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PERVAPORATION OF ETHANOL/WATER MIXTURES USING BACTERIAL CELLULOSE-POLY(VINYL ALCOHOL) MEMBRANE

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งานวิจัยนี้ได้ทำการพัฒนาเยื่อแผ่นแบคทีเรียเซลลูโลสเพื่อใช้สำหรับกระบวนการดึงน้ำออกจากสารละลายเอทานอลโดยวิธีการแช่ลงในสารละลายพอลิไวนิลแอลกอฮอล์ที่ความเข้มข้น 5-12 เปอร์เซ็นต์ (น้ำหนัก ต่อ ปริมาตร) จากนั้นทำการเชื่อมขวางด้วยสารละลายกลูตาราลดีไฮด์ โดยผลที่ได้จากการศึกษาจะถูกนำมาเปรียบเทียบกับเยื่อแผ่นแบคทีเรียเซลลูโลสที่ไม่ผ่านการดัดแปลงและเยื่อแผ่นพอลิไวนิลแอลกอฮอล์ที่ทำการเชื่อมขวางแล้ว เพื่อให้เข้าใจถึงผลของสมบัติของเยื่อแผ่นต่อสมรรถภาพของกระบวนการแยกเพอร์เวเปอร์เรชัน เยื่อแผ่นจะถูกนำไปศึกษาลักษณะทางสัณฐานวิทยาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด, แรงกระทำระหว่างโมเลกุลด้วยเครื่องฟลูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปคโทรมิเตอร์, ความเป็นผลึกด้วยเครื่องวิเคราะห์การเลี้ยวเบนรังสีเอกซ์, ความแข็งแรงเชิงกลด้วยเครื่องเครื่องมือวัดและทดสอบวัสดุเชิงกล, ความชอบน้ำของเมมเบรนด้วยเครื่องวัดมุมสัมผัสของน้ำ และความสามารถในการดูดซับ จากการทดลองกระบวนเพอร์เวเปอร์เรชันโดยใช้สารละลายเอทานอลความเข้มข้น 95 เปอร์เซ็นต์ (ปริมาตร ต่อ ปริมาตร) ที่อุณหภูมิ 30 องศาเซลเซียส ความดัน 10 มิลลิเมตรปรอท พบว่าเยื่อแผ่นแบคทีเรียเซลลูโลสที่แช่ในสารละลายพอลิไวนิลแอลกอฮอล์ที่ความเข้มข้น 10 เปอร์เซ็นต์ให้ค่าการแยกน้ำของเยื่อแผ่นสูงที่สุด (ค่าการแยกน้ำต่อเอทานอล ≈ 125) เมื่อเปรียบเทียบกับเยื่อแผ่นแบคทีเรียเซลลูโลสที่ไม่ผ่านการดัดแปลงและเยื่อแผ่นแบคทีเรียเซลลูโลสที่ผ่านการแช่ในสารละลายพอลิไวนิลแอลกอฮอล์ที่ความเข้มข้น 5,7 และ 12 เปอร์เซ็นต์ ผลจากการศึกษาในส่วนของอุณหภูมิที่ใช้ในสายป้อนพบว่าการเพิ่มอุณหภูมิในสายป้อนทำให้อัตราการไหลผ่านเยื่อแผ่นมากขึ้นแต่ค่าการแยกของเยื่อแผ่นลดลง

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SUPAPORN JEWPRASAT: PERVAPORATION OF ETHANOL/WATER MIXTURES USING BACTERIAL CELLULOSE-POLY(VINYL ALCOHOL) MEMBRANE. ADVISOR: ASSOC. PROF. MUENDUEN PHISALAPHONG, Ph.D., 62 pp.

Modifying bacterial cellulose (BC) membranes by immersing BC in 5-12 (% w/v) poly(vinyl alcohol)(PVA) solution and cross-linking with glutaraldehyde solution were studied for the dehydration of ethanol-water azeotropic mixture. The results were compared with the unmodified BC membrane and cross-linked PVA membrane. To be able to understand the effects of membrane properties on the pervaporation separation performance, the membranes were characterized for the morphology by scanning electron microscopy, intermolecular interactions by Fourier transform infrared spectroscopy, the crystalline of membrane by X-ray diffraction, mechanical properties by Instron testing machine, contact angle measurements and adsorption capacity. According to the pervaporation experiments under the conditions at the feed solution of 95 (% v/v) ethanol, temperature of 30 °C and permeate pressure of 10 mmHg, it was found that the modified BC membranes by immersion in 10% PVA solution gave the highest selectivity toward water ($\alpha_{H2O/EtOH} \approx 125$) when compared with the BC and BC- PVA modified by 5, 7 and 12 % PVA solution. In the study of the influences of feed temperature, the result showed that with the increase in the feed temperature, the permeate flux increased, but selectivity decreased.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER I

INTRODUCTION

1.1 Motivation

Ethanol is a renewable fuel that can be produced through fermentation from renewable biomass. The productions of ethanol from fermentation processes have a final ethanol concentration about 9-12% (v/v). Distillation is usually used to increase ethanol concentration from fermentation broth. However the problem in distillation of ethanol-water solution is ethanol and water form a homogeneous minimum-boiling azeotrope of 95.6 wt% alcohol at 78.1 ^{o}C and cannot be further purified by distillation. Therefore, in order to produce absolute ethanol, other types of separation processes have to be applied. Pervaporation is a membrane separation technology with high selectivity, efficiency and low energy consumption which make it the method of choice for separating azeotropic and close-boiling mixtures or dehydrating temperature-sensitive products (Dubey, Saxena et al. 2002). Pervaporation is a membrane separation process developed to separate, purify and concentrate of mixtures of liquids by partial vaporization through membrane. Pervaporation is a membrane separation process involving the partial vaporization of a liquid mixture through a dense membrane whose downstream side is usually kept under vacuum. Pervaporation has been mostly applied in the following three major fields: (i) dehydration of organic solvents (ii) removal of dilute organic compounds from aqueous solutions and (iii) organic–organic mixture separation. The hydrophilic membrane was initially used in industrial processes for organic solvent dehydration by pervaporation. Until now, dehydration of organic liquids using this type of membrane remains the main application of pervaporation in industries (Smitha 2004).

Pervaporative dehydration of ethanol has been widely studied using membrane based on poly(vinyl alcohol) (PVA), poly(acrylonitrile), chitosan, alginate etc (Li, Xu et al. 2006). PVA is a high hydrophilic polymer with high-abrasion resistance and flexibility. Many researches have shown excellent water permselectivity of PVA membrane in pervaporation dehydration of ethanol (Praptowidodo 2005).

Cellulose nanocomposites have been successfully employed as pervaporation membrane. Recently, cellulose nanofibrous membranes biosynthesis from bacteria, namely bacterial cellulose (BC) has been studied for use in pervaporation because of its several advantageous properties, which include high water-holding capacity, high chemical stability, high tensile strength, high heat resistance and fine web-like network structure. BC synthesized extra-cellularly by *Acetobacter xylinum* is of nano-size, as a result of which hydrogen bonding between fibrils is greater than with plant cellulose in normal paper (Yamanaka, Watanabe et al. 1989). Moreover, the pellicle can be easily flattened, pressed and processed into membranes of desired thickness (Dubey, Saxena et al. 2002).

The BC membrane has been examined for the pervaporation of binary ethanol-water mixtures. It was found that for ethanol-water binary system, the permeate flux was very high but the selectivity was fairly low (Dubey, Saxena et al. 2002).

To improve the pervaporative performance of the BC membrane, in this study, the procedure for the membrane biosynthesis was modified by immersing BC in PVA solution and cross-linking with glutaraldehyde solution. The BC-PVA membrane was then characterized for chemical-physical and mechanical properties. Furthermore, dehydration of ethanol-water mixtures through the BC-PVA membrane by pervaporation was investigated.

1.2 Objectives

1.2.1 To synthesize and characterize BC, BC-PVA/GA and PVA/GA membranes

1.2.2 To investigate the pervaporative performance of the BC, BC-PVA/GA and PVA/GA membrane.

1.3 Scopes of this work

1.3.1 Biosynthesis of BC membrane by *Acetobacter xylinum* (AGR60)

1.3.2 Modification of the BC membrane by:

- immersing BC in PVA solution at: 0, 5, 7, 10, 12% (w/v)

1.3.3 Characterization of the membrane by Scanning electron microscopy(SEM), Fourier transform infrared (FTIR)spectroscopy, Universal testing machine, X-Ray diffractometer (XRD), Contact Angle Meter and Water absorption ability (WAC).

1.3.4 Evaluation of pervaporative performance of the BC, BC-PVA/GA and PVA/GA membrane for ethanol dehydration (in terms of flux and selectivity)

- study the effect of feed temperature in the range of 30, 40, 50 ^{o}C.

1.4 Overview

This present work was organized as follows:

Chapter I present an introduction of this study

Chapter II contains background theory of bacterial cellulose, pervaporation system and the literature review

Chapter III states the details of the experimental procedures and techniques of this research

Chapter IV reviews the experimental results of the characterization BC-PVA membrane and pervaporation.

Chapter V contains the overall conclusion obtained from this research. Future work and recommendations are also stated.

Finally, the additional data of the experiments which had emerged from this study are included in appendixes at the end of this thesis.

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEW

2.1 Pervaporation

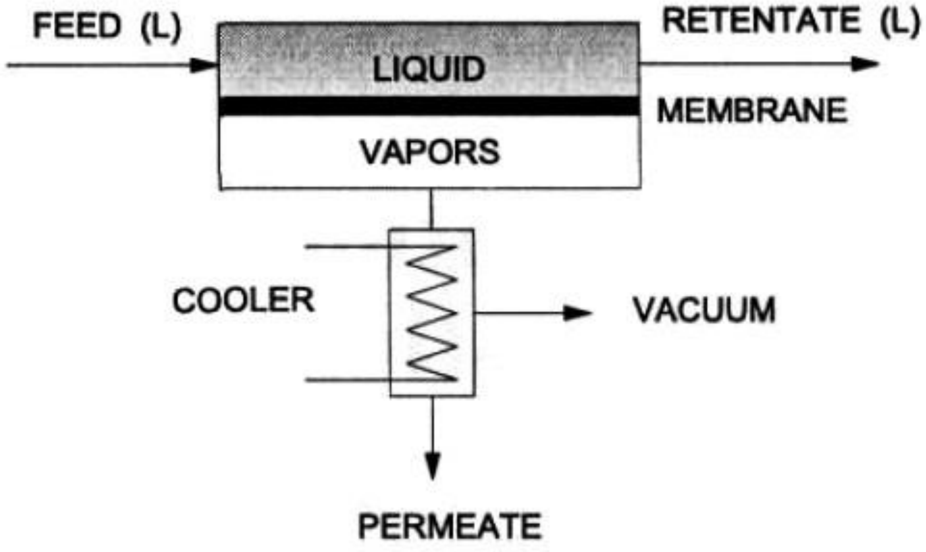


Figure 1 Pervaporation process

Pervaporation in its simplest form is shown in Figure 1. It is an energy efficient combination of membrane permeation and evaporation. It is considered an attractive alternative to other separation methods for a variety of processes. For example, with the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes. Pervaporation is also used for dehydration of organic solvents and removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for separation heat sensitive products, breaking azeotropes, dehydration of solvents and other volatile organics, organic-organic separations such as ethanol or methanol removal, and wastewater purification (S. 2010).

Pervaporation is unique among membrane separations, involving the liquid-vapor phase change to achieve the separation. Pervaporation is separated by partial vaporization through a dense membrane. A liquid feed mixture is in contact with one side of the membrane, the partial vapor pressure is at saturation. The gradient in partial pressure between the feed and the permeate side of the membrane is maintained by a reduction (Kanjanamosit, Muangnapoh et al. 2010). The permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas and then condense.

The transport of the permeate through a nonporous permeate-selective membrane is quite complex. This could be explained in three steps:

1. Separation of the solvent mixture with a permeate-selective membrane on the surface of a nonporous permeate selective membrane.

2. Diffusion of the permeate through the permeate-selective membrane.

3. Permeate desorption on the posterior side of the membrane.

2.1.1 Estimate pervaporation system

- Flux

The performance of membrane in pervaporation is estimated in terms of its selectivity and the permeate flux. The flux of a component i in pervaporation process, J_i , can be described by the following general transport equation:

$$J_i = -L_i \nabla \mu_i \qquad (1)$$

Where, L_i is phenomehological transport coefficient.

μ_i is chemical potential of a component i.

Assuming that transport in the membrane system occurs only in the direction perpendicular to the membrane surface, equation (1) can be rearranged into:

$$J_i = -L_i \frac{d\mu_i}{dx} \qquad (2)$$

Substituting:

$$d\mu_i = \frac{RT}{a_i} da_i \qquad (3)$$

Where, a_i is activity of a component i.

Eq. (2) can be written in the form:

$$J_i = -\frac{L_i RT}{a_i^m} \frac{da_i}{dx} \qquad (4)$$

Where, a_i^mdenotes an activity of component i in the membrane phase.

The estimation of L_i and a_i^m independently from each other would lead to the inaccurate result, so the term $\frac{L_i RT}{a_i^m}$ is summarized and described as a permeability of the membrane in the pervaporation process.

$$J_i = -P_i' \frac{da_i}{dx} \qquad (5)$$

Integration of Eq. (5) over the membrane thickness, leads to the following expression for the permeate pervaporation flux:

$$J_i = -\frac{P_i'}{l}\left(a_{i,p} - a_{i,F}\right) \quad (6)$$

In pervaporation, the activity of components is very low on the permeate side ($a_{i,p} \approx 0$), so Eq. (6) can be rewritten as follows:

$$J_i = \frac{P_i'}{l} a_{i,F} \qquad (7)$$

By including the membrane thickness into the permeability parameter, the final form of the transport equation for pervaporation flux can be presented:

$$J_i = P a_{i,F} \qquad (8)$$

- Selectivity

Selectivity is calculated as the ratio of the permeable component in the permeate is divided by the respective ratio in the feed. The selectivity was calculated using the following equation:

$$\alpha = \frac{\left(C_{water}/C_{org}\right)_{Permeate}}{\left(C_{water}/C_{org}\right)_{Feed}} \qquad (9)$$

The higher the value of α, the greater degree of separationoffered by the membrane. As α →∞, the membrane tends towards being super selective (Chapman, Oliveira et al. 2008).

2.1.2 Factors affecting membrane performance

Performance of pervaporation is dependent not only on the membrane but also on the operating parameters such as feed composition, temperature, and other factors.

- Feed composition and concentration

A change in the feed composition might directly affect membrane properties and the sorption phenomena (degree of swelling) at the liquid membrane interface. The diffusion of the components in the membrane is also dependent on the concentration of the components. The permeation characteristics are hence dependent on the feed concentration. An example this phenomenon is shown in (Figure 2).

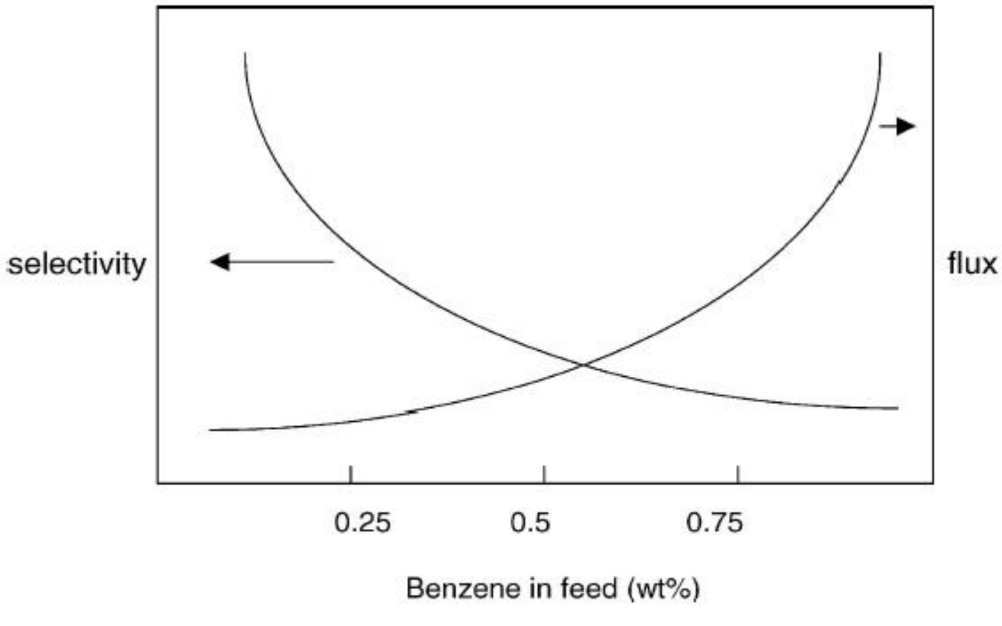


Figure 2 Effect of feed concentration on organic–organic pervaporation separation of benzene–cyclohexane mixture (Smitha 2004)

- Temperature

As the temperature of the feed increases, the permeation rate generally increases following an Arrhenius-type law: $J = J_0 exp(E_p/RT)$. Thus, the selectivity is strongly dependent on temperature. Generally, a decrease in selectivity is observed with increasing temperature. An example this phenomenon is shown in (Figure 3).

