CHAPTER V

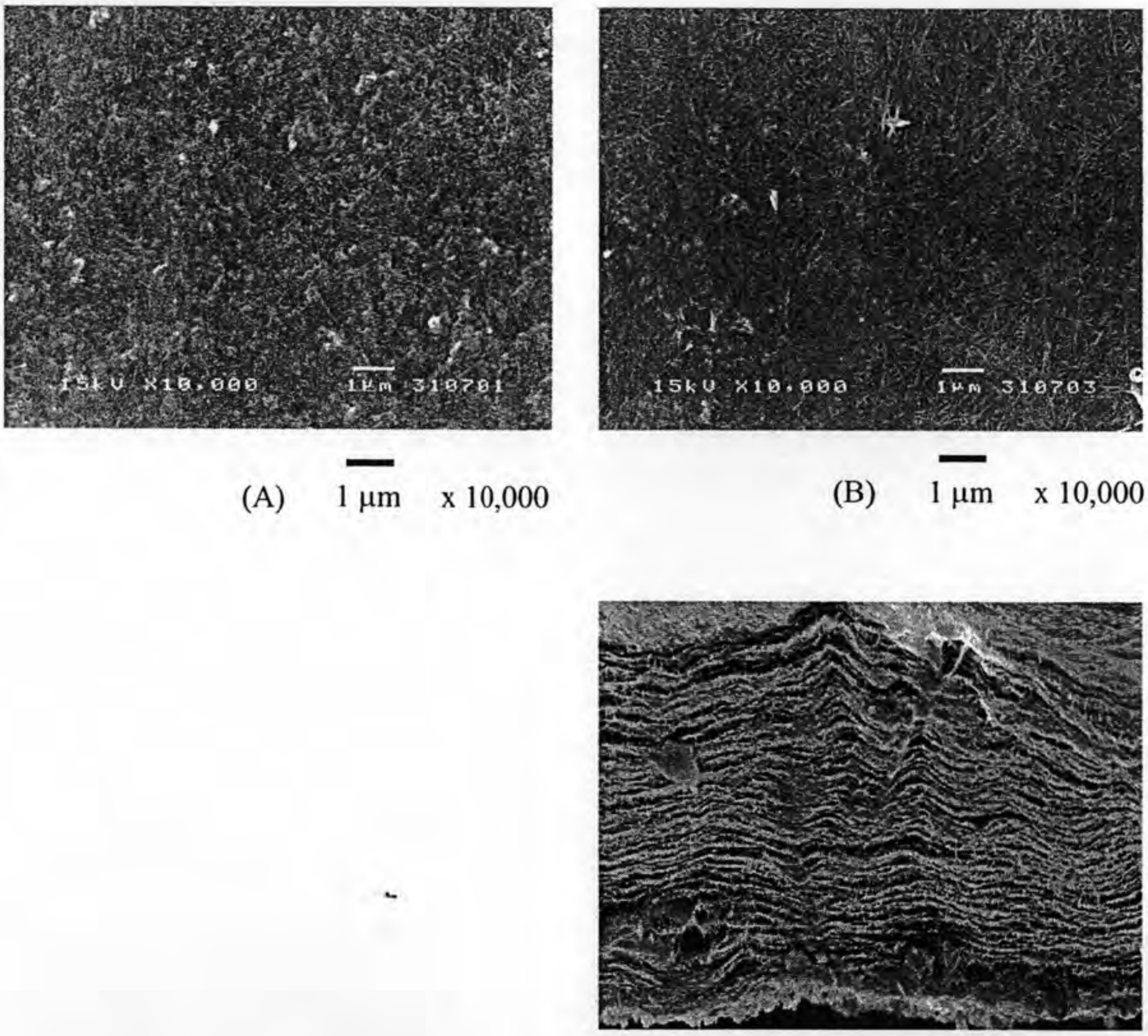
RESULTS AND DISCUSSIONS

5.1 Characterization of BC-alginate membrane

The bacterial cellulose (BC) was synthesized in the form of a pellicle on the surface of a culture medium. Due to the unique physical properties of BC and alginate, it was interesting to add alginate to BC culture medium as it might improve the physical properties of the developed BC-alginate membranes for pervaporation system. Therefore, in this work, the modification of the BC film was performed by the supplementation of alginate (0-1% w/v) during the biosynthesis by *A.xylinum*. The structure, pore morphology, tensile strength, components and chemical structure of the developed BC with the addition of alginate were then investigated and compared with the biosynthesized BC membrane without alginate supplementation.

5.1.1 Surface morphology

In this research, the surface structure of BC and BC-alginate membranes were analyzed by scanning electron microscopy (SEM). In definition, BC and BCA membrane referred to BC membrane without and with addition of alginate in culture medium, respectively. From the static culture, the analyzed SEM images of the developed films at 0%, 0.5%, 0.75% and 1% (w/v) alginate in culture medium, respectively were showed in Figures 5.1 (a) to (d). From this study, adding alginate seemed to be well-bonded into BC fibril network. In the surface of the BCA films especially, the BCA film with 1% alginate added culture medium, we observed many gel particles, which should composed of alginate. Moreover, the apparent pore size of BCA film decreased with increasing the percent of alginate.

