

Synthesis and Characterization of Bacterial Cellulose/Alginate Blend Membranes

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ABSTRACT: Bacterial cellulose and alginate in an aqueous NaOH/urea solution were used as substrate materials for the fabrication of a novel blend membrane. The blend solution was cast onto a Teflon plate, coagulated in a 5 wt % CaCl₂ aqueous solution, and then treated with a 1% HCl solution. Supercritical carbon dioxide drying was then applied for the formation of a nanoporous structure. The physical properties and morphology of the regenerated bacterial cellulose and blend membranes were characterized. The blend membrane with 80% bacterial cellulose/20

wt % alginate displayed a homogeneous structure and exhibited a better water adsorption capacity and water vapor transmission rate. However, the tensile strength and elongation at break of the film with a thickness of 0.09 mm slightly decreased to 3.38 MPa and 31.60%, respectively. The average pore size of the blend membrane was 10.60 Å with a 19.50 m²/g surface area. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3419–3424, 2008

Key words: biopolymers; blends; membranes; synthesis

INTRODUCTION

Cellulose is Earth's major biopolymer from plants and other living systems such as plankton, algae, fungi, and bacteria. Bacterial cellulose (BC), produced by *Acetobacter xylinus*, is distinctly different from cellulose derived from plants and the others. BC is devoid of lignin, hemicellulose, and other complex carbohydrates. Because of the entangled mesh of nanofibrils compacted in the form of an ultrafine network, BC displays unique properties, including high mechanical strength, high water absorption capacity (WAC), and high crystallinity.^{1–5} It is incredibly hydrophilic, absorbing 60–700 times its weight in water.^{1,6} The diameter of BC is about 1/100 of that of plant cellulose, and Young's modulus of BC is higher than that of general organic fibers.⁵

Regenerated cellulose membranes blended with other natural polymers such as alginate (Al),^{7–11} konjac glucomannan,¹² chitosan,¹³ and chitin¹⁴ to modify their properties for applications in many separation fields have been extensively reported. Al, a heteropolysaccharide extracted from marine brown algae, has been widely explored as a substrate material for blend

membranes and a thickener for cellulose fibers. A new blend membrane from cellulose (cotton linter) and Al showed improved performance for the dehydration of ethanol/water in a pervaporation process.⁹ The mechanical properties of the Al membrane were found to be significantly improved by the introduction of cellulose and Ca²⁺ bridges. The crystalline state of the blend membrane from cellulose (cotton linter) and Al prepared in an aqueous NaOH/urea solution was broken completely, and the crystallinity of the blend membranes decreased with an increase in the Al ratio.¹⁰ Although studies of blend membranes from plant-derived cellulose with other biopolymers have been extensively synthesized and characterized,^{7–15} very few, if any, studies using BC as a source of cellulose have been reported.

Because BC displays unique properties considerably different from those of plant cellulose, in this work, we focused on developing a new nanostructure blend membrane from BC and Al in an aqueous NaOH/urea solution. The surface morphology, pore structure, tensile strength, WAC, and water vapor permeability of the blended membranes were examined and compared with those of regenerated bacterial cellulose (RBC) films.¹⁶ To the best of our knowledge, this type of blend combination was first prepared in this work.

EXPERIMENTAL

BC

The BC used in this study was the gel-like cellulose pellicle formed by *A. xylinus* cultures on the surface

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of media containing 0.5% ammonium sulfate, 5.0% sucrose, and 1.0% acetic acid in coconut water. The sheets of BC were purified by washing with deionized (DI) water and then were treated with 1% (w/v) NaOH at 35°C for 24 h to remove bacterial cells and rinsed with DI water until the pH was 7. Afterward, the BC film was air-dried at room temperature (30°C) and stored in plastic film before use.