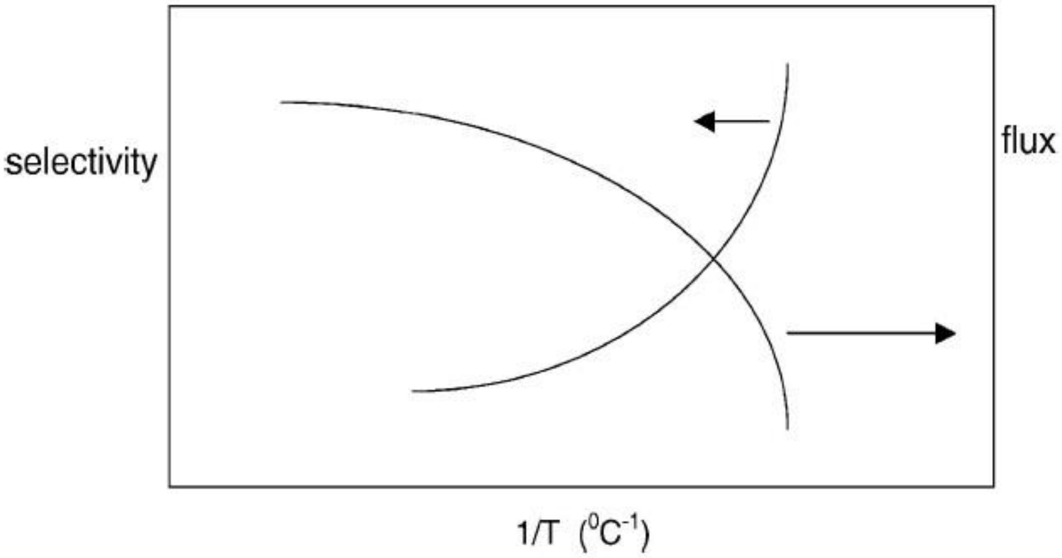


Figure 3 General trends of flux and selectivity with varying temperature for benzene/cyclohexane (Smitha 2004)

2.2 Pervaporation membranes

The separation of compounds using pervaporation methods can be classified into three major fields (i) dehydration of aqueous–organic mixtures (ii) removal of trace volatile organic compounds from aqueous solution and (iii) separation of organic–organic solvent mixtures. The hydrophilic membranes were the first ones, which were used in an industrial application for organic solvent dehydration by pervaporation (Smitha 2004). Pervaporative dehydration of ethanol has been widely studied using membranes based on poly(vinyl alcohol) (PVA), polyamides, chitosan and alginate etc. These membranes are cross-linked by using various types of cross-linking agents to improve mechanical strength, a better separation factor and a higher flux compared with non cross-linked membrane. In the recent years, a significant development of membranes in the pervaporation of the ethanol-water mixture has been reported.

2.2.1 Bacterial cellulose membrane

The bacterial cellulose (BC) originates as a white gelatinous pellicle on the surface of the liquid medium at about 30-35 ^{o}C, in a static culture containing *Acetobacter xylinum*. *A. xylinum* is a rod-shaped aerobic Gram-negative bacterium usually occurring as contaminant invinegar fermentation (Ramana, Tomar et al. 2000). Because BC displays unique properties, including high mechanical strength, high water absorption capacity, high crystallinity and highly pure fiber network structure, it is expected to be a new commodity biochemical with diverse applications (Vandamme, Baets et al. 1998). It has already found application as a food matrix (*nata de coca*) and as dietary fiber, as a temporary dressing to heal skin burns, as an acoustic or filter membrane, as ultra-strength paperand as a reticulated fine fiber network with coating, binding, thickening and suspending characteristics.

Dubey et al. (2002) studied pervaporation of binary ethanol-water mixtures through BC membrane. From this studied, it was found that as the water content in feed mixture increased, the degree of sorption (Q) also increased. The result indicated that BC membrane was a hydrophilic membrane with high selectivity for water (Dubey, Saxena et al. 2002).

Nakayama et al. (2004) studied characterization of BC-gelatin (BC-GE) membrane cross-linked with *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide (EDC) for the separation of ethanol–water solutions. The results of this work showed that fracture strength and elastic modulus under compressive stress were on the order of megapascals, which were several orders of magnitudes higher than those of gelatin gel and almost equivalent to those of articular cartilage (Nakayama, Kakugo et al. 2004).

Dubey et al. (2005) studied pervaporation performance of ethanol-water mixtures through BC membrane immersing in chitosan solution (CTSN–BCM) compared with the blends of chitosan and poly(vinyl alcohol) solution (CTSN–PVA).

The results of this work showed that the selectivity of CTSN–PVA were higher than CTSN–BCM but a lower flux (Dubey, Pandey et al. 2005).

Pandey et al. (2005) studied pervaporative characteristics of aqueous organic mixtures through BC membrane. Five binary mixtures systems were chosen, acetone/water (Ac/H_2O), formalin/water (HCHO/H_2O), ethanol/water (EtOH/H_2O), ethylene glycol/water (EG/H_2O) and glycerol/water (Gly/H_2O) for the study of permeate flux and selectivity. Gly/H_2O binary mixtures system showed the highest selectivity but the lowest flux while EtOH/H_2O binary mixtures system showed the highest flux but lower selectivity. From studying influenced of temperature for ethanol-water binary mixtures system, it was found that as the temperature increased, the flux also increased but the selectivity decreased (Pandey, Saxena et al. 2005).

Kanjanamosit et al. (2010) studied pervaporation separation of ethanol–water mixtures through BC-alginate membrane for the dehydration of ethanol aqueous solution. The composite membranes were prepared by adding 0.5-1% (w/v) of alginate in the culture medium during biosynthesis. The results of this work showed that the BC membrane with 1% (w/v) alginate added culture medium gave the improved selectivity when compared with the unmodified BC membrane. The membrane selectivity was increased with the alginate content in membranes (Kanjanamosit, Muangnapoh et al. 2010).

2.2.2 Poly(vinyl alcohol) membrane

Poly(vinyl alcohol) (PVA) is one of the important membrane pervaporation materials for the dehydration of organic mixtures owing to its good chemical stability, film-forming ability and high hydrophilicity, especially high water permselectivity in pervaporation separation of aqueous ethanol solutions (Ye, Liu et al. 2007). However, the swelling of the PVA membrane in an aqueous solution results in increase in both the solubility and diffusivity of the organic component, consequently lowers the water permselectivity and simultaneously reduces the strength of the PVA membranes. To improve the membrane stability and permeation properties, the PVA membranes were cross-linked with an organic chemical such as glutaraldehyde, polyacrylic acid, tetraethoxysilane etc. Glutaraldehyde is frequently used to cross-link with PVA membranes to enhance water permselectivity (Gimenes, Liu et al. 2007).

Praptowidodo et al. (2005) studied degree of cross-linking in copolymer membranes of PVA, poly(vinyl alcohol-co-itaconic acid) (PVA-It) and poly(vinyl alcohol-co-N-3-trimethyl-ammonio-propyl-acrylamide-chloride) (PVA-N) affecting pervaporation performance. The PVA-based membranes were cross-linked with glutaraldehyde for separation of ethanol-water mixtures. The results showed that as glutaraldehyde concentrations increased, the swelling degree decreased, and leading to an increase in selectivity but decrease in permeation flux. On the other hand, for the swollen membrane, the distance between polymer chains was enhanced, which caused ethanol and water passing across the membrane freely (Praptowidodo 2005).

Li et al. (2006) studied chitosan-poly(vinyl alcohol)/poly(acrylonitrile) (CS–PVA/PAN) composite membranes for the separation of ethanol–water solutions. The CS–PVA/PAN membranes were cross-linked with glutaraldehyde and sulfuric acid for separation of ethanol-water mixtures. From this studied, it was found that as PVA concentration in the CS–PVA polymer increased, the separation factor of CS–PVA/PAN composite membranes also increased while permeation flux decreased. The increase of membrane thickness strongly enhanced the selectivity but the permeation flux decreased. From studying influenced of temperature, it was found that as the temperature increased, the permeation flux of PVA/PAN and CS–PVA/PAN composite membranes also increased (Li, Xu et al. 2006).

Ye et al. (2007) studied pervaporation performance and structure of PVA blended with poly(ethylene glycol) (PEG) followed by cross-linking with tetraethoxysilane (TEOS). The results of this work showed that the membrane cross-linked with 10 wt% TEOS gave the improved selectivity. From studying influenced of annealing temperature, it was found that the annealing temperature potentially affected membrane selectivity (Ye, Liu et al. 2007).

Zhang et al. (2007) studied pervaporation performance of ethanol-water mixtures through the blend of PVA with γ-aminopropyl-triethoxysilane (APTEOS). The hybrid membranes were prepared by sol–gel reaction. The results showed that permeation flux and water permselectivity were increased with an increase of APTEOS content. The hybrid membrane containing 5 wt% APTEOS has highest separation factor (Zhang, Liu et al. 2007).

Zhang et al. (2009) studied pervaporation performance of ethanol-water mixtures through quaternized poly(vinyl alcohol) (q-PVA) membrane followed by cross-linking with glutaraldehyde. The experimental results showed that the water permeability and permselectivity of the q-PVA membranes increased with increasing degree of quaternization (DQ). The quaternary ammonium groups enhanced the hydrophilicity and water permselectivity (Zhang, Zhang et al. 2009).

Zhou et al. (2013) studied poly (vinyl alcohol)/cellulose acetate (PVA/CA) blended membranes for the pervaporation separation of ethanol-water mixtures. The results of this work showed that the flux was increased with an increase of CA content in the membranes while the separation factor was decreased. The increase of CA loading led to a decrease in the membrane hydrophilicity and an increase in the radius of free volume cavity in the blended membranes (Zhou, Zhang et al. 2013).

Hong et al. (2014) studied pervaporation performance of poly(ether sulfone)/poly(vinyl alcohol) blend membrane modified with gelatin (GE/PVA-PES) for separation of ethanol-water mixtures. The PVA-PES membranes were cross-linked with glutaraldehyde. The gelatin layer was crosslinked with glutaraldehyde to improve the structural stability and separation performance. An increase in PVA concentrations enhanced both separation factor and permeation flux. Moreover the GE/PVA-PES membrane has stability in long-term operation (Wu, Lu et al. 2014).

2.2.3 Other membranes

Chen et al. (2001) studied lithiated polysulfone membrane (PSF) for the separation of ethanol–water solutions. From this studied, it was found that the water permeation rate decreased and separation factor increased with increasing the degree of lithiation of polysulfone membrane up to 0.75. Beyond the degree of substitution 0.75, the permeation rate increased and separation factor decreased with increasing the substitution (Chen, Liou et al. 2001).

Jiraratananon et al. (2002) studied pervaporation performance of ethanol-water mixtures through chitosan/hydroxyethylcellulose (CS/HEC) composite membranes. The composite membranes were prepared from chitosan blended with hydroxyethylcellulose using cellulose acetate as a porous support. The experimental results showed that an increase of temperature, feed flow rate and feed concentration enhanced permeate flux but reduced separation factor. Pervaporation experiments with low permeate pressure increased both flux and separation factor (Jiraratananon, Chanachai et al. 2002).

Kanti et al. (2004) studied dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation. The membranes was prepared by blending 84% deacetylated chitosan and sodium alginate biopolymers followed by crosslinking with glutaraldehyde solution. It was shown that at constant membrane thickness, the membranes selectivity improved with decreasing pressure (Kanti, Srigowri et al. 2004).

Chen et al. (2007) studied chitosan membrane for the separation of ethanol–water solutions. The chitosan (CS) was cross-linked with 3-aminopropyl-triethoxysilane (APTEOS) to prepare chitosan–silica hybrid membranes (CSHMs). The results show that both the permeation flux and water permselectivity increased remarkably with increasing APTEOS content; CSHM-10 containing 10 wt% APTEOS has the highest separation factor of 597 with a flux of 0.887 kg/(m^2 h) in pervaporation of 85 wt% feed ethanol at 323 K (Chen, Liu et al. 2007).

Kalyani et al. (2008) studied sodium alginate (SA) membranes. A sodium alginate dense membrane was prepared by the casting sodium alginate solutions on an acrylic plate, followed by cross-linked with phosphoric acid for the separation of ethanol–water mixtures at 30°C by the pervaporation method. The experimental results showed that the sodium alginate dense membrane with 3wt% of sodium alginate gave the highest selectivity. When weight percentage of water in the feed mixture increased, the permeation flux of SA membranes also increased while separation selectivity decreased. Increasing membrane thickness decreased the flux but had a less profound effect on the separation factor. Higher permeate pressure caused a reduction in both flux and selectivity (Kalyani, Smitha et al. 2008).

Nawawi et al. (2008) studied chitosan-clay composite membranes for the separation of ethanol–water solutions. The composite membranes were prepared by blending the chitosan with small amount of clay and casting on a porous support which prepared from polysulfone to produce composite membrane. The effects of feed temperature and ethanol concentrations were investigated. From this studied, it was found that as ethanol concentration increased, the separation factor also increased while permeation flux of the membrane decreased. At higher operating temperature, the membrane exhibited a higher permeation flux and a lower selectivity (Nawawi, Sadikin et al. 2008).

Uragami et al. (2010) studied for pervaporation separation of ethanol-water mixtures through sodium carboxymethylcellulose (CMCNa) membrane followed by cross-linking with glutaraldehyde (GA) or tetraethoxysilane (TEOS). The effects of the GA or TEOS content on the water/ethanol selectivity and permeability of these CMCNa/GA cross-linked and CMCNa/TEOS hybrid membranes were investigated. The cross-linked and hybrid membranes containing up to 10 wt% GA or 10 wt% TEOS exhibited higher water/ethanol selectivity than CMCNa membrane without any cross-linker (Uragami 2010).

Zhao et al. (2011) studied for pervaporation separation of ethanol-water mixtures through gelatin/polyacrylonitrile (GE/PAN) blend membrane followed by cross-linking with GA. The composite membranes of GE/PAN were prepared by dip-coating method. The results showed that the GE/PAN membrane with 2 wt% GE concentration at mass ratio of GA to GE of 2.50 wt% in the membrane casting solution exhibited the highest pervaporation performance (Zhao, Ma et al. 2011).

Table 1 Studies on pervaporation of ethanol-water mixtures

Membrane support	Modifier/ Cross-linker	Ethanol in feed (%)	Thickness (μm)	Permeate pressure (mmHg)	Temp (°C)	Total flux (g/m^{2}h)	Selectivity	Reference
BC	-	60	80	1	35	614	12	Pandey et al.,(2005)
BC	-	70	100	1	30	112	287	Dubey et al.(2002)
BC	CS	95	200	10	24	214	9.2	Dubey et al.,(2005)
PVA	CS/GA	90	100	-	90	470	450	Lee et al.,(1992)
PVA	PEG/ TEOS	85	2	15	50	46	300	Li Yi Ye et al.,(2007)
PAN	PVA-CS/GA	95	18	0.225	50	320	93.7	Li et al.,(2006)

BC = Bacterial cellulose membrane, CS = Chitosan, GA = Glutaraldehyde,

PAN = Poly(acrylonitrile), PEG = Poly(ethylene glycol), PVA = Poly(vinyl alcohol)

and TEOS = Tetraethoxysilane

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Microbial strains

The A. *xylinum* (AGR60) was isolated from *nata de coco*. The stock culture waskindly supplied by PramoteTammarat, the Institute of Food Research and ProductDevelopment, Kasetsart University, Bangkok, Thailand.

3.1.2 Chemicals substances

The details of chemicals used in this experiment are shown in Table 2.

Table 2 The chemicals used in this experiment

Chemical	Supplier
Poly(vinyl alcohol)	Chem-supply
Sucrose	Ajax Finechem
Ammonium sulfate	Carlo Erba
Sodium hydroxides	Carlo Erba
Acetic acid	BDH
Ethanol absolute	BDH

3.1.3 Equipments

- Scanning electron microscopy, SEM (JEOL JSM-7610F, Japan).

- Fourier Transform Infrared (FTIR) spectrometer (Nicolet SX-170, USA).

- Universal testing machine (ASD8-82A.TSX, UK).

- X-ray Diffractometer (D8, Karlsruhe Germany).

- Contact Angle Meter (Tantec).

- Autoclave (Model Tomy Autoclave SS-325, Nerima-ku, Tokyo, Japan).

- Vacuum pump (Model RV5 Edwards, England).

3.2 Membrane preparation

The medium for the inoculum was coconut-water supplemented with 5.0% sucrose, 0.5% ammonium sulfate and 1.0% acetic acid. The medium was sterilized at 110^{o}C for 5 mins. Precultures were prepared by a transfer of 50 ml stock culture to 1000 ml in 1500 ml bottle and incubated statically at 30^{o}C for 7 days. After the surface pellicle was removed, a 5% (v/v) preculture broth was added to sterile medium and statically incubated at 30^{o}C for 7 days in a Preti-dish. All sample membranes were first purified by washing with DI water and then was treated with NaOH at room temperature to remove bacterial cells followed by a rinse with 1% acetic acid (w/v) and DI water and until pH came to 7. The BC hydrogel was then immersed in PVA solution at 5, 7, 10 and 12% (w/v) at 60^{o}C. After approximately 7 days, the BC Hydrogel was saturated with PVA solution. Saturated BC was washed with DI water and air dried at room temperature. The BC membrane was cross-linked with 0.1 % (v/v) glutaraldehyde solution and washed with DI water. Afterward, the BC-PVA membrane was air-dried at 30^{o}C and stored in plastic film at room temperature.