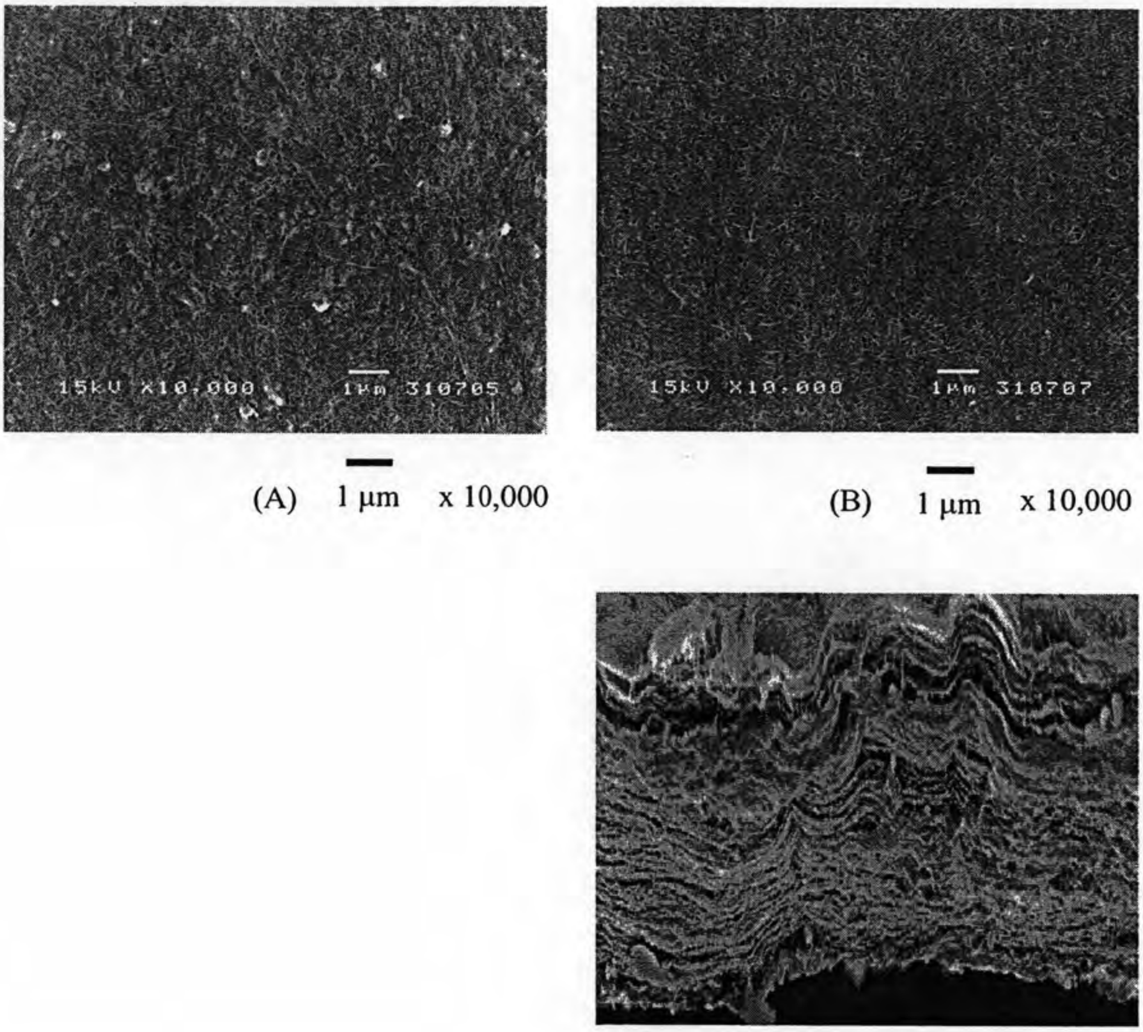


(A) 1 µm x 10,000

(B) 1 µm x 10,000

(C) 10 µm x 2,000

Figure 5.1 (a) SEM images of surface morphology of the dried films at 0% alginate supplement : (A) Top view; (B) Bottom view and (C) Cross-section