Preparation of the membranes

Preparation of the BC/Al blend film

To prepare a slurry of BC, 3 wt % BC was dissolved in a 4 wt % NaOH/3 wt % urea aqueous solution and stirred for 10 min at room temperature. The BC slurry was then cooled to -5°C in a freezer and held at -5°C until it became a solid frozen mass for 12 h. The frozen solid was then allowed to thaw and was stirred extensively at room temperature to obtain a clear BC solution. After that, the insoluble parts were isolated by centrifugation at 6000 rpm and 10°C for 30 min. Sodium alginate (3 wt %) was dissolved in distilled water at room temperature to form a gel-like solution. Then, the prepared solution of BC was mixed with the Al solution to produce mixtures having BC/Al weight ratios of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100. The mixtures were stirred energetically at room temperature for 24 h to form clear solutions. The casting solutions were spread over a Teflon plate. The thickness of this solution was controlled at 2.3 mm by manual adjustment of the height of the casting blade. The thickness of the membranes was measured with a micrometer (Mitutoyo, Tokyo, Japan) at various parts of a particular membrane. All of the casting solutions were coagulated in a 5 wt % CaCl₂ aqueous solution for 30 min and treated with a 1% HCl solution for 10 min. After that, the membranes were washed with DI water until the drain water reached a pH of 7, and then they were air-dried at room temperature.

Preparation of the nanoporous structure

Supercritical drying was applied to the preparation of a porous structure. First, the films were dipped in DI water for 24 h. After that, to replace water with ethanol, the swollen films were immersed in 10, 30, 50, and 70% (w/v) ethanol for 30 min in each step, and then they were immersed in 100% (w/v) ethanol for 1 h. Lastly, the swollen membranes were dried by supercritical CO₂ drying. In the drying procedure, the films were placed in a vessel inside a high-pressure cell with an inner diameter of 10 cm. The cell was immediately filled with supercritical CO₂ and controlled at 40°C and 1200 psi (the critical

point of CO₂; critical pressure = 1072 psi, critical temperature = 31°C). The temperature and pressure were selected so that the CO₂ and ethanol inside the membrane were fully miscible. Subsequently, the cell was flushed by the addition of fresh CO₂ for 2 h to replace the residual ethanol inside, and then the system was slowly depressurized at a constant rate of 150 psi/min to remove the CO₂.

Characterization of the membranes

Elemental analysis of the membranes

The membranes were cut into particles and vacuum-dried for 24 h before the analysis of the elemental contents. The contents of nitrogen in the membranes were determined with a Leco (St. Joseph, MI) CHN-2000 elemental analyzer. The contents of calcium and sodium were determined with an Oxford Ed (Oxford, UK) 2000 X-ray fluorescence (XRF) spectrometer.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used primarily to identify the chemical structure of the membrane. The FTIR spectra of the membranes were recorded with a Nicolet (Madison, WI) SX-170 FTIR spectrometer.

WAC

To determine WAC, the dried membranes were immersed in DI water at room temperature until equilibration. After that, the membranes were removed from the water, and excess water at the surface of the membranes was blotted out with Kim-wipes paper. The weights of the swollen membranes were measured, and the procedure was repeated until no further weight change was observed. The water content was calculated with the following formula:

$$\text{WAC (\%)} = \frac{W_h - W_d}{W_d} \times 100 \quad (1)$$

where W_h and W_d are the weights of the hydrate and dry membrane, respectively.

Tensile property testing

All the membranes under study in the dry form were tested for the tensile strength and elongation at break. The film samples were cut into strip-shaped specimens 10 mm wide and 10 cm long. The maximum tensile strength and break strain of RBC films were determined with a Lloyd (Southampton, UK) 2000R universal testing machine. The test conditions

followed ASTM D 882. The tensile strength and break strain were the average values determined from 10 specimens.

Scanning electron microscopy (SEM)

The films were frozen in liquid nitrogen, immediately snapped, vacuum-dried, and then sputtered with gold and photographed. Images were taken on a JOEL (Tokyo, Japan) JSM-5410LV scanning electron microscope.

Water vapor permeability measurement

The water vapor transmission rate (WVTR) of the dry RBC membrane and the dry RBC/Al blend membrane with an area of 50 cm² were determined with a Lyssy (Zollikon, Switzerland) L80-4000 water vapor permeation tester. The test conditions followed ISO 15106-1. The determination of WVTR was done under 38°C and 90% relative humidity. As water solubilized into the membrane and permeated through the sample film, nitrogen gas swept and transported the transmitted water vapor molecules to a calibrated infrared sensor. The response was reported as a transmission rate.