3.3 Pervaporation experiment

A schematic diagram of pervaporation experiments is shown in Figure 4. It consisted of a stirred batch reactor where the feed solution was contained in it. The upper part of the reactor holds the feed solution at atmospheric pressure, and the lower part holds the membrane. The effective area of the membrane was 19.625 cm^2. The feed solution was kept vigorously stirred during the pervaporation by a magnetic stirrer. The reactor was provided with an inlet port for temperature measurement. The permeate was condensed and collected in a liquid nitrogen trap and the permeation rate was determined from the weight of the collected samples.

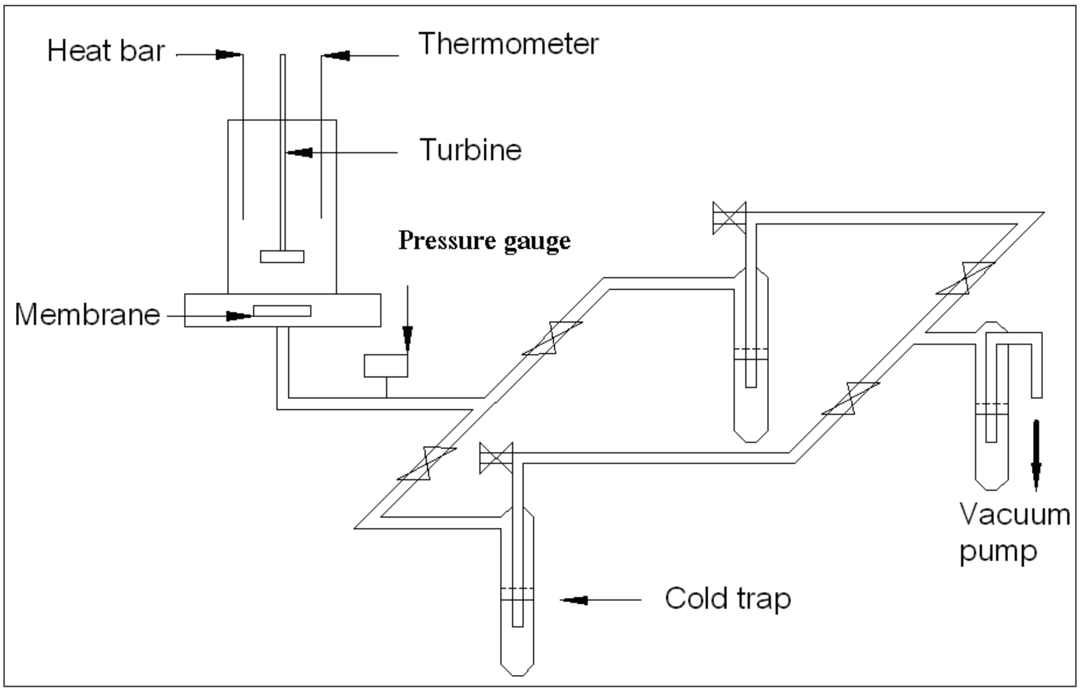


Figure 4 Schematic diagram of the pervaporation system (Kanjanamosit, Muangnapoh et al. 2010)

3.4 Characterization of Membrane

3.4.1 Scanning electron microscope (SEM)

The examination of the surface properties was performed by scanning electron microscopy (SEM). Scanning electron micrographs were taken with JEOL JSM-7610F microscope at Scientific and technological research equipment centre, Chulalongkorn University. The BC membranes were frozen in liquid nitrogen, immediately snapped, and vacuum-dried. Then, the membranes were sputtered with gold and photographed. The coated specimens were kept in dry place before experiment. SEM was obtained at 1-2 kV which was considered to be a suitable condition since too high energy can be burnt the samples.

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used primarily to identify the chemical structure of the sample. FTIR spectra of the membranes were recorded with a Nicolet FT-IR Spectrometer (SX-170) in the region of 4000–500 cm^{-1}, at Scientific and technological research equipment centre, Chulalongkorn University.

3.4.3 X-ray diffraction (XRD)

The examination of the structure of crystalline materials was performed by X-ray Diffractometer (D8, Karlsruhe Germany) at Department of Materials Science, Faculty of Science, Chulalongkorn University. The determination of crystalline property was done under BC membrane was cut into strip-shaped specimens 4 cm in width and 5 cm in length. At least two specimens were used for each blend composition.

3.4.4 Tensile properties testing

In this study, the tensile strength of the membrane was measured by Instron Testing Machine (ASD8-82A.TSX, NY, USA) at Scientific and technological research equipment centre, Chulalongkorn University. The test conditions follow ASTM D882. The determination of tensile property was done under BC membrane was cut into strip-shaped specimens 1 cm in width and 10 cm in length. At least five specimens were used for each blend composition.

3.4.5 The adsorption capacity

The adsorption capacity of membranes was determined by immersing the dried membrane in distilled water and absolute ethanol solution (≥99.5% (v/v)) at room temperature until equilibration. The membrane was then removed from the water and ethanol solution. After that, the surface of the membrane was blotted out with tissue paper, the weight of the swollen membrane was measured and the procedure was repeated until there was no further weight change. The adsorption capacity was calculated using the following formula:

$$The\ adsorption\ capacity\ (\%) = \frac{(W_h - W_d)}{W_d} \times 100$$

Where W_h and W_d denoted the weight of hydrate and dry membrane, respectively.

3.4.6 Contact angle measurements

In this study, the hydrophylic of the membrane was measured by Contact angle meter (Tantec) at Department of Materials Science, Faculty of Science, Chulalongkorn University. The samples were placed onto the specimen holder under the syringe needle then drop water on surface sample and wait for the droplet to stabilize. The sample stages were move to the measure position and read the contact angle on the scale.

CHAPTER IV

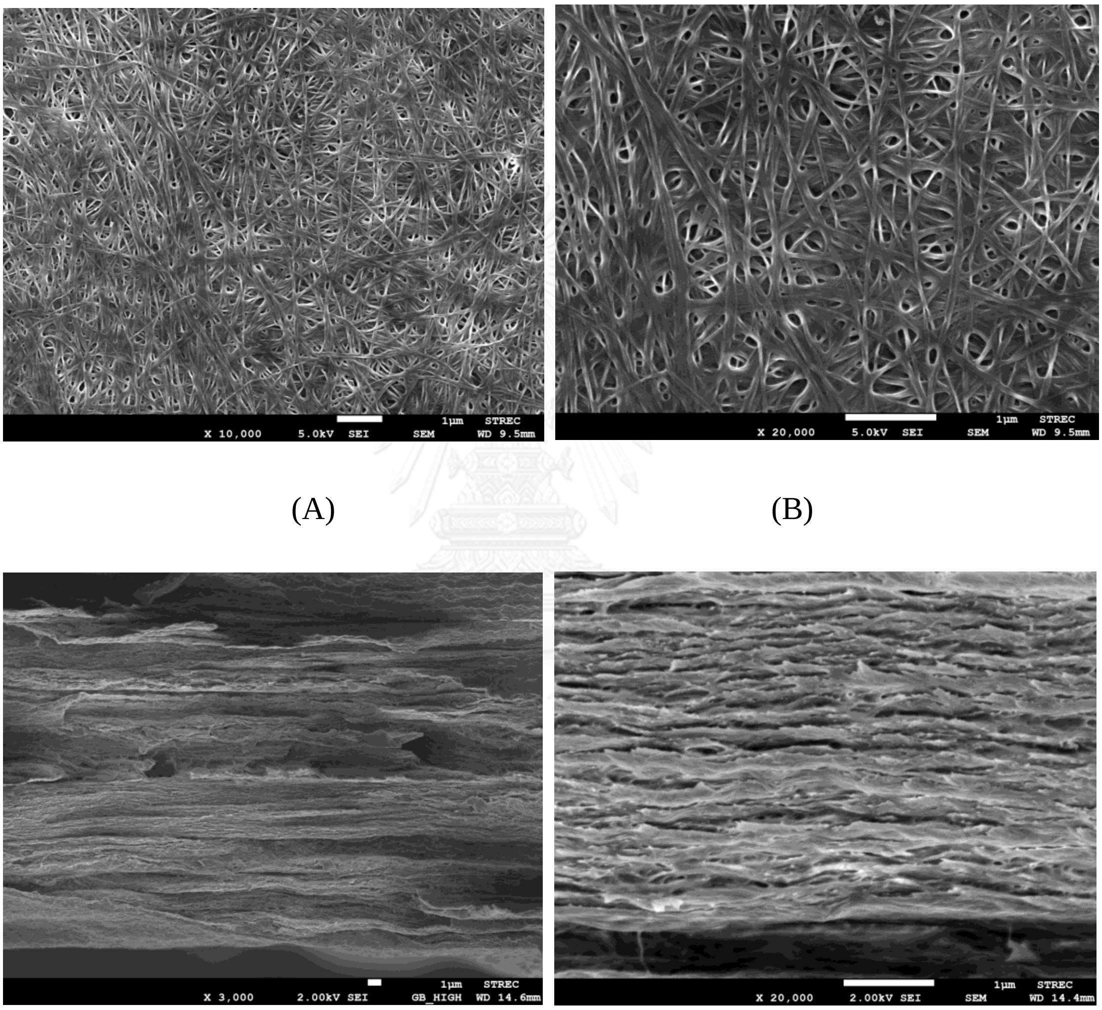
RESULTS AND DISCUSSIONS

4.1 Characterization of BC-PVA membrane

The Composite membranes composed of bacterial cellulose (BC) and poly(vinyl alcohol) (PVA) was prepared by immersing BC in PVA solution and cross-linking with glutaraldehyde (GA) solution. Due to the unique properties of BC and PVA, it might improve the performance of the developed composite membranes for pervaporation system. The effect of PVA concentrations in solution was investigated. In this work, the modification of the BC membrane was performed by immersing wet BC membranes in differences PVA solution followed by cross-linking with GA. In definition BC, BC-5PVA/GA, BC-7PVA/GA, BC-10PVA/GA and BC-12PVA/GA membrane referred to the unmodified BC and the BC membrane immersing in 5, 7, 10 and 12% (w/v), respectively. PVA/GA is the PVA membrane prepared by 10% (w/v) PVA solution followed by cross-linking with GA. morphology, chemical structure, crystallinity properties, mechanical properties and adsorption capacity of the composite membranes were investigated and compared with those of BC membrane and cross-linked PVA membrane.

4.1.1 Surface morphology

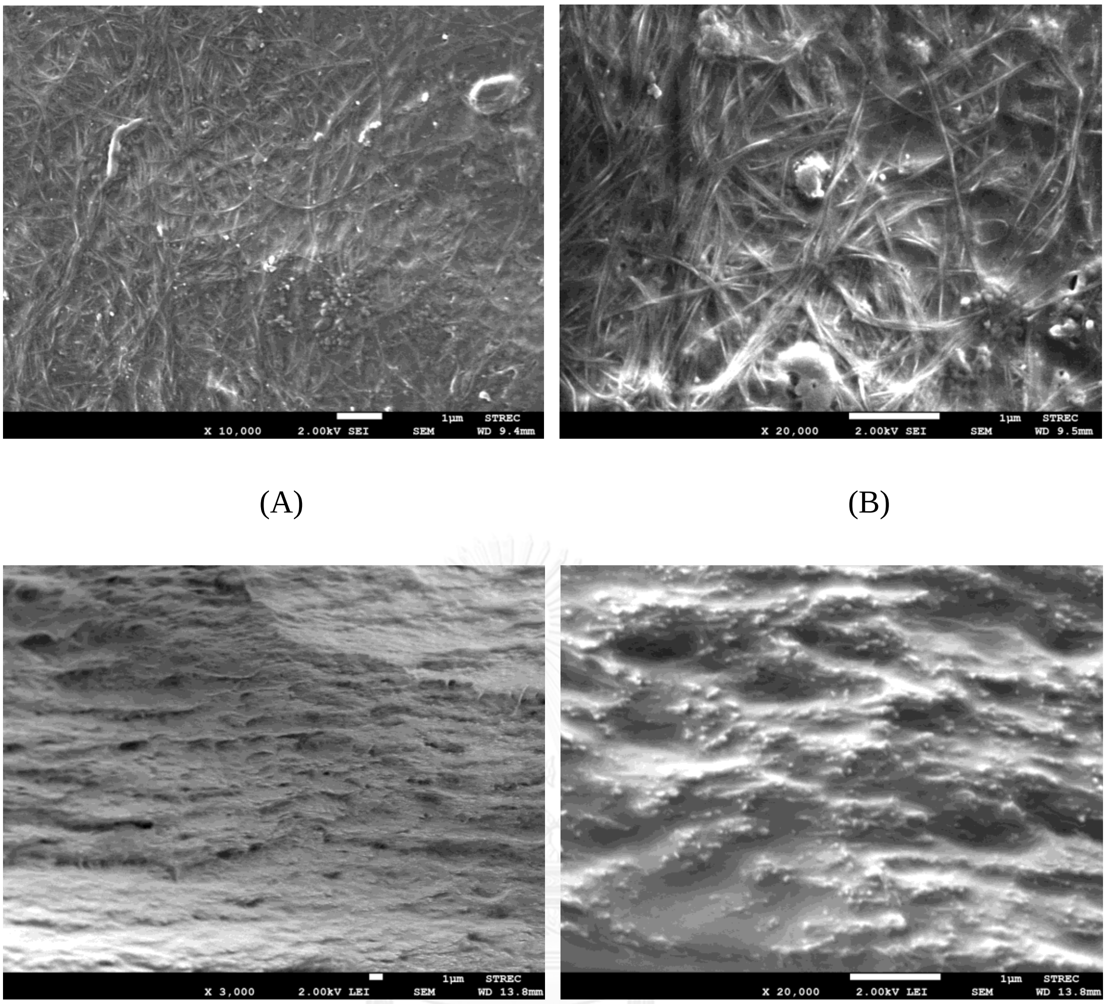
It was expected that BC nanofibers would have modified morphology by immersion method. In this research, the morphologies of dried BC, PVA/GA and BC-PVA/GA membranes were studied by scanning electron microscopy (SEM). Figure 5 showed the three-dimensional structure of BC as a fibrous, porous network of un-oriented nanofibers. All dried BC-PVA/GA membranes can observe fibrous pattern as shown in Figures 6 to 9. Moreover, BC nanofiber network on the surface were more hardly to be observed with increasing the PVA content, while PVA alone exhibits a flat homogeneous surface, without any defects and no visible pores on the surface (Figure 10). By the immersion method, PVA seemed to be well-bonded into BC network. PVA were filled inside pore of BC membrane randomly, rising the overall density of the hydrogels. In the surface of the BC films especially, the BC film with 10% PVA, we observed very good mixing of both components, resulting in less visible fibres and an almost completely flat area on the surface (Figure 8). Figures 6 to 9 show clearly that PVA could penetrate into the BC network structure and filled pores and voids within the BC matrix. PVA molecules were embedded within BC fibers, thus forming uniform composite structures with altered properties.