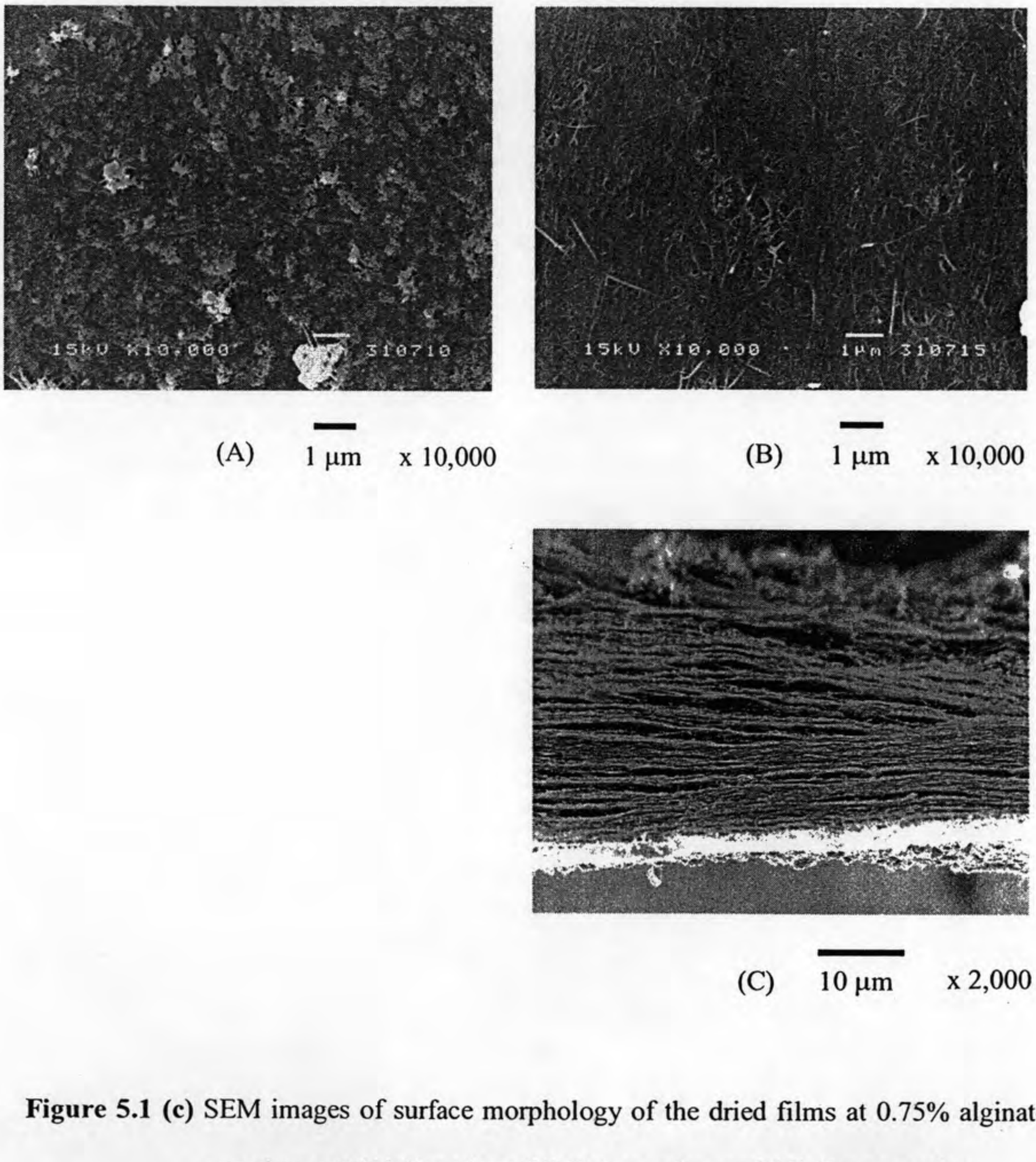


(A) 1 µm x 10,000

(B) 1 µm x 10,000

(C) 10 µm x 2,000

Figure 5.1 (b) SEM images of surface morphology of the dried films at 0.5% alginate supplement: (A) Top view; (B) Bottom view and (C) Cross-section

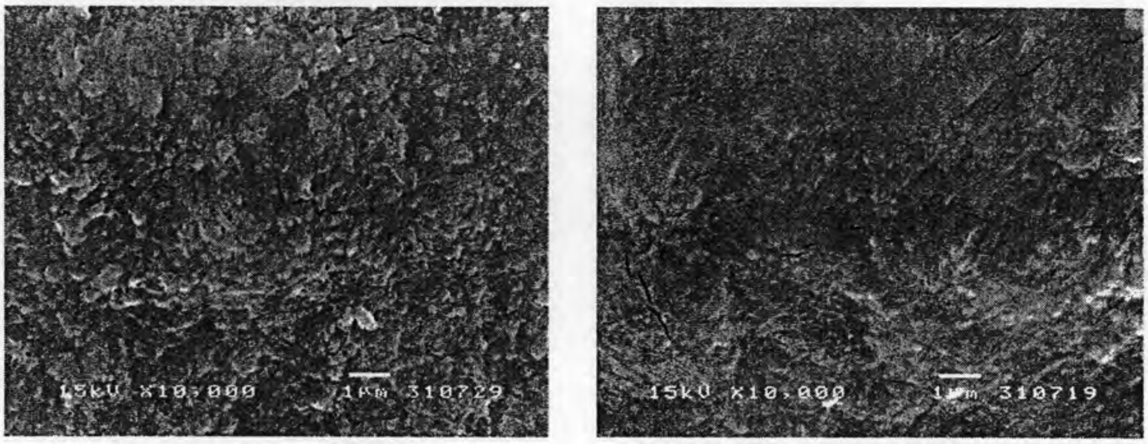


(A) 1 µm x 10,000

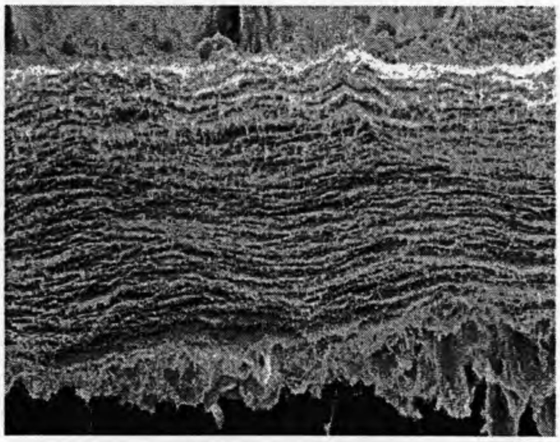
(B) 1 µm x 10,000

(C) 10 µm x 2,000

Figure 5.1 (c) SEM images of surface morphology of the dried films at 0.75% alginate supplement: (A) Top view; (B) Bottom view and (C) Cross-section