Brunauer–Emmett–Teller (BET) surface analysis

The pore size and surface area of the membranes were determined with a BET surface area analyzer. To remove moisture from the film samples, the samples were placed in sample cells, which were then heated up to 373 K for 2 h and cooled to room temperature before the BET analysis. The BET pore size and surface area were determined with N₂ adsorption at 77 K in a Micromeritics (Atlanta, GA) ASAP 2020.

RESULTS AND DISCUSSION

Membrane compositions

Elemental analysis revealed the absence of nitrogen in the fabricated membranes. Therefore, urea was completely removed from the membrane during the coagulation and washing. The XRF spectra indicated that the calcium content was less than 0.005 wt % in the blend membrane with ≤40 wt % Al and increased to 0.010–0.019 wt % in the blend membranes with greater than 40 wt % Al. No sodium peak was observed in any of the membranes, and this suggested that NaCl and NaOH were completely removed from the developed membranes. A small amount of Al/calcium complex as calcium bridges was previously reported in Al membranes.^{9,17} Therefore, the calcium accumulation in the BC/Al blend membranes should be due to the

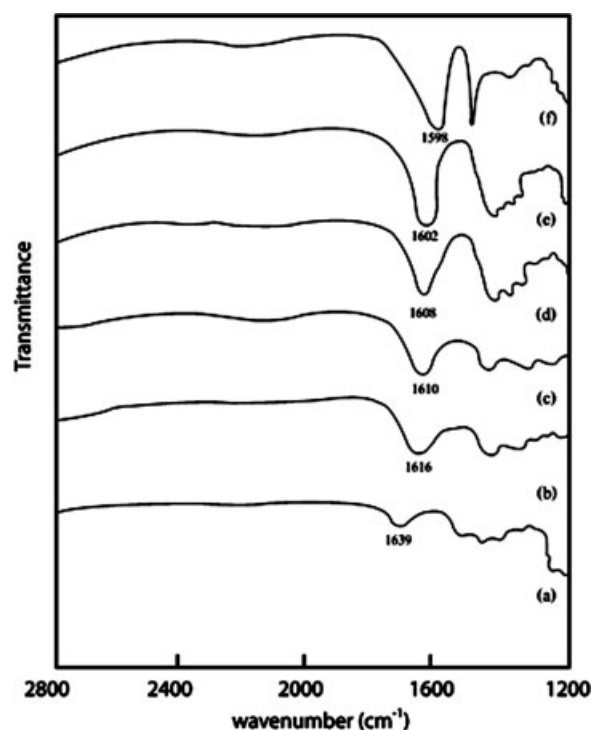


Figure 1 FTIR spectra of the BC/Al blend membranes. The BC/Al ratios were (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100.

formation of a calcium/Al gel network by crosslinking with Ca²⁺ ions.

FTIR analysis of the blend membrane

FTIR spectroscopy was used to investigate the nature of mixing between the two biopolymers in this study. The FTIR spectra of the RBC, Al, and blend membranes were measured at wave numbers ranging from 2800 to 1200 cm⁻¹. The FTIR spectra of the RBC membrane [Fig. 1(a)] showed a band at 1639 cm⁻¹, which was attributed to glucose carbonyl of cellulose. The strong band of the Al membrane at 1598 cm⁻¹ [Fig. 1(f)] indicated the presence of the carboxyl group. The FTIR spectra of BC/Al blend membranes [Fig. 1(b–e)] were characterized by the presence of absorption bands in the pure components, whose intensities were roughly related to the blending ratio. The carboxyl group bands for the blend membranes with BC/Al at 20/80, 40/60, 60/40, and 80/20 ratios were shifted from 1598 to 1602, 1608, 1610, and 1616 cm⁻¹, respectively. The result, therefore, implied that there might be some specified interaction between the hydroxyl group of cellulose and carboxyl group of Al. Similar observations were previously discussed in the preparation of cotton cellulose/Al blend membranes.⁹

