decreased resulting from the increase of proportion of ion-exchangeable AAc.

Fig.3 shows current-voltage (I-V) curves of various membranes. The untreated BC did not show 3 typical characteristic regions. This is caused that co-ions permeated through the membrane due to large pore channels and low ion-exchange sites. On the other hand, the AAc-20-BC membrane showed them, demonstrating the feasibility of manufacturing an IEM with BC. However, the transport number (Tn) of the AAc-20-BC membrane was somewhat lower than that of CMX (e.g., Tn: 0.98) because the dense structure of the membrane did not reject co-ions (Cl-) completely.

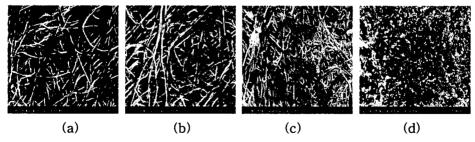


Fig. 1. FE-SEM micrographs of the surfaces of untreated bacterial cellulose (a) and AAc-treated bacterial cellulose membranes prepared with 5 min (b), 10 min (c), and 20 min (d) of UV-irradiation time.

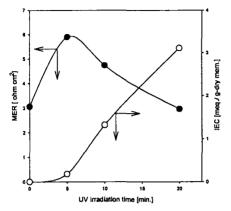


Fig. 2. Relationships of MER and IEC as a function of UV-radiation time.

Fig. 3. I-V curves of the CMX and prepared membranes.

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