(A) 1 µm x 10,000 (B) 1 µm x 10,000



(C) 10 µm x 2,000

Figure 5.1 (d) SEM images of surface morphology of the dried films at 1% alginate supplement: (A) Top view; (B) Bottom view and (C) Cross-section

5.1.2 FTIR analysis

Fourier Transform Infrared (FTIR) spectroscopy has often been utilized as the useful tool in determining specific functional groups or chemical bonds that exist in a material (Lee et at., 1994). Therefore, in this research, the sample of BC and BCA membranes were analyzed by FTIR. The presence of peak at a specific wave number would indicate the presence of a specific chemical bound. As showed in Figure 5.2 and Figure 5.3, the FTIR spectra of the BC, BCA and alginate membranes were measured at wave number ranging from 3200-800 $cm^{-1}$and 2000-800 cm^{-1} respectively. The BC membrane showed a band at 1647 cm^{-1} as in Figure 5.2 (a), which was attributed to glucose carbonyl of cellulose. The strong band of the alginate membrane at 1613.98 cm^{-1} was assigned to the carboxyl group as showed in Figure 5.6 (e). All the characteristic bands of the BC film was present in the spectra of the BCA films. However, the carbonyl group band for BCA films [Figure 5.2 (a-d)] were shifted from 1647 cm^{-1} to 1645.63, 1645.42 and 1646.43 cm^{-1}, respectively. The difference between the absorption bands of the membranes could be attributed to the interaction between the component biopolymers. The result might imply that there were the specified intermolecular hydrogen bonds between hydroxyl group of cellulose and carboxyl group of alginate. From the previous report of alginate-cellulose blend membrane (Zhou et al., 2007), a significant change in the region of 1,472-1,548 cm^{-1} (-COO stretching vibrations) was observed, which was suggested that there were hydrogen bands between group of BC and alginate.