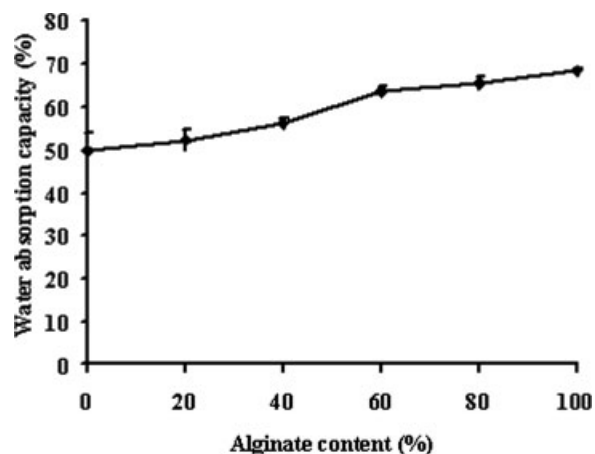


Figure 2 WAC (%) of the RBC/Al blend membranes as a function of the Al content.

WAC

WAC of the membranes as a function of the Al content is illustrated in Figure 2. WAC of the RBC membrane was 49.67%, whereas WAC of the Al membrane was 68.40%. The increase in the Al content in the membranes resulted in an increase in the water absorption ability of the blend membranes. The hydrogen bonds in regenerated cellulose formed very tightly packed crystallites, and these crystals could be so tight that water hardly penetrated them. Water molecules were found to be easily absorbed into the Al membrane crosslinked with glutaraldehyde because of its high hydrophilic property.¹⁸ The blending of RBC with Al reduced hydrogen bonding of cellulose chains in the membranes, resulting in the increase in the water absorption ability of the membranes. Besides the composition of the membranes, the drying conditions also affected the water absorption of the membranes. In a previous report,¹⁹ the water retention values of wet-state BC, freeze-dried BC, BC air-dried up to 100°C, and typical plant

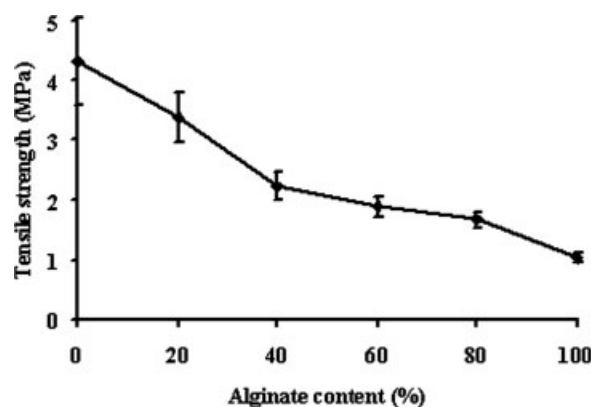


Figure 3 Tensile strength of the BC/Al blend membranes as a function of the Al content.

cellulose (cotton linters) were 1027, 629, 106, and 60%, respectively. In our works,^{6,16} WAC of natural BC films after air drying at 30°C was 509%, whereas WAC of the fabricated RBC films decreased to 49.67%, which was about that of typical plant celluloses.

Mechanical properties of the membranes

Figure 3 presents the tensile strength of the blend membranes as a function of the Al content. The tensile strengths of the RBC membrane and the Al membrane with the thickness of 0.09 mm were 4.32 and 1.01 MPa, respectively. Increasing Al from 20 to 80% decreased the tensile strength of the blend membranes from 3.38 to 1.67 MPa. Figure 4 shows the elongation at the break of the blend membranes as a function of the Al content. The elongation at break of the RBC membrane was 35.20%, whereas the elongation at break of the Al membrane was 15.50%. In the same way, it was found that the elongation at break of the blend membranes decreased from 31.60 to 19.20% with the increase in the Al content from 20 to 80 wt %.