(A) (B)

(C) (D)

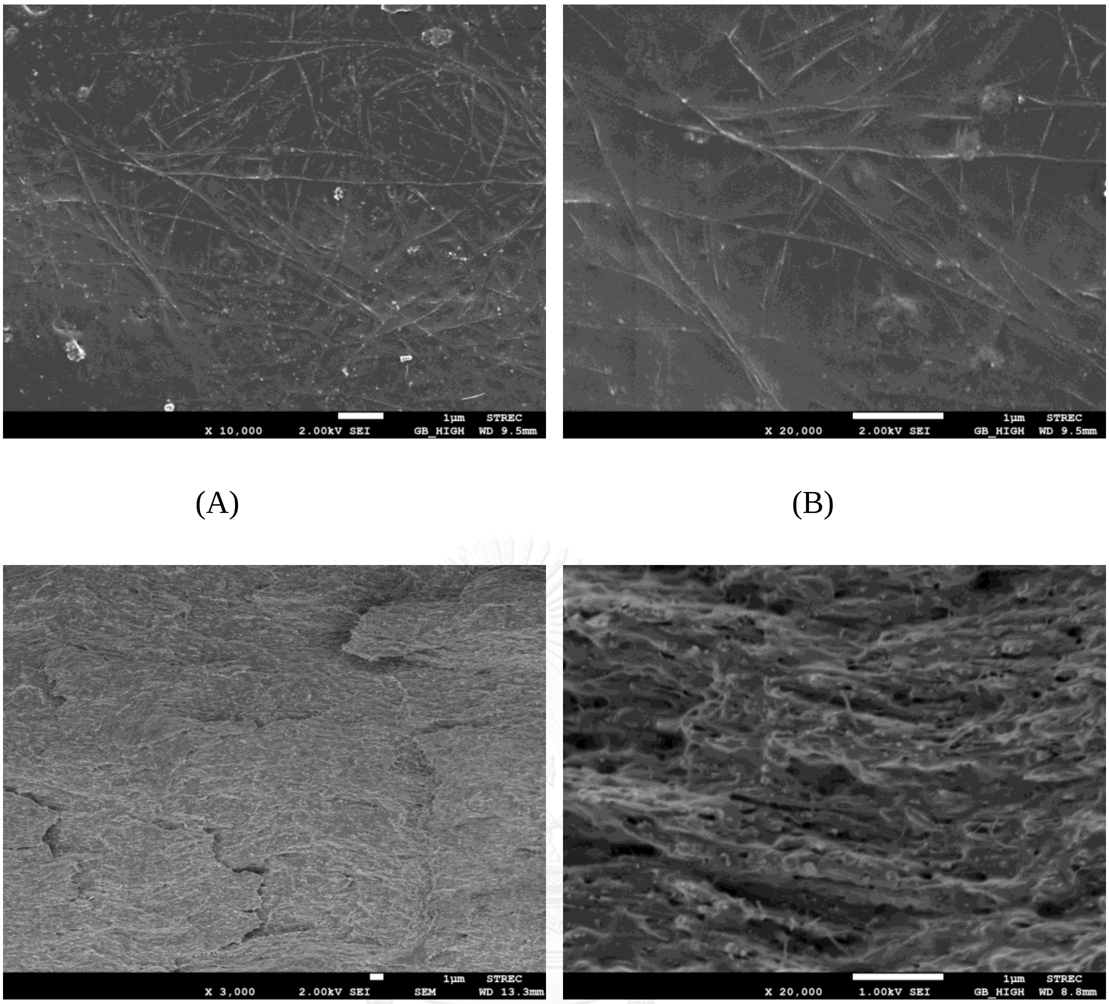
Figure 5 SEM images of the dried BC membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



(A) (B)

(C) (D)

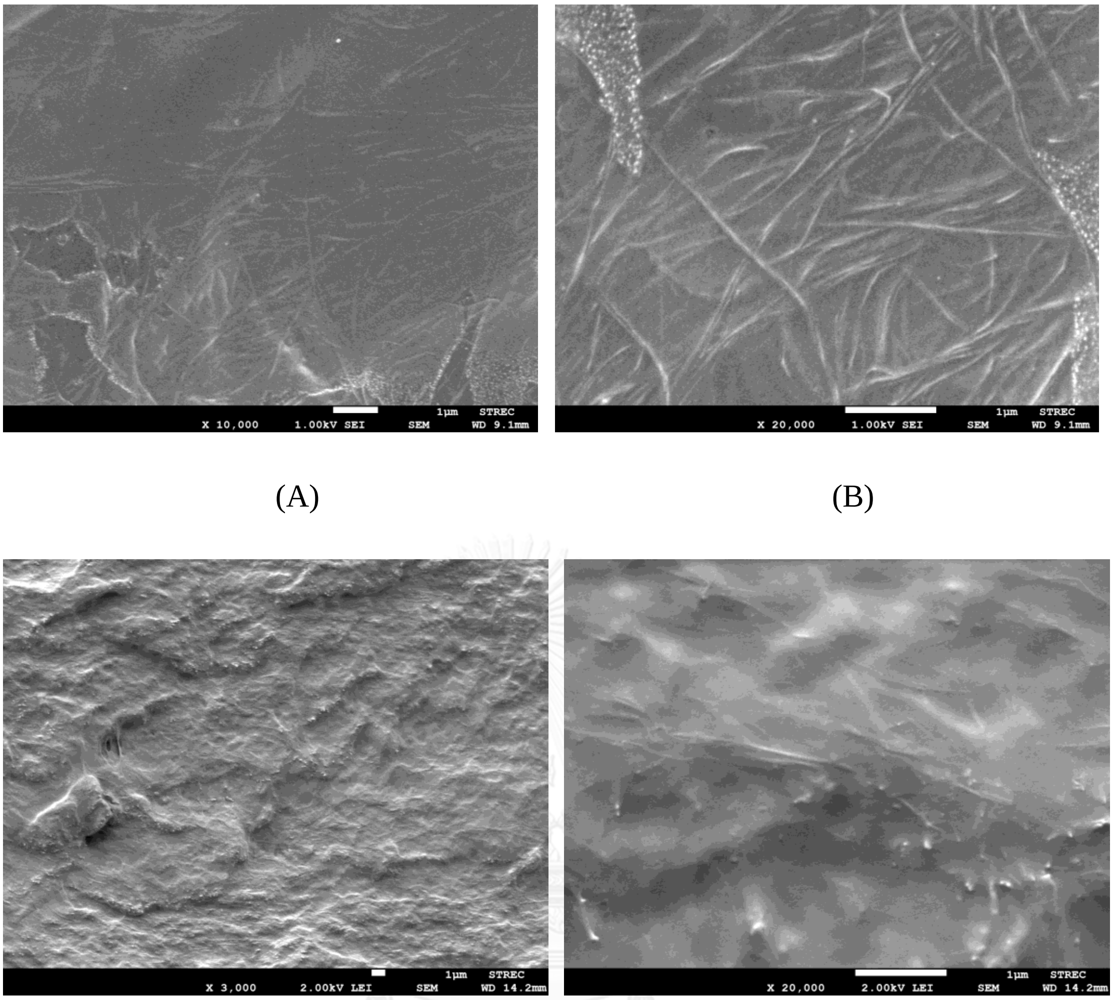
Figure 6 SEM images of the dried BC-5PVA/GA membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 μm



(A) (B)

(C) (D)

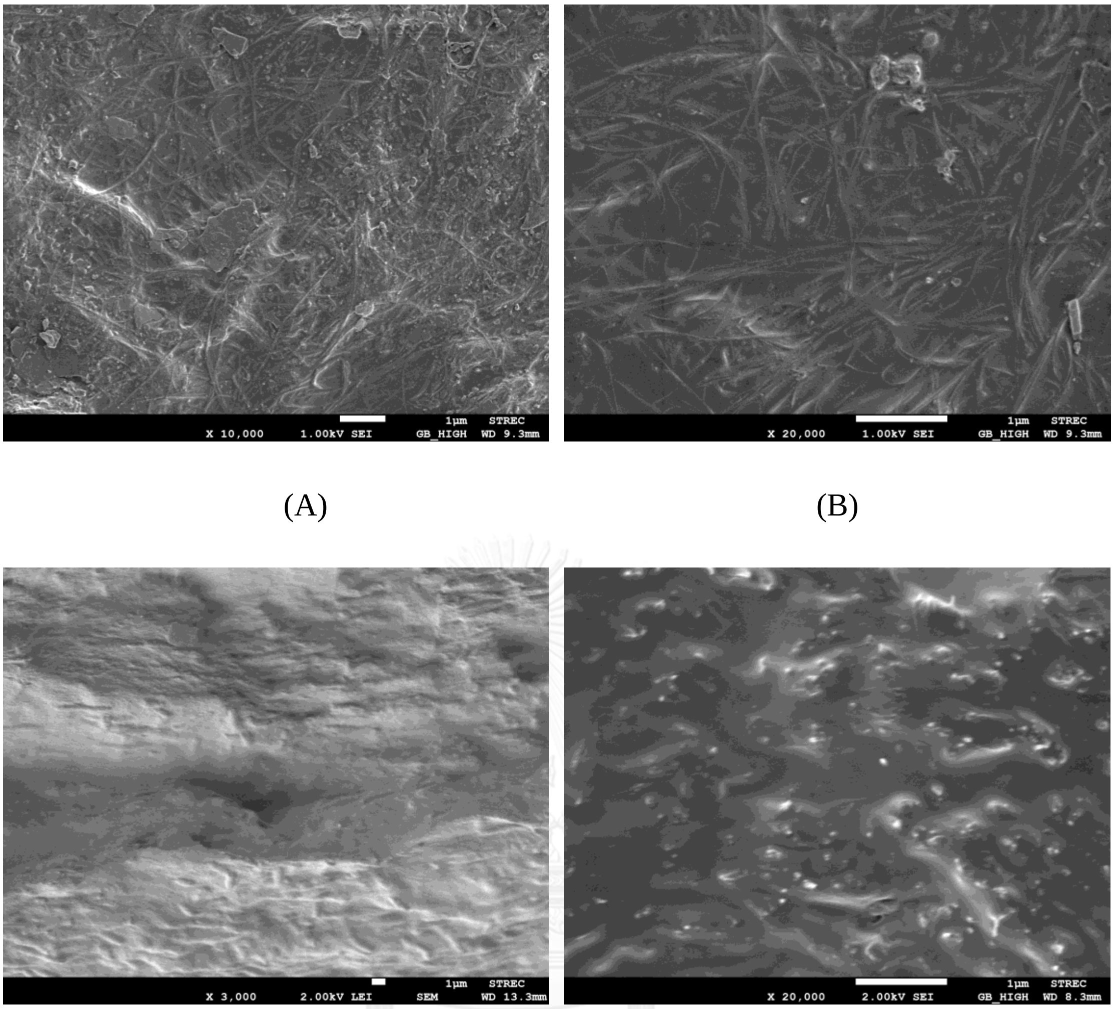
Figure 7 SEM images of the dried BC-7PVA/GA membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



(A) (B)

(C) (D)

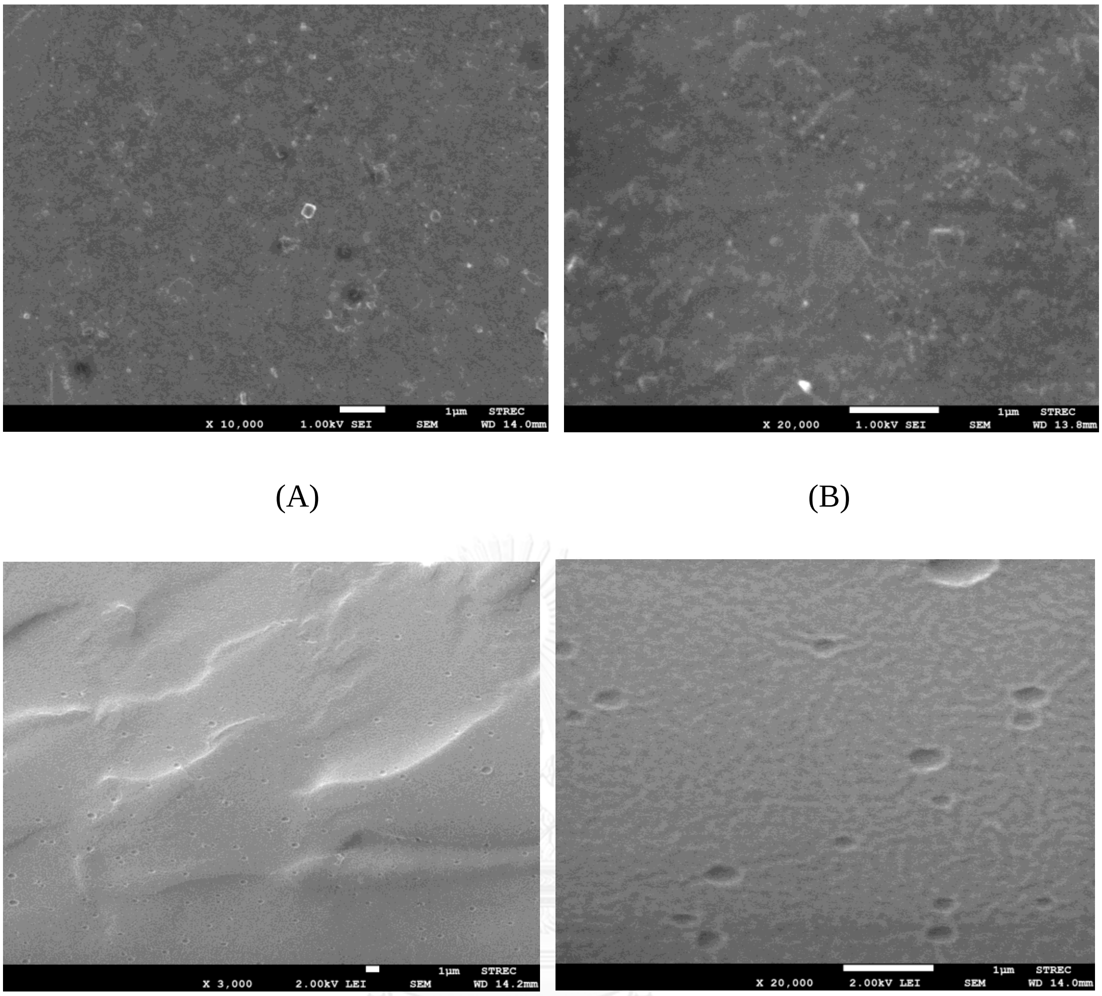
Figure 8 SEM images of the dried BC-10PVA/GA membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



(A) (B)

(C) (D)

Figure 9 SEM images of the dried BC-12PVA/GA membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



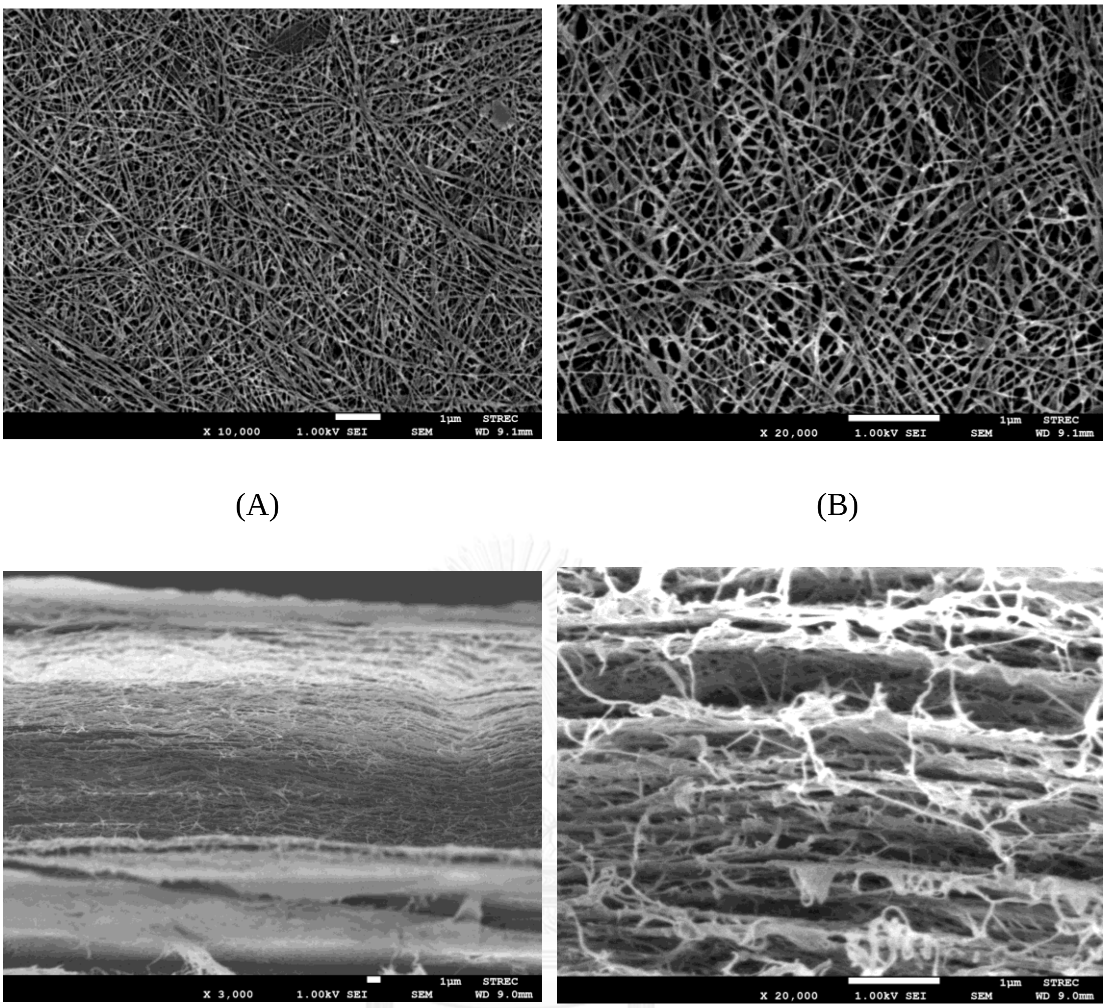
(A) (B)

(C) (D)

Figure 10 SEM images of the dried 10PVA/GA membrane: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) 20,000x (D). The scale bars represent 1 μm

In this research, the morphology of membranes in both deionized (DI) water and absolute ethanol were investigated by scanning electron microscopy (SEM). The SEM images of the BC, BC-10PVA/GA and PVA/GA with 10% (w/v) PVA in DI water were shown in Figure 11 to 13, respectively. The considerable increases in pore size of the swollen membranes in water were clearly observed in the BC and BC-10PVA membranes. It is noticeable that as compared to the unmodified BC, the pore size of the BC-PVA/GA was more enhanced in water. As shown in Figure 12, PVA well integrated into the original BC hydrogel forming an interpenetrated network. PVA inside the BC membrane randomly bridge individual BC fibers. The similar results were previously reported in morphology of BC and BC/PVA membranes study, before and after an initial drying step (Leitão, Silva et al. 2013). As shown in Figure 13, it is observed that the morphology of PVA/GA have densely compacted structure. The morphology of BC, PVA/GA and BC-PVA/GA membranes in absolute ethanol are shown in Figure 14 to 16, respectively. All samples presented quite similar morphological characteristics of denser structure as observed in the dry membranes.