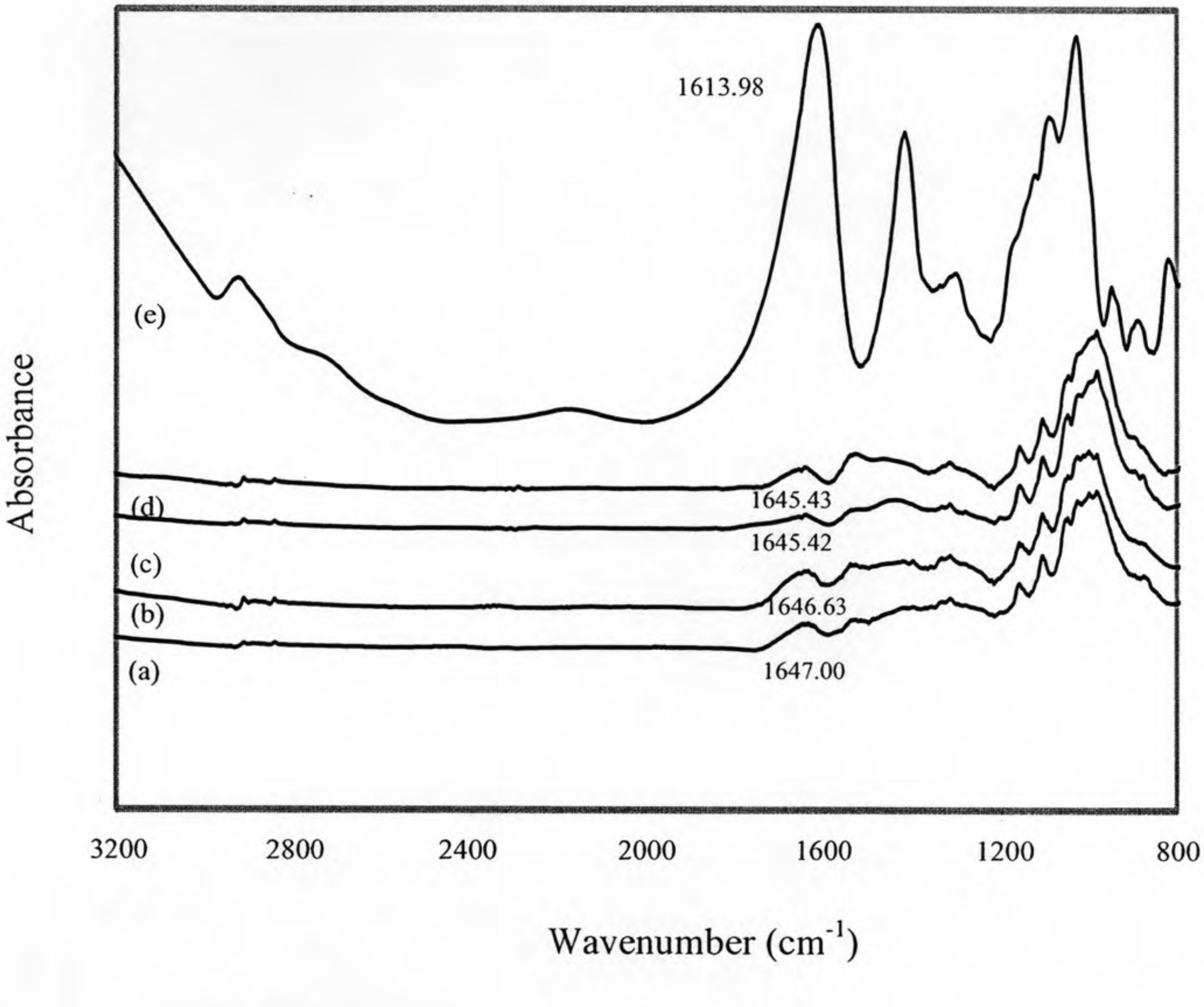


Figure 5.2 The FTIR spectra of BC and BCA membranes in wave numbers ranging from 3200 to 800 cm^{-1}: (a) BC; (b) 0.5% alginate; (c) 0.75% alginate; (d) 1% alginate and (e) alginate.

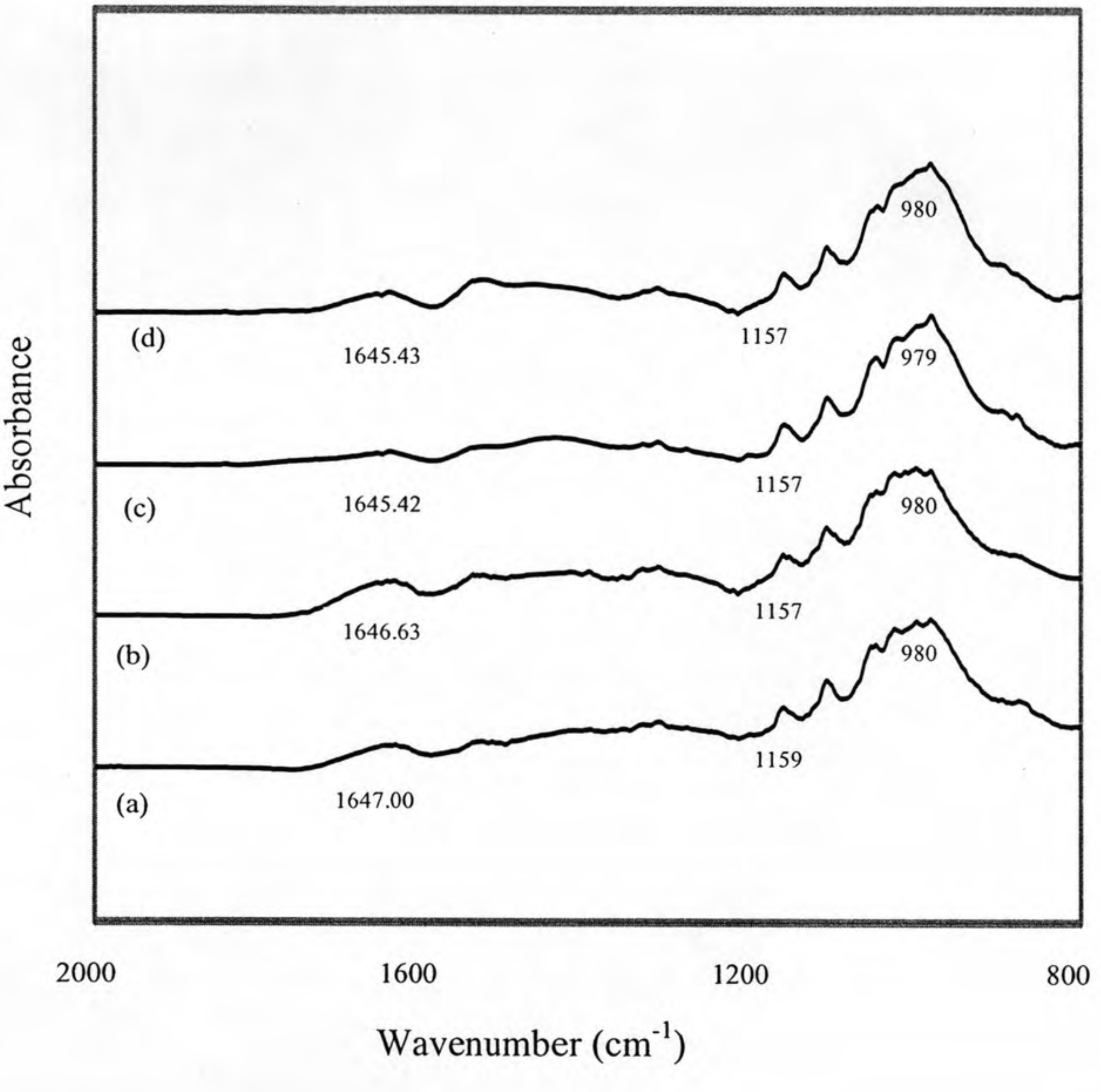


Figure 5.3 The FTIR spectra of BC and BCA membranes in wave numbers ranging from 2000 to 800 cm^{-1}: (a) BC; (b) 0.5% alginate; (c) 0.75% alginate; (d) 1% alginate and (e) alginate.