The effect of the Al content on the mechanical properties of the blend membranes was similar to that of cotton cellulose/Al blend membranes.^{7,10} The sodium alginate membrane was mechanically weak, but its mechanical properties were obviously improved by the introduction of cellulose and cross-linking with Ca²⁺. The interaction between cellulose and Al molecules based on their structural similarities was supposed to be hydrogen-bonding formation between the hydroxyl groups of cellulose and the carboxyl groups of Al. The presence of Al chains could enhance the molecular motion of cellulose in the blend and perturbed the strong hydrogen bond of pure cellulose because of the formation of new intermolecular interactions between the two biopolymers.⁹ The morphological structure, tensile proper-

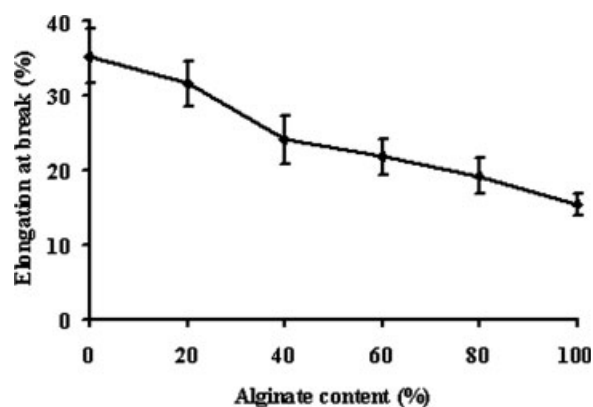


Figure 4 Elongation at break of the BC/Al blend membranes as a function of the Al content.

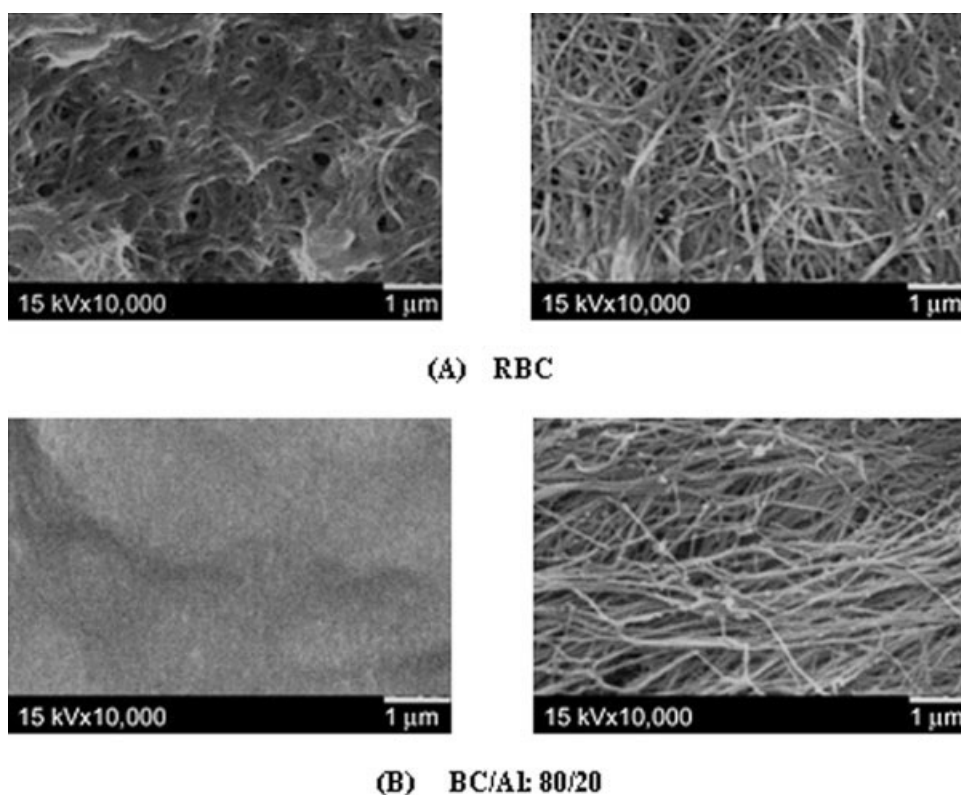


Figure 5 SEM images of the surface morphology of (A) RBC membranes and (B) 80/20 BC/Al blend membranes before (left) and after (right) reswelling in DI water and supercritical drying.