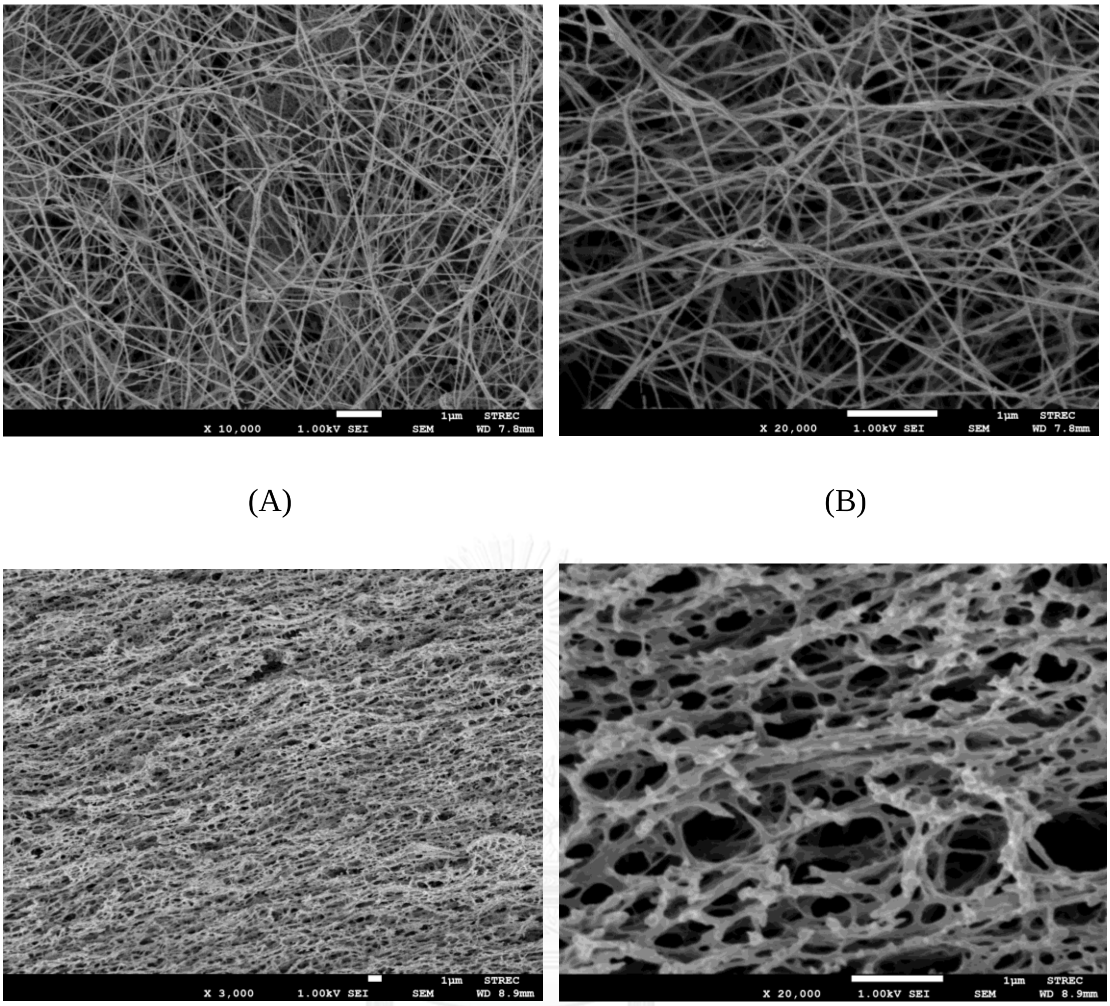
Comparison between the morphology of the BC and BC-PVA/GA membranes in DI water and absolute ethanol showed clear and marked structural differences as could be observed in Figure 11 to 12 and Figure 14 to15, respectively. Figures 12 and 15 showed that in DI water, the pore size of membranes greatly increases, which could lead to the increase in permeability of water and other components across the membrane. The result showed that the permeability of BC-PVA/GA in water should be higher than that in ethanol. Here, we show that changes in water content of a feed alter the structure of BC and BC composite membranes and thus should have effects on pervaporation performance.



(A) (B)

(C) (D)

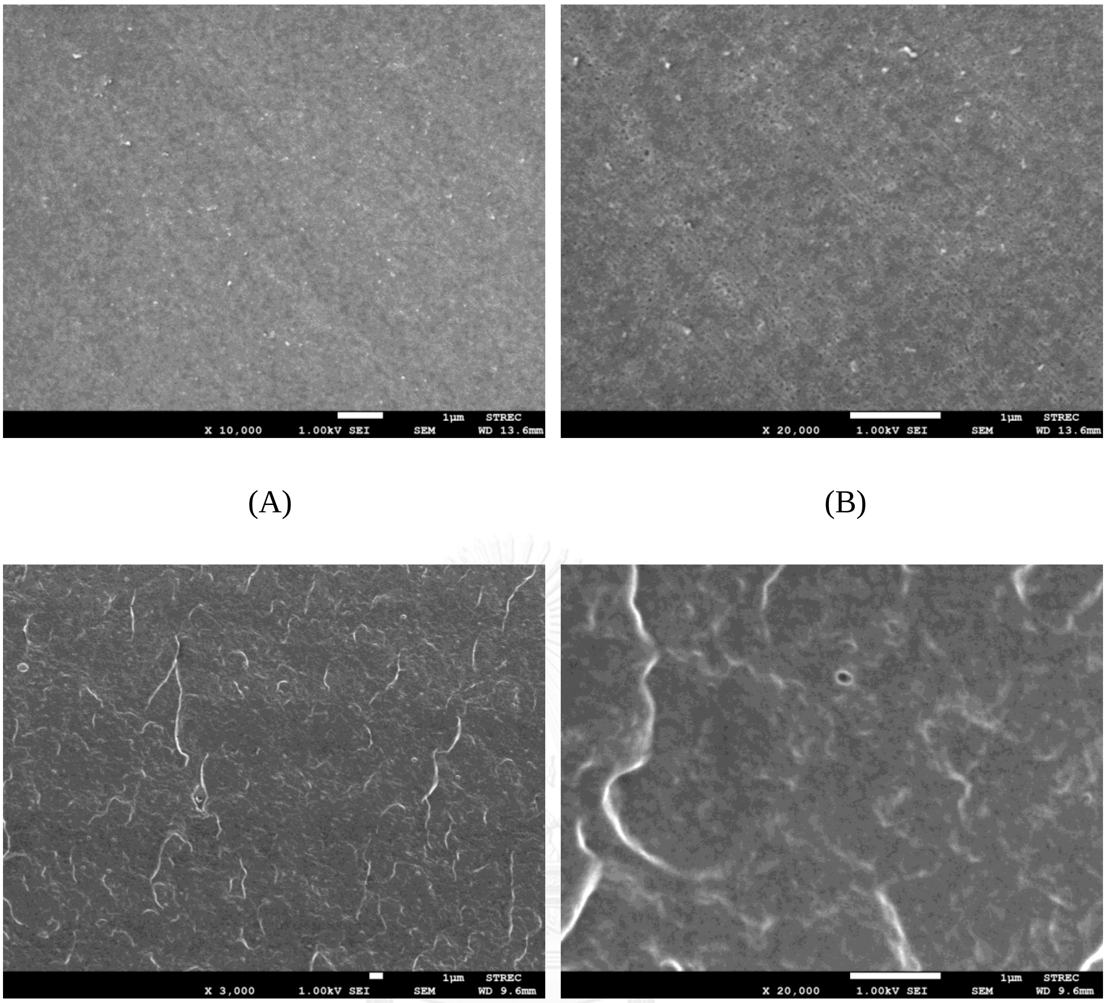
Figure 11 SEM images of the BC membrane in DI water: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 μm



(A) (B)

(C) (D)

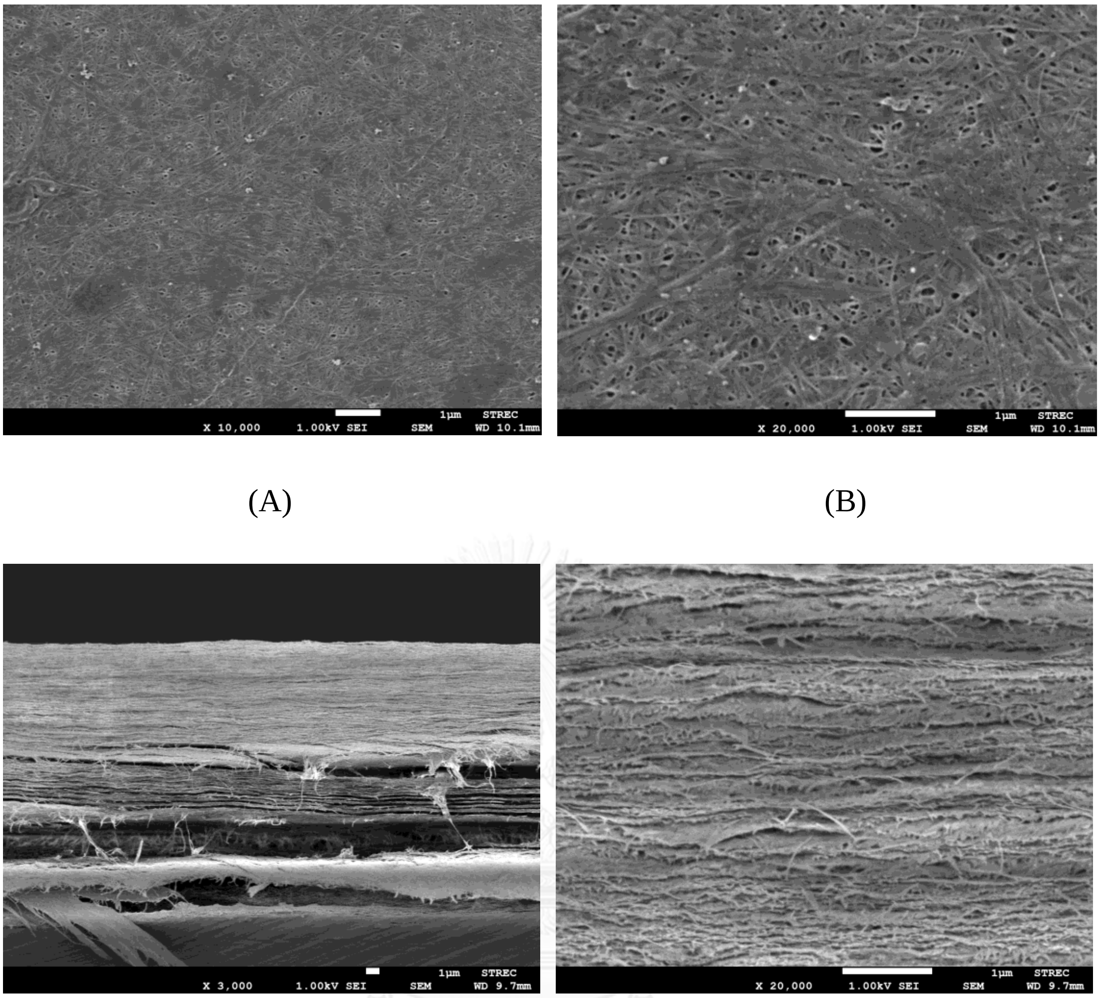
Figure 12 SEM images of the BC-10PVA/GA membrane in DI water: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



(A) (B)

(C) (D)

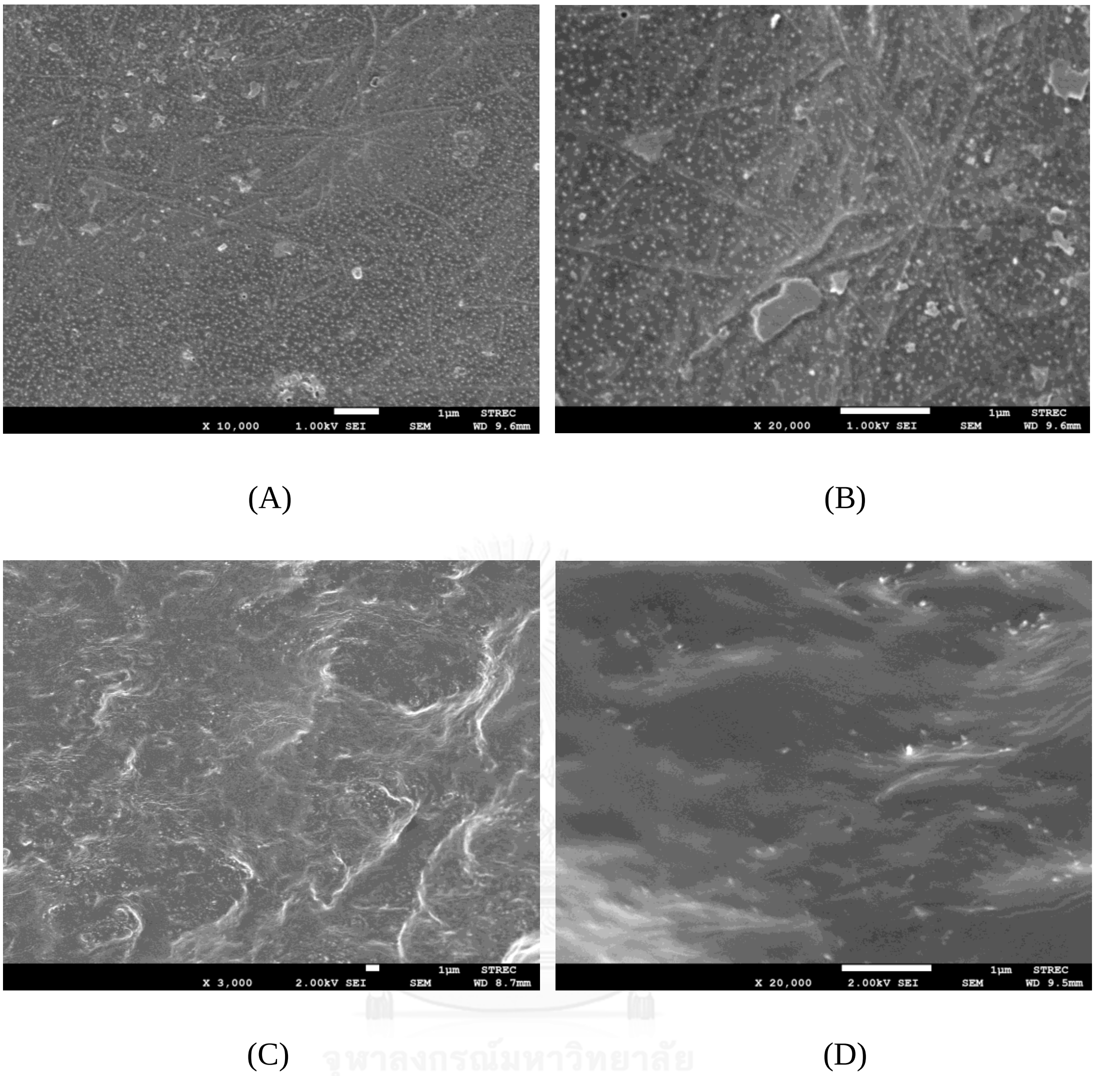
Figure 13 SEM images of the 10PVA/GA membrane in DI water: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 μm



(A) (B)

(C) (D)

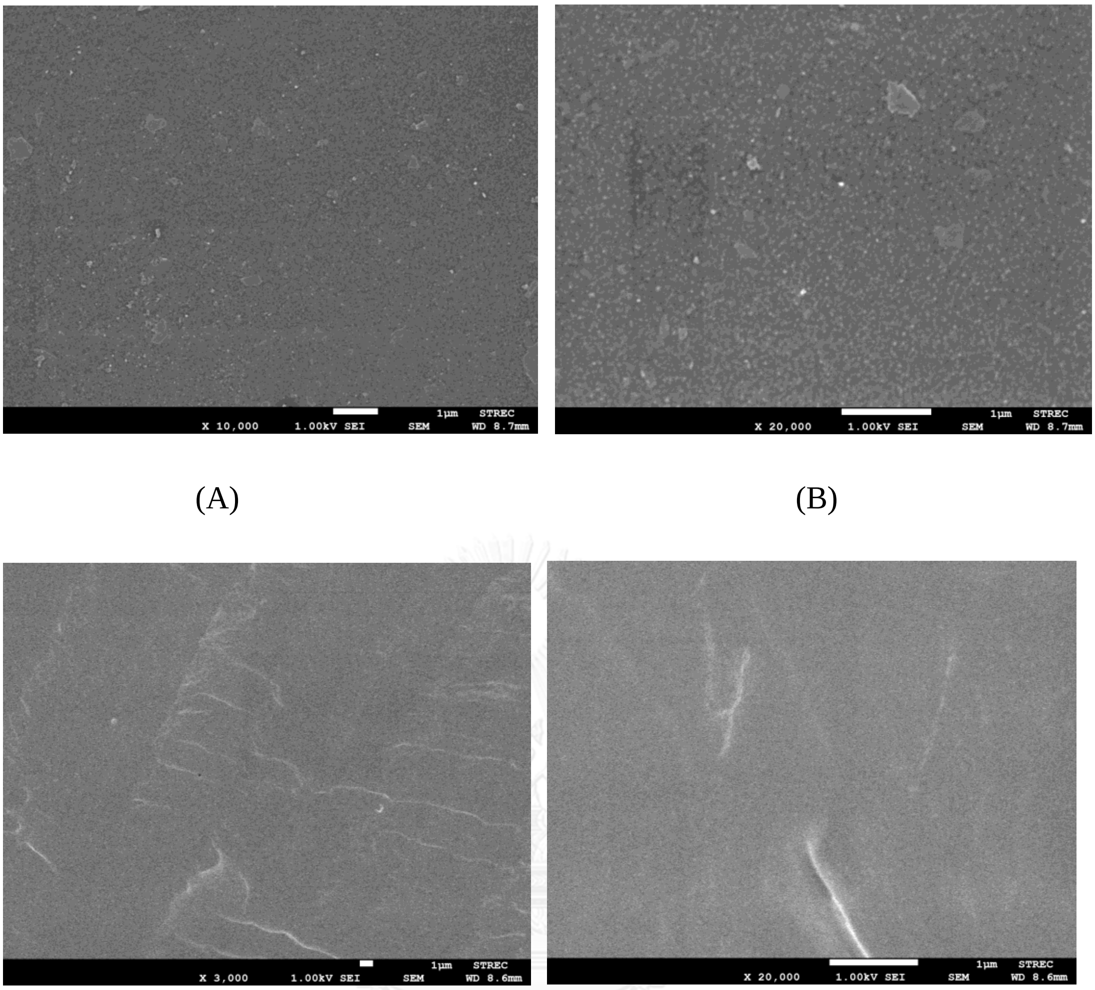
Figure 14 SEM images the BC membrane in absolute ethanol: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 μm.