5.1.3 Mechanical properties

The mechanical properties, among all the properties of materials, are often one of the most important properties because virtually all service condition and the majority of end-use applications involve some degree of mechanical loading. Therefore, in this study, the mechanical properties such as the tensile strength, Young's modulus and elongation at break were examined.

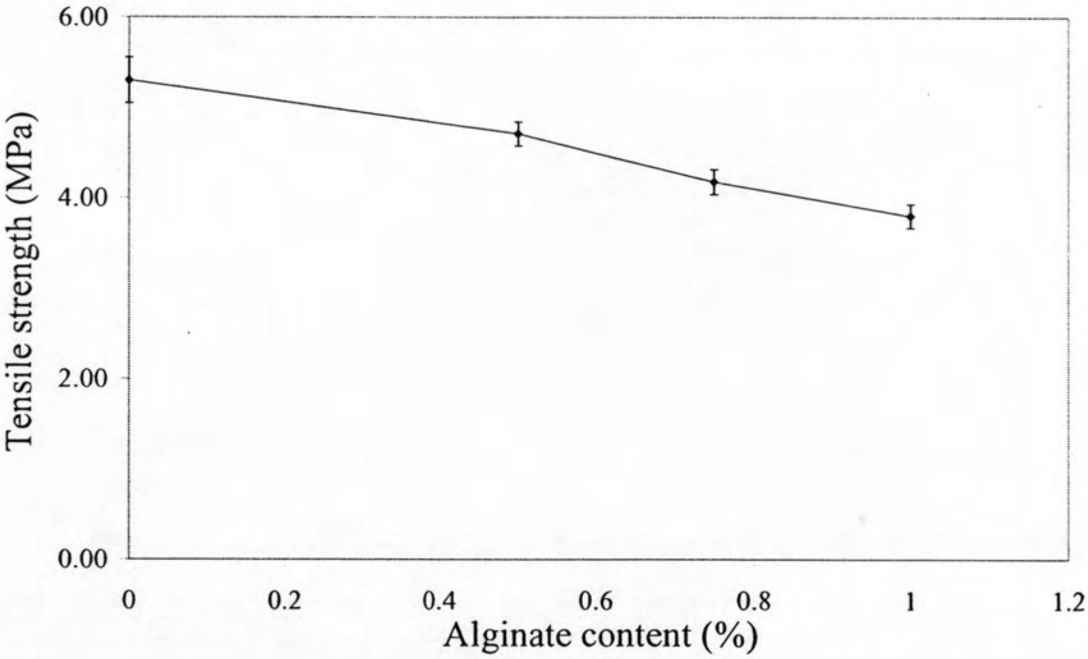


Figure 5.4 The tensile strength of the BC-alginate membranes as a function of alginate content in culture medium.

Figure 5.4 illustrated the change of tensile strength of membranes as a function of alginate content. The tensile strength of BC membrane at the average thickness of 40 μm was 5.30 MPa. The tensile strength of membranes decreased from 5.30 to 3.84 MPa when alginate content was increased from 0% to 1 %. This indicated that the decreasing of tensile strength of BC-alginate membranes depended on the amount of alginate content.

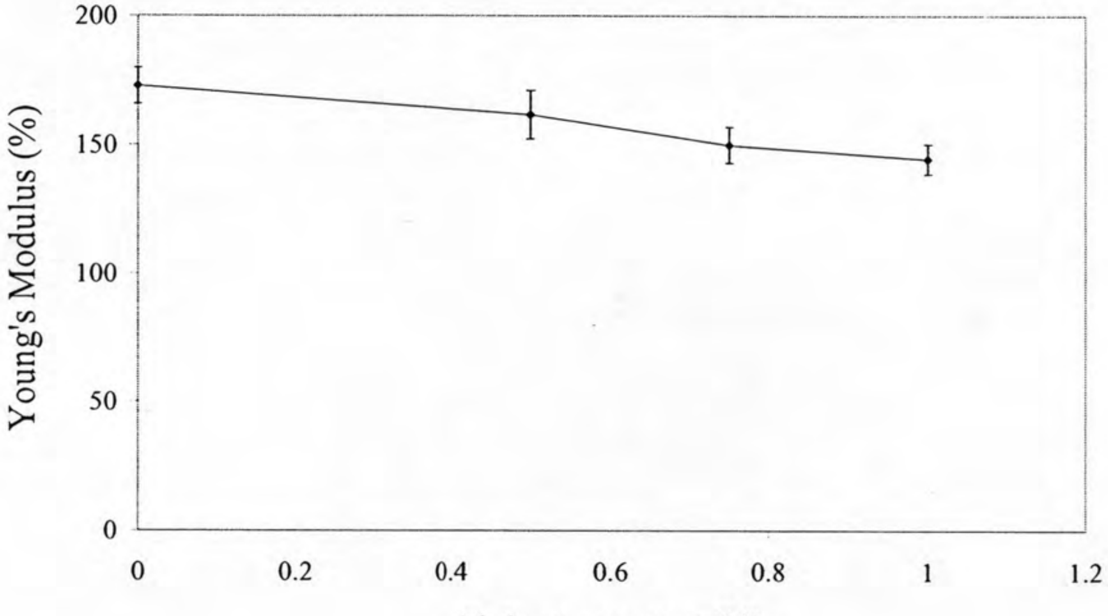


Figure 5.5 The young's modulus of the BC-alginate membranes as a function of alginate content in culture medium.