ties, and permeability of the cellulose membrane could also depend on the coagulation conditions.²⁰

Surface morphology

The RBC and blend membranes exhibited dense nanoporous structures. The surface morphology of the membranes before and after reswelling in DI water at 30°C and supercritical drying is presented in Figure 5. In the case of the blend membrane composed of 80 wt % BC and 20 wt % Al, SEM displayed a homogeneous structure, which exhibited a certain level of miscibility of the blend. It was shown that the fibers of the blend membrane were more orderly nonwoven than the pure RBC membrane. Furthermore, the apparent pore size of the blend membrane decreased with the increase in the Al content. By the introduction of more than 20 wt % Al, the miscibility of the blend membrane was less orderly, and the structure became less homogeneous (figure not shown). Therefore, the optimum ratio of the BC/Al blend membrane was 80/20 wt %.

Water vapor permeability

The water vapor permeability of the dry films was determined by a water vapor permeation tester, with the test conditions following ISO 15106-1. However,

with this analysis, there might be a lag time during which water solubilized in the membrane before permeation. Overall, WVTR of the RBC membrane was 0.25 g/cm² day, whereas that of the Al membrane was 0.56 g/cm² day (Fig. 6). WVTR of the blend membranes was significantly improved by the introduction of Al. WVTR of the blend membrane with 20% Al content was 0.51 g/cm² day or 2.1 times that of the unblended RBC membrane. The considerable improvement in WVTR of the blend membrane was

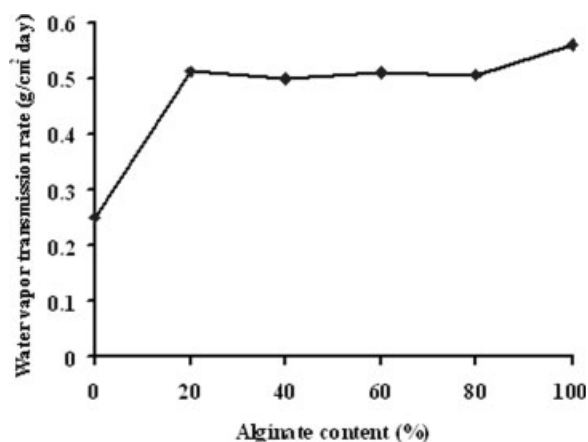


Figure 6 WVTR of the BC/Al blend membranes as a function of the Al content.

TABLE I
Characteristics of RBC and the Blend Membrane

Membrane	Tensile properties		WAC (%)	WVTR (g/cm ² day)	Pore diameter (Å)	Surface area (m ² /g)
	Tensile strength (MPa)	Elongation at break (%)				
RBC	4.32	35.20	49.67	0.25	12.63	17.57
80/20 RBC/Al blend	3.38	31.60	52.25	0.51	10.60	19.50

due to the high hydrophilic property of Al, which formed the strong interaction between water molecules and $-\text{COO}^-$ and $-\text{OH}$ functional groups.⁹ More water molecules binding to the surface of the blend membranes led to a greater driving force of the concentration gradient across the membrane, resulting in the enhancement of water transportation through the membrane.

Porosity

The average pore diameters of the RBC membrane and the blend membrane with 20% Al, characterized by a BET analyzer, were 12.63 and 10.60 Å with surface areas of 17.57 and 19.50 m²/g, respectively. The pore sizes of the RBC membrane and the blend membrane were approximately 1/20 of that of the biosynthesis BC membrane (224.0 Å).⁶ In comparison with the BC membrane with the total surface area of 12.62 m²/g,⁶ the surface areas of the RBC and blend membranes were increased by 39.2 and 54.5%, respectively. Table I gives a summary of the characteristics of the blend membrane versus the RBC membrane.