(A) (B)

(C) (D)

Figure 15 SEM images of BC-10PVA/GA membrane in absolute ethanol: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm



(A) (B)

(C) (D)

Figure 16 SEM images of 10PVA/GA membrane in absolute ethanol: surface at magnification of 10,000x (A) and 20,000x (B); cross-section at magnification of 3,000x (C) and 20,000x (D). The scale bars represent 1 µm

4.1.2 FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. Therefore, in this research, the samples of BC, PVA/GA and BC-PVA/GA membranes were analyzed by FTIR. The presence of peak at a specific wave number would indicate the presence of a specific chemical bound. As shown in Figure 17 and Figure 18, the FTIR spectra of the BC, BC-PVA/GA and PVA/GA membranes were measured at wave number ranging from 3800-2600 cm^{-1}and 3700-700 cm^{-1}, respectively. From Figure 17, A broad band at 3200–3500 cm^{-1}, wavenumber seen in all spectra, is a result of the hydroxyl (O–H) stretching vibration resulting from the strong hydrogen bonds of intra-molecular and inter-molecular type (Qiu and Netravali 2012). The BC membrane showed a band at 3343.3 cm^{-1}. However, the band at 3294.04 cm^{-1} observed in the PVA spectrum is much broader, which indicates the hydrogen bond’s formation. As shown in Figure 17 for all BC-PVA/GA membranes, the broadened O-H stretch band at 3290–3300 cm^{-1} is observed. This broadening could be due to the intermolecular hydrogen bonding between PVA and BC that was also seen in PVA-soaked cellulose (Adhikari, 2005; Aldona Długa, 2014). The absorption band observed between 2820 and 3000 cm^{-1} wavenumber is due to the stretching of aliphatic C–H bond. From Figure 18, PVA showed C-H stretching at wave number 2938.75 cm^{-1}. Figures 18 (b) to (e) show that the bands of for BC-5PVA/GA, BC-7PVA/GA ,BC-10PVA/GA and BC-12PVA/GA membranes slightly shifted to 2919.89 cm^{-1}, 2937.61 cm^{-1}, 2939.03 cm^{-1} and 2938.8 cm^{-1}, respectively. The shift of the C-H stretching absorption band was previously observed in a precipitated cellulose and PVA blend (Pritchard 1970, Salama 2004) and it was suggested that it could be a simultaneous effect of the shifting peak of the isotactic stereosequence vibration (Pritchard 1970) from 835.93 cm^{-1} of PVA to around 834-837 cm^{-1} of the nanocomposites. The peak shift could indicate a change in morphology or crystallinity of PVA as its isotactic stereosequence was altered. Here, the changes of C-H stretching and bending at the absorption bands around 2900 and 800 cm^{-1}were observed. The FT-IR results could imply molecular interactions between PVA and BC through hydrogen bonding and crystallinity change.

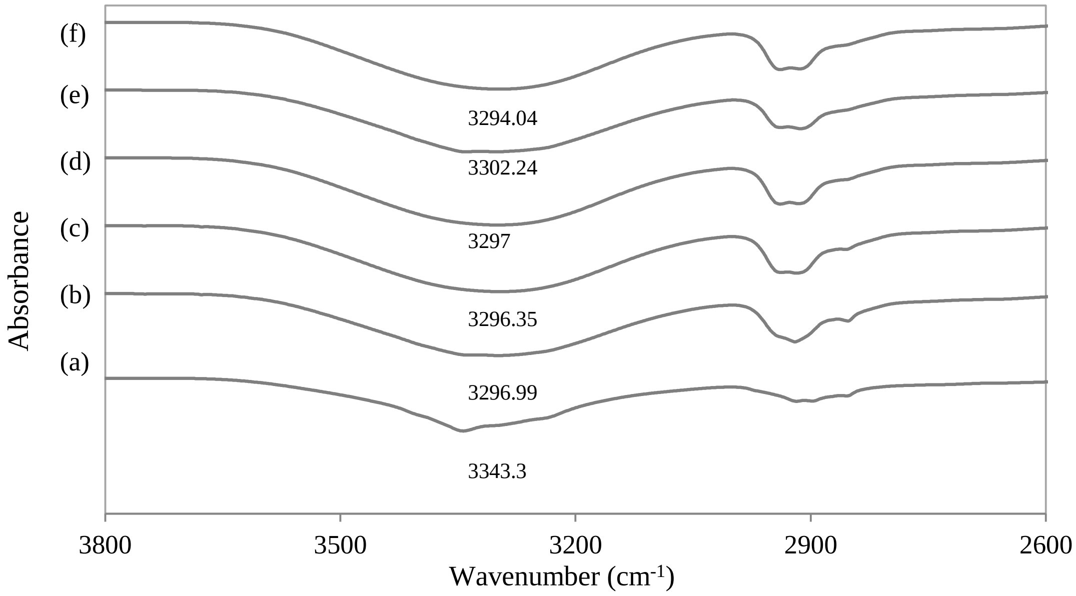


Figure 17 The FTIR spectra of BC, BC-PVA/GA and PVA/GA membrane in wave numbers ranging from 3800 to 2600 cm^{-1}: (a) BC; (b) BC-5PVA/GA; (c) BC-7PVA/GA; (d) BC-10PVA/GA; (e) BC-12PVA/GA and (f) 10PVA/GA

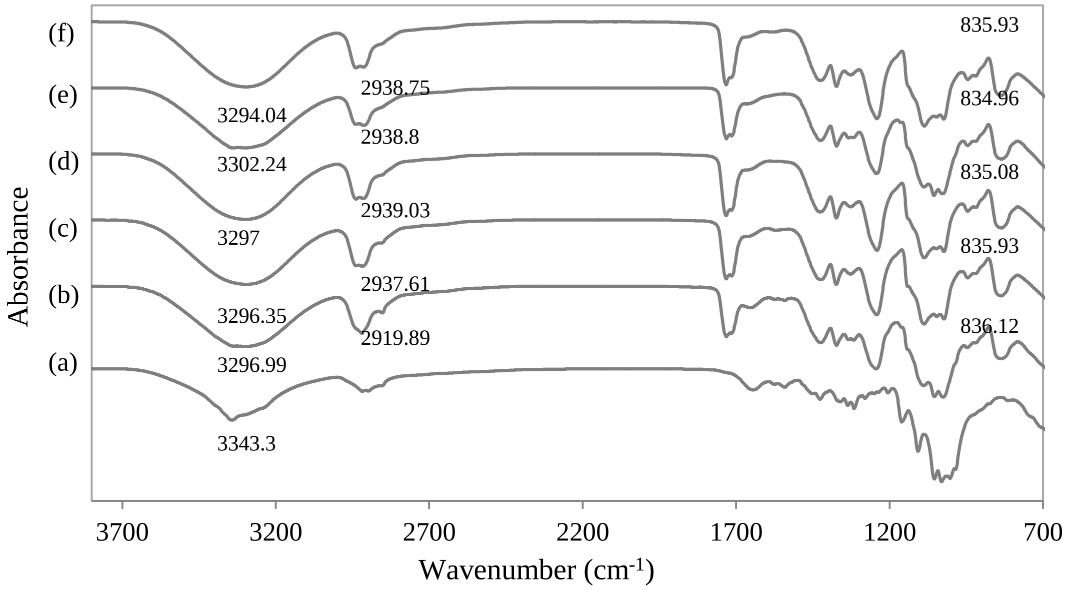


Figure 18 The FTIR spectra of BC and BC-PVA membranes in wave numbers ranging from 3700 to 700 cm^{-1}: (a) BC; (b) BC-5PVA/GA; (c) BC-7PVA/GA; (d) BC-10PVA/GA; (e) BC-12PVA/GA and (f) 10PVA/GA

4.1.3 XRD analysis

XRD was used to evaluate the crystallinity of membranes. The crystallinity (%) values for individual specimens were calculated using a ratio of crystalline area to the combined crystalline and amorphous areas in the XRD patterns. The XRD patterns of BC, PVA/GA and BC-PVA/GA membranes were shown in Figures 19.

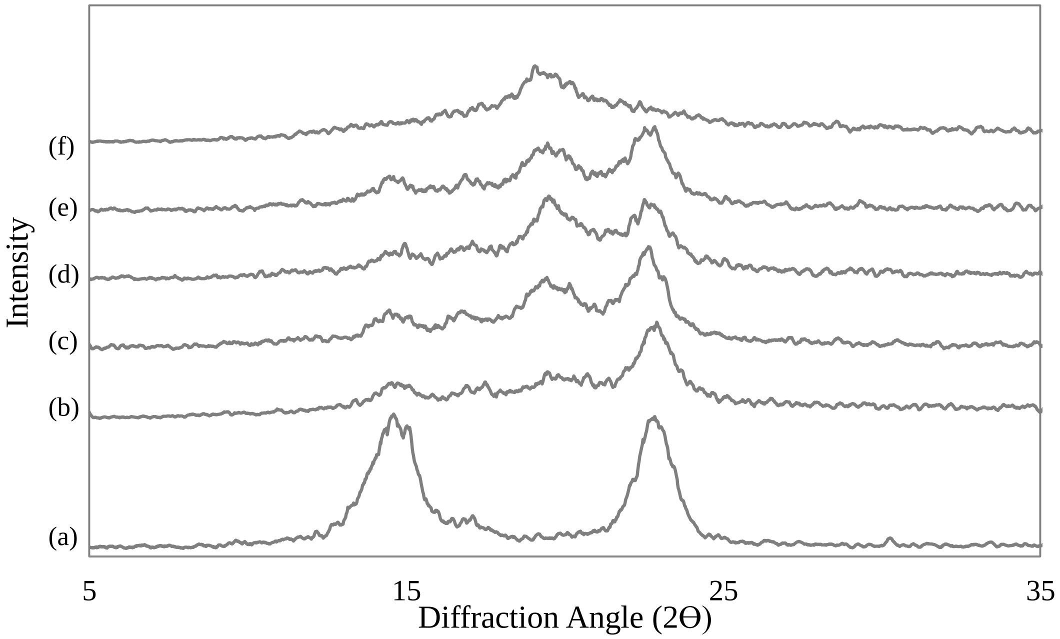


Figure 19 The XRD patterns obtained for (a) BC; (b) BC-5PVA/GA; (c) BC-7PVA/GA; (d) BC-10PVA/GA; (e) BC-12PVA/GA and (f) 10PVA/GA

In Figure 19, the diffractograms of BC showed three peaks located at 2θ = 14.65°, 17.121°, and 22.81° corresponding to the primary diffraction of the $(1\bar{1}0)$, (110), and (200) planes of polymorph cellulose I (Klechkovskaya 2003). The diffractograms of PVA/GA was showed a distinct peak located at 2θ = 19.22° correspond to the presence of crystalline microstructure, similarly to previously reported in the as-electrospun PVA fibers (Wang and Hsieh 2010). The diffractograms of BC-PVA/GA display both characteristics of BC and PVA as shown in Figure 19 (b) to (e). From these data it can be concluded that the presence of PVA has effect on the crystal structure of BC-PVA/GA membranes.

Table 3 shows that the crystallinity of BC was 74.97%, which was the highest value in all samples tested in this study, whereas the crystallinity of PVA/GA was 34.97%. The crystallinity of the BC-PVA/GA membranes was lower than that of the BC membrane. However, it is notable that the BC film membrane 10% PVA was showed highest the crystallinity when compared with BC-PVA/GA at 5, 7 and 12% PVA. This indicated that the crystallinity of BC-PVA/GA membranes depended on the amount of PVA concentration. Considering from the homogeneous dispersion of PVA in BC matrix and its crystalline structure, the optimal concentration of PVA for the preparation of BC-PVA/GA membranes in this study is 10% w/v.

Table 3 The crystallinity of membranes

Membranes	The crystallinity (%)
BC	74.97
BC-5PVA/GA	30.7
BC-7PVA/GA	33.38
BC-10PVA/GA	38.19
BC-12PVA/GA	34.75
PVA/GA	34.97

4.1.4 Mechanical properties

The mechanical properties, among all the properties of materials, are often one of the most important properties, essentially for almost all applications. BC is known for its high tensile strength, varying according to the membrane’s density, dimensions, treatment and preparation methods. Generally, BC is regarded as lacking elastic properties, since hydrogen bonds formed between individual BC strands contribute to the stiffness of the hydrogel. PVA, on the other hand, is known for its elasticity and relatively low tensile strength (Leitão, Silva et al. 2013). Therefore, in this study, the mechanical properties such as the tensile strength, Young's modulus and elongation at break of BC, BC-PVA/GA and PVA/GA were examined.

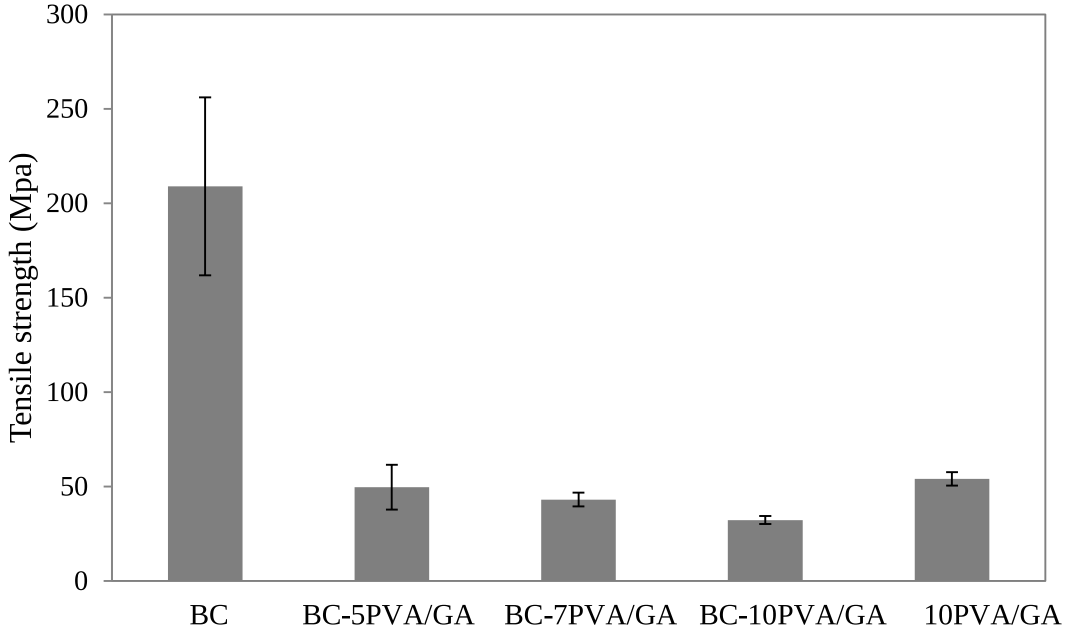


Figure 20 The tensile strength of the BC-PVA membranes as a function of PVA concentration in solution, in comparison with BC and PVA/GA membranes

Figure 20 presented the change of tensile strength of BC-PVA/GA membranes as a function of PVA concentration, in comparison with BC and PVA/GA membranes. The results showed that the tensile strength of BC membrane at the average thickness of 45 µm was 208.94 MPa, while the tensile strength of PVA/GA membrane was 54.03 MPa. The tensile strength of membranes decreased from 208.94 to 32.29 MPa with PVA concentration in solution was increased from 0% to 10%. Decreasing of tensile strength of BC-PVA/GA membranes depended on the amount of PVA concentration in the composite.