Figure 5.5 shows the change of young's modulus of the BC-alginate membranes as a function of alginate content with the average thickness of 40 μm. The young's modulus of the BC membrane was 172.8 MPa, which was the maximum observed value in the test. The minimum young's modulus was 144.4 MPa at the BCA with 1% alginate supplement. It was found that the young's modulus of the BCA membranes were lower than the BC membrane and it decreased with increasing alginate content.

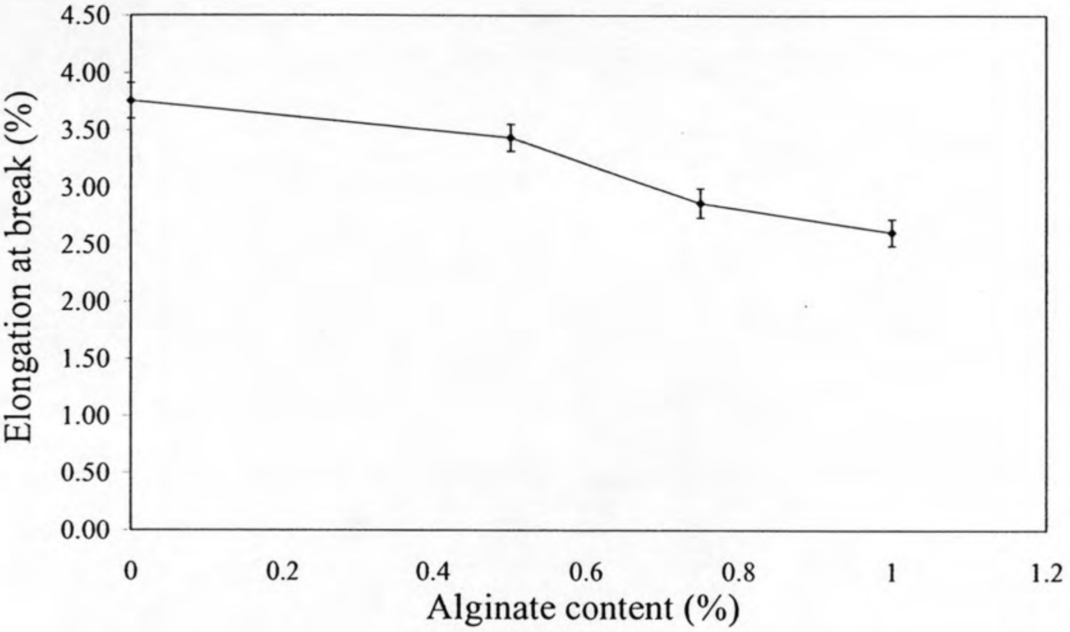


Figure 5.6 The Elongation at break of the BC-alginate membranes as a function of alginate content in culture medium.

Figure 5.6 illustrated the change of elongation at break of membranes as a function of alginate content. The elongation at break of BC membrane at the average thickness of 40 μm was 3.76%. The elongation at break of BCA membrane at 1%

alginate was 2.61% and it was found that the elongation at break also decreased when increasing the alginate content in the similar way as it was observed previously on the tensile strength and young's modulus.

The effect of alginate content on mechanical properties of the bacterial cellulose/alginate membranes was similar to that of cotton cellulose alginate blend membranes. Zhang et al. (1997) prepared the ion exchange blend membranes of cotton cellulose and alginate. They found that the mechanical properties of blend membranes decreased with increasing alginate content. The similar result was reported in the study of cotton cellulose/alginate blend membrane from the solution of NaOH/urea solvent (Zhou et al., 2001). Although the alginate membrane and its blend membranes were mechanically weak, they showed promising performance for the pervaporation dehydration (Yang et al., 2000).

5.1.4 Porosity

BET is one of the most widely used for finding the surface area of material by physical adsorption of gas molecules (Brunauer et al., 1938). Surface area and porosity are important characteristics, capable of affecting the quality and utility of many materials. The result data from BET analysis were summarized in Table 5.1.

Table 5.1 Surface area and pore diameter of the BC and BCA analyzed by BET analyze

Alginate content (%)	Average Pore diameter (Å)	Surface area (m^2/g)
0	224	12.6
0.5	97	12.1
0.75	64	11.8
1	39	11.2

The result data showed that the BCA membranes had the average pore size much less than that of the BC membrane (Sanchavanakit et al., 2006) and the average pore diameter of membranes decreased with increasing alginate content; whereas, the surface area slightly decreased. The similar result was reported in the study of bacterial cellulose/alginate film developed by blending in an aqueous NaOH/urea solution (Phisalaphong et al., 2008).