CONCLUSIONS

The nanoporous membranes were satisfactorily prepared with mixtures of BC/Al solutions as substrate materials. BC (3 wt %) was dissolved in a 4 wt % NaOH/3 wt % urea solution, and this was followed by a freeze-thaw process. The mixture of BC and sodium alginate solutions was spread over a Teflon plate and was then coagulated in a 5 wt % CaCl₂ solution and treated with a 1% HCl solution. The chemical structure, surface morphology, porosity, water vapor permeability, and mechanical properties were determined with FTIR, SEM, BET surface analysis, water vapor permeation testing, and tensile property testing. The blend membrane of 20 wt % Al and 80 wt % RBC demonstrated a homogeneous structure with a certain level of miscibility of the blend. The FTIR spectra displayed the specified interaction between the hydroxyl group of cellulose and the carboxyl group of Al. The mechanical properties of the blend membranes were slightly decreased compared to those of the pure RBC membrane; however, WVTR and the degree of swelling

in water were significantly improved. The tensile strength and elongation at break of the blend membrane with a 0.09-mm thickness were 3.38 MPa and 31.6%, respectively. WAC and WVTR of the blend membrane were 52.25% and 0.51 g/cm² day, respectively. The membrane pore was classified as a micropore with an average diameter of 1.06 nm and a total surface area of 19.50 m²/g. Because the developed membrane had a nanoporous structure and exhibited chemical stability, high mechanical strength, high water adsorption capacity, and high WVTR, its potential use in membrane separation processes is expected. The evaluation of the blend BC/Al film as a separation membrane in pervaporation processes is ongoing.

References

- Brown, R. M. In *Cellulose: Structural and Function Aspects*; Kennedy, J. F.; Phillips, G. O.; Williams, P. A., Eds.; Ellis Horwood: Chichester, England, 1989.
- Iguchi, M.; Yamanaka, S.; Budhiono, A. *J Mater Sci* 2000, 35, 271.
- Yamanaka, S.; Ishihara, M.; Sugiyama, J. *Cellulose* 2000, 7, 213.
- Yamanaka, S.; Watanabe, K.; Kitamura, N. *J Mater Sci* 1989, 24, 3141.
- Wan, Y. Z.; Hong, L.; Jia, S. R.; Huang, Y.; Zhu, Y.; Wang, Y. L.; Jiang, H. J. *Compos Sci Technol* 2006, 66, 1825.
- Sanchavanakit, N.; Sangrungraungroj, W.; Kaomongkolgit, R.; Banaprasert, T.; Pavasant, P.; Phisalaphong, M. *Biotechnol Prog* 2006, 22, 1194.
- Zhang, L.; Zhou, D.; Wang, H.; Cheng, S. *J Membr Sci* 1997, 124, 195.
- Zhang, L.; Zhou, J.; Zhou, D.; Tang, Y. *J Membr Sci* 1999, 162, 103.
- Yang, G.; Zhang, L.; Peng, T.; Zhong, W. *J Membr Sci* 2000, 175, 53.
- Zhou, J.; Zhang, L. *J Polym Sci* 2001, 39, 451.
- Krishna Rao, K. S. V.; Subha, M. C. S.; Vijaya Kumar Naidu, B.; Sairam, M.; Mallikarjuna, N. N.; Aminabhavi, T. M. *J Appl Polym Sci* 2006, 102, 5708.
- Yang, G.; Xiong, X.; Zhang, L. *J Membr Sci* 2002, 201, 161.
- Zhuang, X. P.; Liu, X. F. *J Appl Polym Sci* 2006, 102, 4601.
- Liang, S.; Zhang, L.; Xu, J. *J Membr Sci* 2007, 287, 19.
- Zhou, J.; Zhang, L.; Cai, J.; Shu, H. *J Membr Sci* 2002, 210, 77.
- Phisalaphong, M.; Suwanmajo, T.; Sangtherapitikul, P. *J Appl Polym Sci* 2008, 107, 292.
- Yalpani, M. *Polysaccharides: Synthesis Modifications and Structure/Property Relations*; Elsevier: Amsterdam, 1988, p 370.
- Lee, K. H.; Yeom, C. K.; Jegal, J. G. *Polym Mater Sci Eng* 1997, 77, 345.
- Klemm, D.; Schumann, D.; Udhardt, U.; Marsch, S. *Prog Polym Sci* 2001, 26, 1561.
- Cao, Y.; Tan, H. *J Appl Polym Sci* 2006, 102, 920.