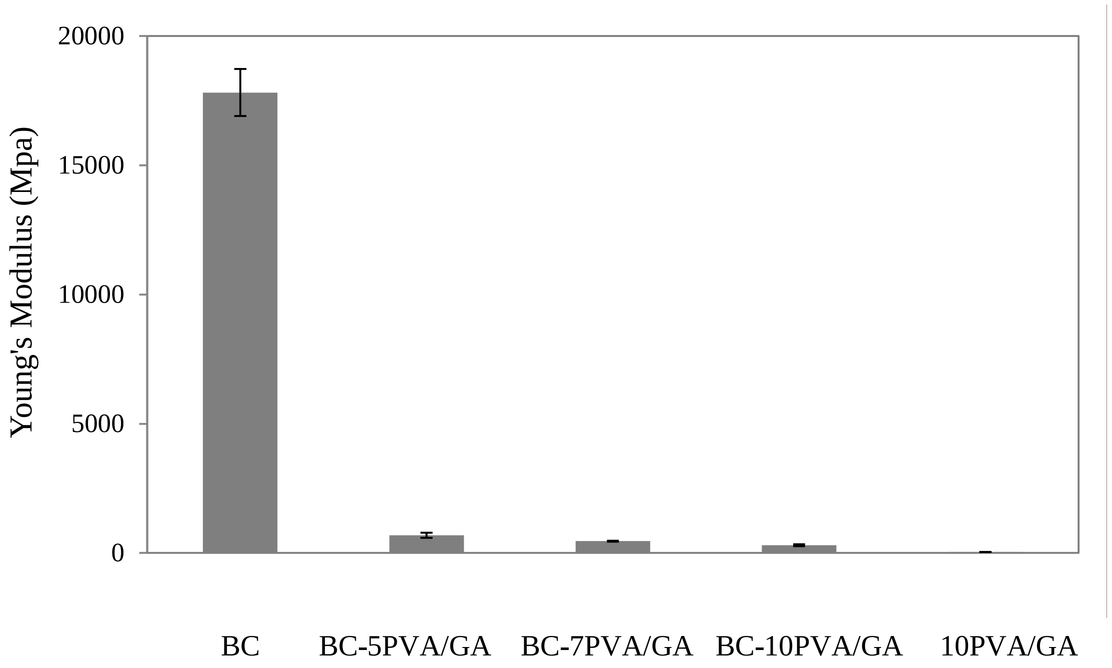


Figure 21 The young's modulus of the BC-PVA membranes as a function of PVA concentration, in comparison with BC and PVA/GA membranes

Figure 21 shows the change of young’s modulus of the BC-PVA membranes as a function of PVA concentration in solution, in comparison with BC and PVA/GA membranes. The young’s modulus of BC membrane at the average thickness of 45 µm was 17816.72 MPa, which was the maximum observed value in all samples tested in this study. The PVA/GA membrane has minimum young’s modulus at 37.72 MPa. It was found that the young’s modulus of the BC-PVA/GA membranes were 688.2 -303.9 MPa, relatively decreasing with the increase of PVA concentration in solution. The similar results were previously reported in the study of the effect of PVA content of the BC/PVA membranes on mechanical properties. They found that the young’s modulus values of the BC–PVA composites were between those obtained for BC and PVA and the young’s modulus of the BC–PVA composites decreased with the increase in PVA content as well (Castro, Vesterinen et al. 2014).

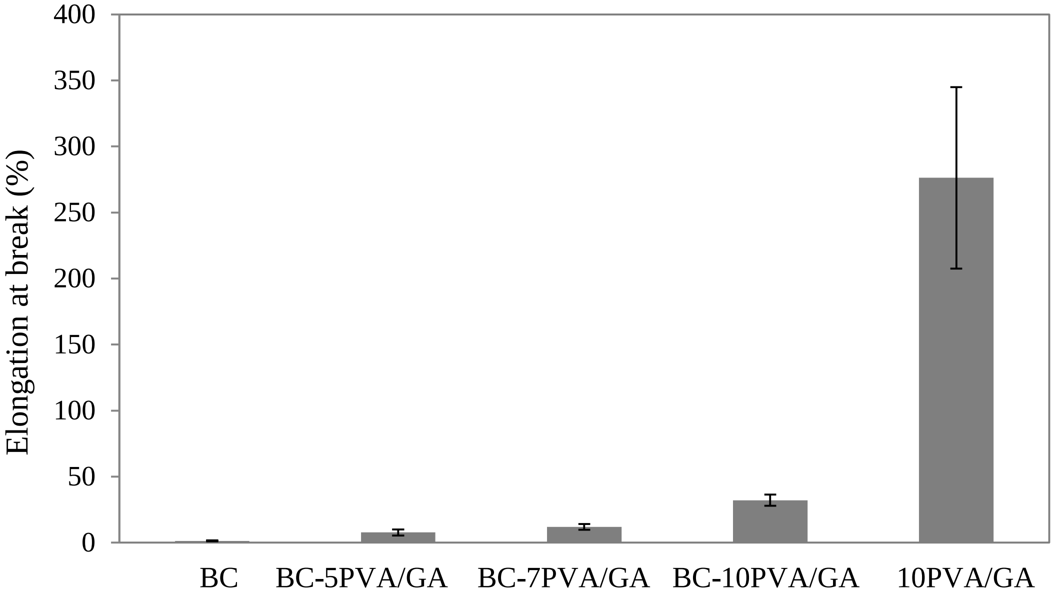


Figure 22 The elongation at break of the BC-PVA membranes as a function of PVA concentration in solution compare with BC and PVA/GA membranes

Figure 22 presented the change of elongation at break of the BC-PVA membranes as a function of PVA concentration in solution, in comparison with BC and PVA/GA membranes. The elongation at break of BC membrane at the average thickness of 45 µm was only 1.32% when the PVA/GA membranes showed the elongation at break at 276.2%, which was the highest value in all the samples tested in this study. The elongation at break of membranes increased from 1.32% to 32.14% with PVA concentration was increased from 0% to 10%. It was found that the elongation at break also increased with increasing PVA concentration in solution. The result indicated that the BC–PVA/GA membranes have more elastic behavior than the BC membranes. The similar results were previously reported in the study of the effect of PVA content of the BC/PVA membranes on mechanical properties. They found that the BC–PVA composite shows an initial elastic behavior followed by a plastic yielding. They suggested that this effect occurred because the yielding may be due to PVA’s high ductility and breaking of some BC nanofibers that are in the stress direction and possible alignment of the remaining nanofibers. Once that process was over, BC–PVA composites showed elastic behavior until the fracture point.

The effect of PVA content on mechanical properties of the BC/PVA membranes was similar to those of the composites BC/PVA membranes (Qiu and Netravali 2012, Castro, Vesterinen et al. 2014). Castro et al. (2014) studied effect of PVA content of nanocomposites of poly(vinyl alcohol) (PVA) reinforced with bacterial cellulose (BC) crosslinking with glyoxal on mechanical properties. They found that young’s modulus and tensile strength of nanocomposites decreased with increasing PVA content. The similar observation was previously reported (Qin and Netravali et al., 2012). They studied the effect of BC content in the BC–PVA composites on mechanical properties. The BC composites were produced by immersing wet BC pellicles in PVA solution, followed by crosslinking with glutaraldehyde. They found that when the PVA content increased, the mechanical properties of the BC–PVA composites decreased. However, the elongation at break increased with increasing PVA concentration in solution. Therefore, immersing BC membrane in PVA solution can increase elastic behavior of BC membranes.

4.1.5 The adsorption capacity

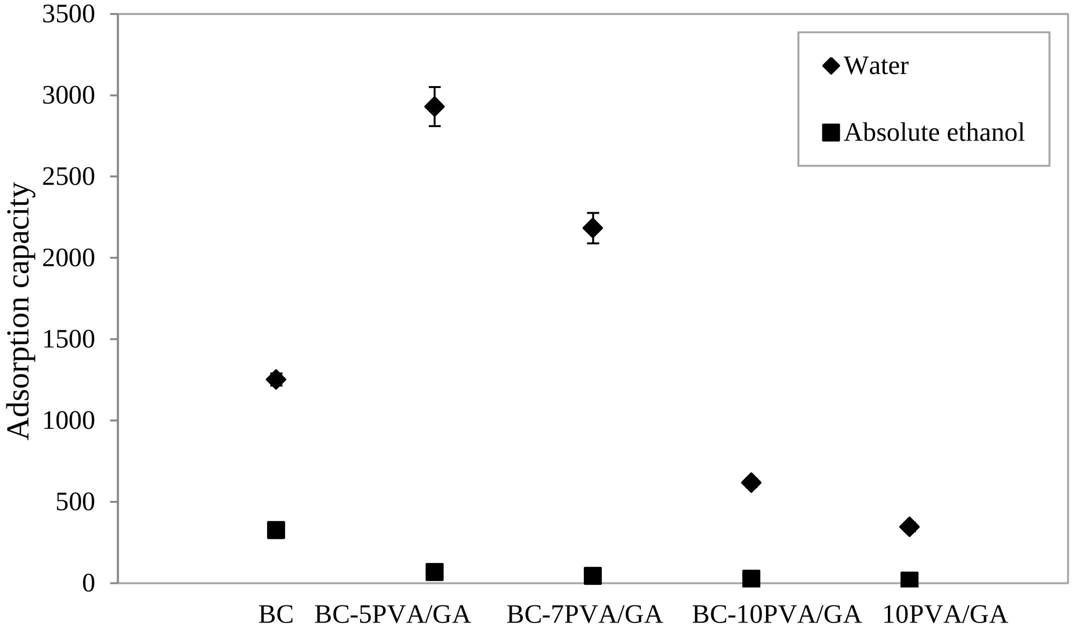


Figure 23 The adsorption capacity of the BC-PVA/GA membranes as a function of PVA concentrations compare with BC and PVA/GA membranes

The adsorption capacity of the membranes can infer the ability of a membrane to specifically absorb the liquid. The adsorption capacity of BC, BC-PVA/GA (5, 7 and 10% (w/v)) and PVA/GA membrane in both DI water and absolute ethanol (≥99.5% (v/v)) are shown in Figure 23. The adsorption capacity of BC was 1252% in water, 325% in ethanol, whereas the adsorption capacity of PVA/GA was only 345% in water, 15% in ethanol. In this study, it demonstrated the effect of PVA content in the BC-PVA/GA membranes on adsorption capacity. The BC-PVA/GA membranes prepared with 5 and 7% (w/v) PVA have higher water absorption capacity than the BC and PVA/GA membranes. However, the adsorption capacity of the BC-PVA/GA membranes in DI water decreased with increasing PVA content. On the other hand, the adsorption capacity in ethanol of the BC membrane was higher than BC-5PVA/GA, BC-7PVA/GA, BC-10PVA/GA and PVA/GA membranes, respectively. According to the results, it was shown that the absorption capacity of the membrane depends not only on its structure (porosity and crystallinity) but also on its hydrophilic/hydrophobic property. Praptowidodo (2005) studied influence swelling degree on flux and selectivity of PVA membrane. From this studied, it was found that the selectivity increased when the adsorption capacity in pure water decreased. They suggested that in swollen membrane, the distance between polymer chains increase that will promote ethanol and water pass across the membrane freely, leading to the decrease of membrane selectivity. The results from Figure 23 showed that the adsorption capacity of BC-PVA/GA membrane in water was higher than in ethanol at the same PVA concentration. This indicates that the membranes have more affinity to water, which is due to the presence of the hydrophilic BC and PVA in the composite film. Previously, it has been reported that the adsorption capacity of both BC and PVA membranes increase with increasing water content because both BC and PVA membranes are hydrophilic in nature and sorb more water than ethanol (Dubey, Saxena et al. 2002, Praptowidodo 2005). Likewise, the BC-PVA membrane is hydrophilic. It has greater affinity towards water than ethanol. The BC-PVA membrane also showed good stability in water and ethanol, therefore, it has the potential to be applied as a membrane for the pervaporation dehydration of ethanol–water.

4.1.6 Contact angle analysis

Contact angle measurements of liquid droplets on substrate surfaces are used to characterize surface wettability, surface cleanliness and the hydrophilic/ hydrophobic nature of the surface. Generally, if the water contact angle is smaller than 90^{o}, the solid surface is considered hydrophilic and if the water contact angle is larger than 90^{o}C, the solid surface is considered hydrophobic (Renate Förch 2009). In this study, we are focus hydrophilic properties of membranes for pervaporation of binary ethanol-water mixtures. The results from Table 4 showed that the contact angle of BC membrane have value was 81.13 Ө while PVA/GA was 71.56 Ө. The results of this work showed that the contact angle was decreased with an increase of PVA concentration. This indicates that the addition of PVA in BC membrane increases hydrophilic property of the membranes

Table 4 Contact angle of membranes

Membranes	Contact angle (Θ)
BC	81.13
BC-5PVA/GA	79.83
BC-7PVA/GA	73.61
BC-10PVA/GA	70.17
BC-12PVA/GA	74.27
PVA/GA	71.56

4.2 Pervaporation results

The pervaporation process combines the evaporation of volatile components of a mixture with their permeation through a polymeric membrane under reduced pressure conditions. The pervaporation performance of a membrane is assessed in terms of two important parameters, namely, the total permeation flux (J) is the mass crossing the membrane per unit area in a unit time, and the selectivity (α) towards the preferentially permeated component (Dubey, Pandey et al. 2005). The BC-PVA/GA membranes prepared in this study were hydrophilic in nature and hence, were water selective. The effect of temperature in pervaporation process was studied. The pervaporation performances of the PVA/GA membranes were investigated and compared with those of the BC membrane.

4.2.1 The effect of PVA content

Figure 24 and 25 showed the influences of PVA concentration in solution in the composites membranes on pervaporation performances at permeate pressure of 10 mmHg, 30^{o}C and feed solution of 95 wt% ethanol. Figure 24 showed that when PVA concentration in solution increased from 0, 5, 7 to 10% PVA, the total permeation decreased from 12625 to 73 g/m^{2}h, while the selectivity increased from 1.47 to 125, respectively. With increasing PVA concentration from 0 to 10% in the solution, the prepared BC-PVA/GA membranes had higher hydrophilic property; as a result, the membranes had higher affinity towards water. However, the total permeation of BC-12PVA/GA membrane increased while the selectivity decreased when compared with 10BC-PVA/GA membrane. This phenomenon can be explained the result observed from SEM images and crystallinity. Those previous results showed that BC-10PVA/GA membrane had the better structure in terms of homogeneous dispersion of PVA in BC matrix and higher crystallinity in comparison to BC-12PVA/GA membrane. The more ordered crystalline structure could lead to higher H_2O/EtOH selectivity of the membrane with a lower permeate flux rate. The experimental result showed that under a feed solution of 95 wt% ethanol aqueous solution, 30 °C and permeate pressure of 10 mmHg, BC-10PVA/GA membrane gave the highest selectivity at 125 with the total permeate flux of 73 g/m^{2}h. However, under these operating conditions, the total permeate flux of~0 g/m^{2}h was obtained by using the PVA/GA membrane. This result could be explained by the observation of very dense structure of the PVA/GA membrane in both DI water and ethanol. As previously shown in Figures 11 to 16, the PVA/GA has much more densely compacted structure as compared to BC and BC-PVA/GA membranes.

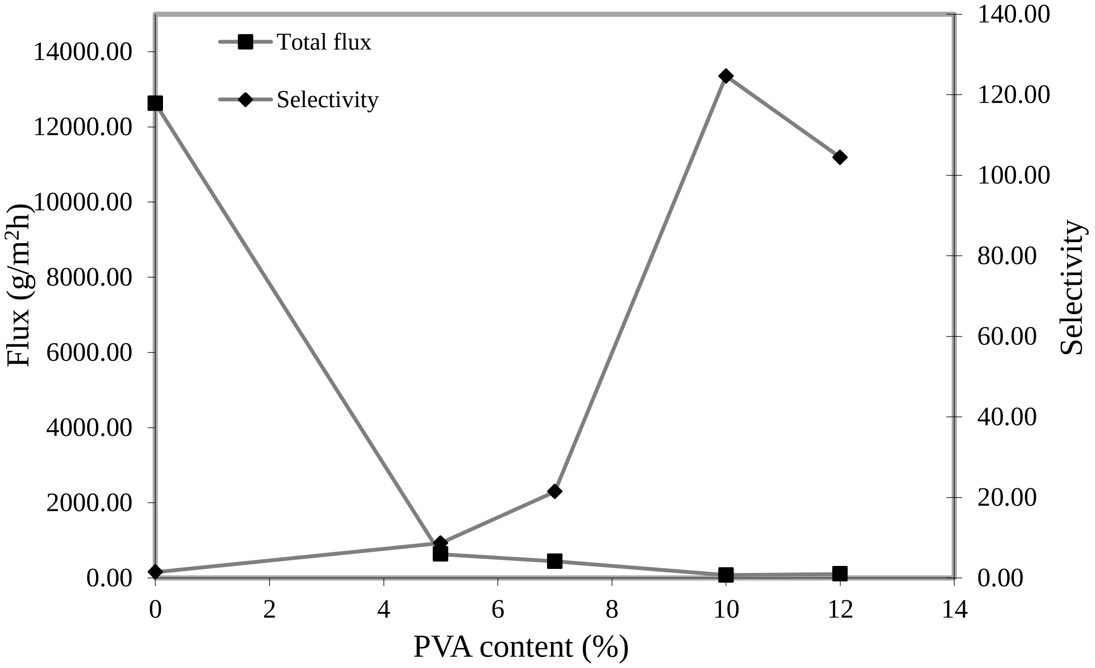


Figure 24 The effect of PVA concentration on total flux and selectivity

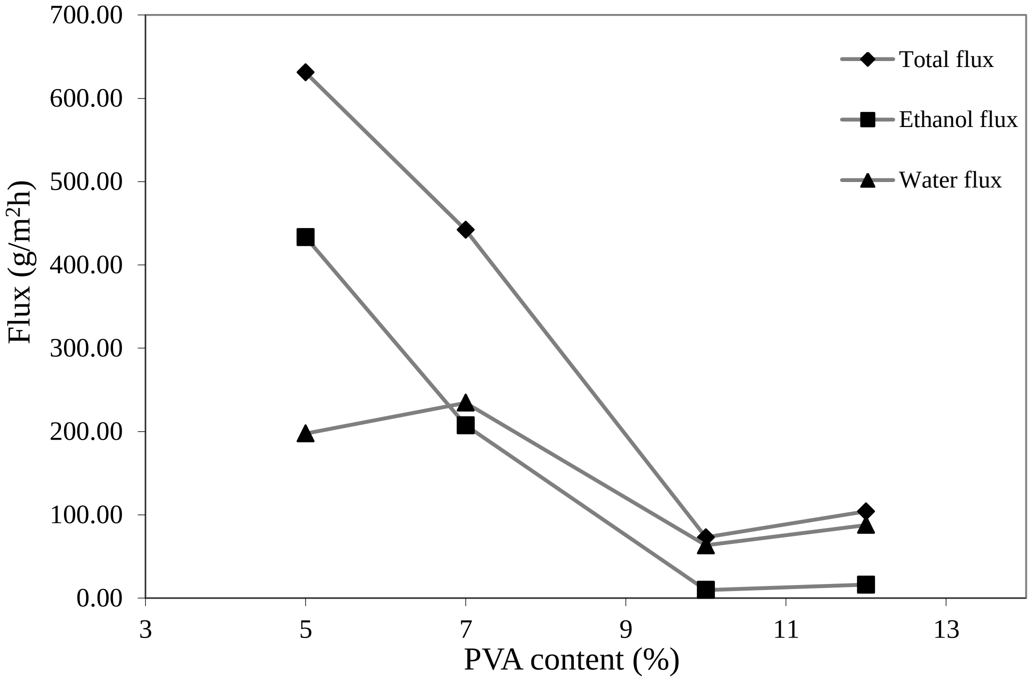


Figure 25 The effect of PVA concentration in solution on total flux, ethanol flux and water flux

4.2.2 The effect of temperature

The pervaporation process is known to be temperature dependent as both flux and selectivity are influenced by the change in temperature (Dubey, Pandey et al. 2005, Pandey, Saxena et al. 2005). As a representative study, the dependence of pervaporation of 95 wt% ethanol aqueous solution was investigated at temperatures ranging from 30 ◦C to 50◦C. The influences of feed temperature on pervaporation performances using the BC-10PVA/GA, which wet BC membranes immerse in 10% PVA solution followed by cross-linking with GA is shown in Figure 26 and 27. As expected, when temperature was increased, the total permeation flux slightly increased from 73 g/m^{2}h at 30 ◦C to 130 g/m^{2}h at 50 ◦C, while the selectivity decreased from 124.59 to 31.44. This phenomenon occurred because the temperature affected the transport of components in the liquid feed and in the membrane. Both mass transfer coefficient of components in the liquid and sorption of components into the membrane increase with increasing feed temperature Jiratananon et al., (2002). The increase in flux at higher temperature may be attributed to the increased free volume of the polymers and enhanced kinetic energy of the permeants which assists their diffusivity through the matrix of the membrane. In addition, the polymer chains were more flexible at higher temperature and caused larger available free volume of polymer matrix for diffusion. The latter effect also causes the decrease in selectivity as the diffusivity of both the permeants is enhanced. Therefore, the selectivity decreased with increasing temperature. The similar results were previously reported in the pervaporation study by BC membranes (Dubey, Pandey et al. 2005, Pandey, Saxena et al. 2005).

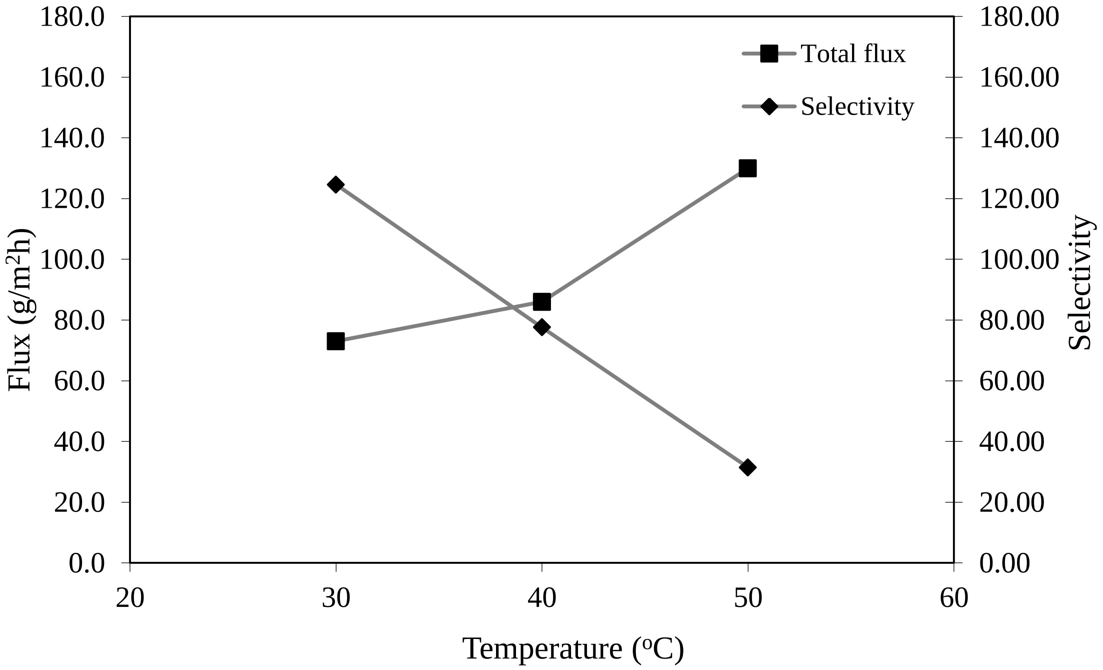


Figure 26 The effect of temperature on total flux and selectivity at 95% ethanol in feed.

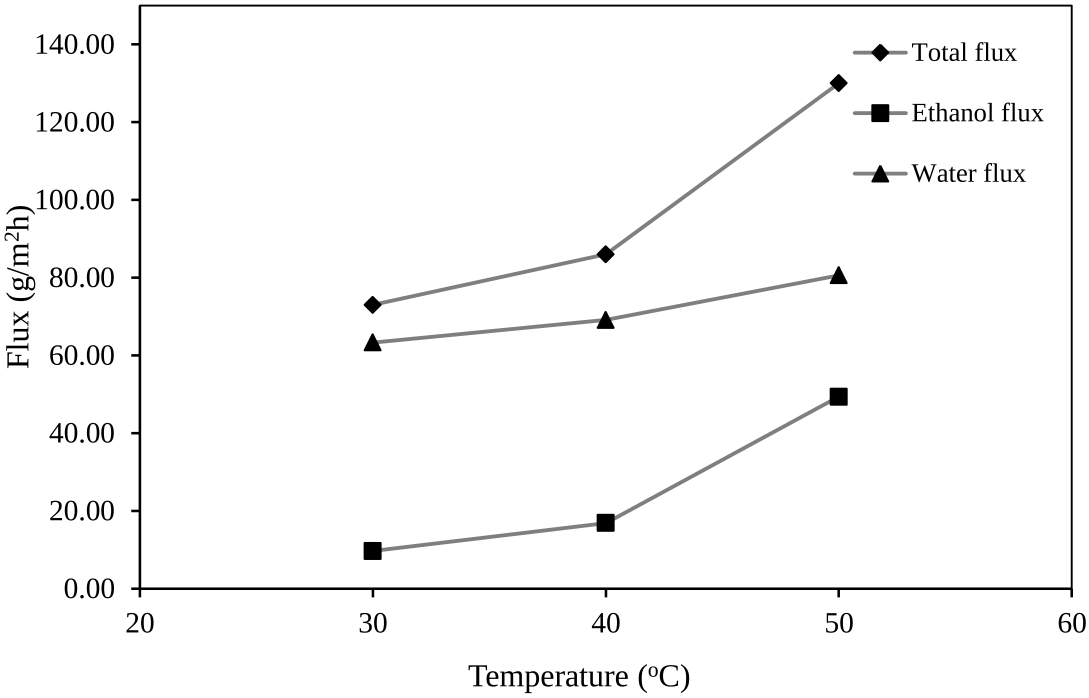


Figure 27 The effect of temperature on total flux, ethanol flux and water flux at 95% ethanol in feed

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, BC membrane was modified by immersing bacterial cellulose in poly(vinyl alcohol) solution and chemical crosslinking with glutaraldehyde solution. It indicated that this modified membrane was more hydrophilic than the unmodified BC membrane. From SEM images of surfaces morphologies, all BC-PVA/GA composite membranes had denser structures. The membrane porosity decreased with increasing PVA content. The BC membrane with 10% PVA showed good compatibility between BC and PVA. From XRD patterns, the presence of PVA has effect on the crystal structure of all BC-PVA/GA membranes. The BC-10PVA/GA had the highest crystallinity when compared with BC-PVA/GA membranes of 5, 7 and 12 % PVA. FTIR spectroscopy result indicated interactions between PVA and BC. The BC–PVA/GA composite membranes had higher elastic behavior than the BC membrane. The elongation at break of the BC-10PVA/GA membrane was more than 30 times of that of the BC membrane. The adsorption capacity of BC, BC-PVA/GA and PVA membrane in water was considerably higher than that in ethanol. This result indicates that the membranes have a higher affinity for water than ethanol.

For the BC membrane, the crystallinity, the tensile strength, Young's modulus, the elongation at break, the water adsorption capacity, the contact angle were 74.97%, 208.94 MPa, 17816.72 MPa, 1.32%, 1252% and 81.13 Ө, respectively.

For BC-PVA membrane immersing with 10% PVA concentration in solution, the crystallinity, the tensile strength, Young's modulus, the elongation at break, the water adsorption capacity, the contact angle were 45.8%, 32.29 MPa, 303.91 MPa, 32.14%, 617% and 70.17 Ө, respectively.

The study of the influences of PVA concentration in the BC-PVA/GA membranes and feed temperature on pervaporation performances was performed under a feed solution of 95 wt% ethanol aqueous solution, feed temperature at 30 °C and permeates pressure of 10 mmHg. The BC-10PVA/GA membrane gave the highest selectivity at 125 with the total permeate flux of 73 g/m^{2}h. The selectivity for water over ethanol of the BC-10PVA/GA membrane was about 83-fold of that of the BC membrane. Furthermore, in the study of the influences of feed temperature, the result showed that with the increase of the feed temperature from 30 ◦C to 50 ◦C, the permeation flux of the BC-10PVA composite membrane increased but the selectivity decreased.

5.2 Recommendations for future studies

Based on this study, further studies for improvement of bacterial cellulose film as a membrane for pervaporation seperation are recommended.

1. Modification of bacterial cellulose membrane by combining other natural polymers.

2. Modification of bacterial cellulose membrane by using surface modification of polymers.

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APPENDIX

APPENDIX A

DATA OF MEMBRANE CHARACTERIZATION

Table A1 Thickness of membrane

Membrane	Thickness (mm)
BC	0.05
BC-5PVA/GA	0.2517
BC-7PVA/GA	0.7632
BC-10PVA/GA	0.646
BC-12PVA/GA	0.31
PVA/GA	0.378

Table A2 Data of Figure 20

Membrane	Tensile strength (MPa)					Average	S.D.
	1	2	3	4	5		
BC	273.12	196.03	236.34	150.43	188.78	208.94	47.08
BC-5PVA/GA	50.70	29.09	54.82	59.13	54.23	49.59	11.85
BC-7PVA/GA	39.08	42.22	48.53	44.59	41.15	43.11	3.62
BC-10PVA/GA	33.45	29.31	31.29	34.75	32.64	32.29	2.09
BC-12PVA/GA	76.79	66.88	102.68	97.38	104.24	89.59	16.78
PVA/GA	55.31	52.76	48.42	57.07	56.58	54.03	3.56

Table A3 Data of Figure 21

Membrane	Young's Modulus (MPa)					Average	S.D.
	1	2	3	4	5		
BC	16347.69	18161.92	17789.26	18828.77	17955.98	17816.72	911.26
BC-5PVA/GA	534.46	720.79	736.48	798.26	651.16	688.23	100.64
BC-7PVA/GA	476.3	438.3	461.2	453.9	479.1	461.76	16.77
BC-10PVA/GA	309.69	259.68	275.76	359.61	314.79	303.91	38.74
BC-12PVA/GA	1916.22	2081.95	1748.53	1919.16	1793.64	1891.9	130.06
PVA/GA	42.03	38.04	33.63	43.59	31.3	37.72	5.27

Table A4 Data of Figure 22

Membrane	Elongation at break (%)					Average	S.D.
	1	2	3	4	5		
BC	1.5	1.55	1.55	0.84	1.18	1.32	0.31
BC-5PVA/GA	9	3.56	8	9.36	8.64	7.71	2.37
BC-7PVA/GA	12.9	15.38	10.66	9.82	11.44	12.04	2.18
BC-10PVA/GA	28.5	27.6	38	33.6	33	32.14	4.22
BC-12PVA/GA	5	4	6.7	5.84	6.52	5.61	1.12
PVA/GA	219.5	314	258	213.5	376	276.2	68.68

Table A5 Data of Figure 23

Membrane	The degree of swelling (%) at absolute ethanol					Average	S.D.
	1	2	3	4	5		
BC	321.31	323.08	250.94	353.7	378.43	325.49	47.90
BC-5PVA/GA	56.44	82.08	53.91	79.44	69.64	68.30	12.89
BC-7PVA/GA	51.05	42.4	44.83	34.12	46.09	43.70	6.21
BC-10PVA/GA	15.44	30.51	24.89	26.61	31.75	25.84	6.45
PVA/GA	11.63	11.09	13.17	20.27	20.25	15.28	4.61

Table A6 Data of Figure 23

Membrane	The degree of swelling (%) at pure water					Average	S.D.
	1	2	3	4	5		
BC	1259.09	1284.79	1213.73	1214.05	1289.36	1252.2	36.83
BC-5PVA/GA	2905.3	2919.65	3129.77	2885.19	2807.97	2929.58	119.92
BC-7PVA/GA	2066.33	2284.53	2129.68	2163.4	2270.81	2182.95	93.35
BC-10PVA/GA	639.13	593.05	586.85	623.38	644.07	617.3	26.2
PVA/GA	353.93	344.37	313.94	385.3	328.53	345.21	27.11

APPENDIX B

DATA OF PERVAPORATION EXPERIMENTS

Table B1 Data of Figure 24 and 25

Membrane	Selectivity	Total Flux (g/(m^{2}h))	Ethanol Flux (g/(m^{2}h))	Weter Flux (g/(m^{2}h))
BC	1.47	12625	11716	909
BC-5PVA/GA	8.63	631	433.37	197.63
BC-7PVA/GA	21.41	442	207.43	234.57
BC-10PVA/GA	124.59	73	9.69	63.31
BC-12PVA/GA	104.40	104	16.18	87.82

Table B2 Data of Figure 26 and 27

Temperature (^{o}C)	Selectivity	Total Flux (g/(m^{2}h))	Ethanol Flux (g/(m^{2}h))	Weter Flux (g/(m^{2}h))
30	124.59	73	9.69	63.31
40	77.61	86	16.86	69.14
50	31.44	130	48.87	81.13

APPENDIX C

NOMENCLATURE

Greek symbols

α = activity factor [-] β = enrichment factor [-]

i_{μ} = chemical potential of a component i [-]

Symbols

i_a = activity of a component i [-]

i_c = molar concentration of a component i [mol kg^{-1}]

i_J = membrane flux of a component i [kg m^{-2}h^{-1}]

l = membrane thickness [m]

i_L = phenomehological transport coefficient [mol s^{-1}m^{-3}]

P = permeability coefficient [mol s^{-1}m^{-2}]

R = gas constant [J mol^{-1}K^{-1}]

T = absolute temperature [K]

Subscripts

P = permeate

F = feed

Superscript

i = component

m = membrane phase

VITA

Miss Supaporn Jewprasat was born on June 1st, 1990 in Samutsakorn, Thailand. She received the Bachelor Degree of Chemical Engineering from Faculty of Engineering, King Mongkut's University of Technology Thonburi in 2013. She continued Master degree at Chulalongkorn University in June, 2013.