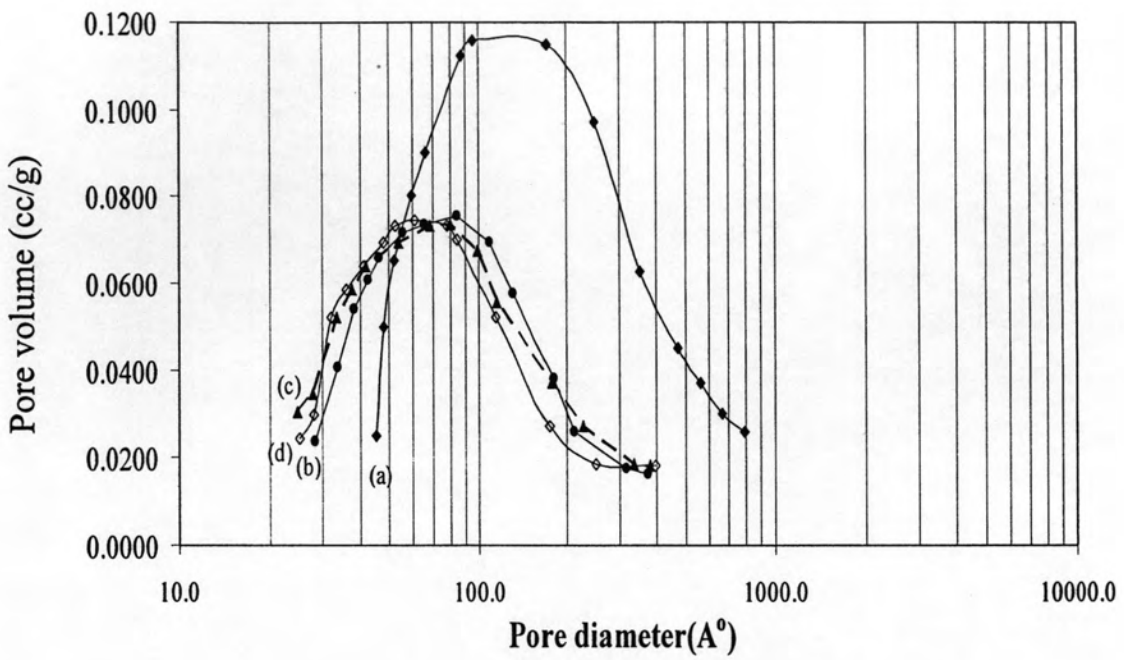


Figure 5.6 The typical pore size distribution of BC and BCA membranes; (a) BC; (b) 0.5% alginate; (c) 0.75% alginate and (d) 1% alginate

5.1.5 The degree of swelling

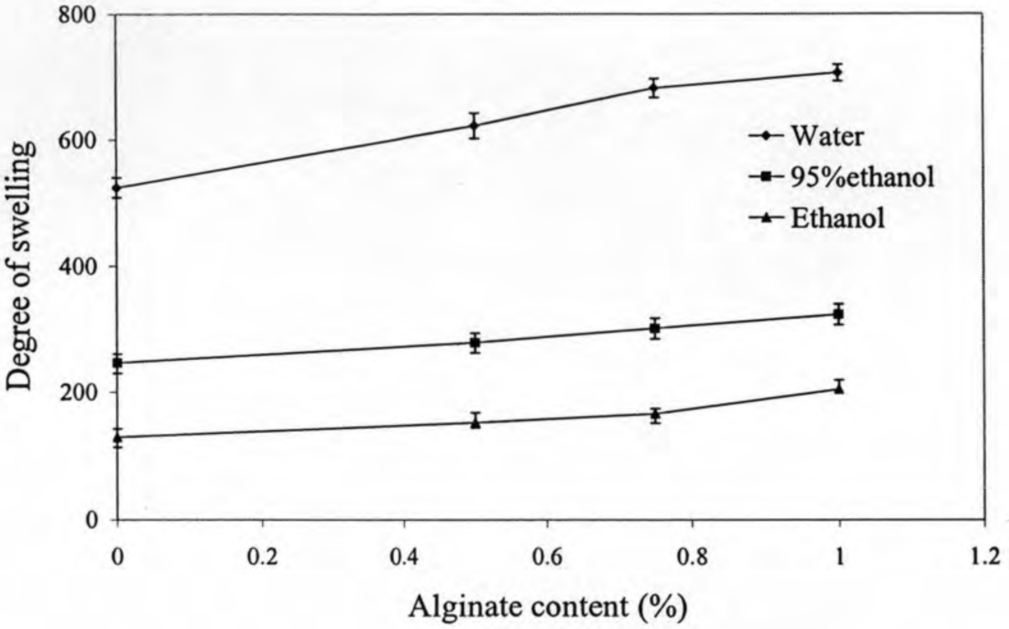


Figure 5.8 The degree of swelling of the BC-alginate membranes as a function of alginate content in culture medium.

From Figure 5.8, the degree of swelling of BC was 542% in water, 129% in ethanol; the degree of swelling of BCA membrane at 1% alginate was 706% in water, 205% in ethanol. It was found that degree of swelling increased when increasing the alginate content. Lee et al. (1997) suggested that the water molecules were easily sorbed into the alginate membrane due to its high hydrophilic property.

The results from Figure 5.8 showed that the degree of swelling of membrane in water was higher than that in ethanol at the same alginate content. Dubey et al. (2002)

and Kalyani et al. (2008) studied the degree of swelling of BC and alginate membrane respectively. They found that the degree of swelling of both BC and alginate membrane also increased with increasing water content because both BC and alginate membrane were hydrophilic in nature and sorbed more water than ethanol. Likewise, the BCA membrane was hydrophilic. It had greater affinity towards water than ethanol. Therefore, it should be suitable to apply on a pervaporation membrane for dehydration of ethanol-water mixtures.

5.1.6 Water vapor permeability test (WVTR)

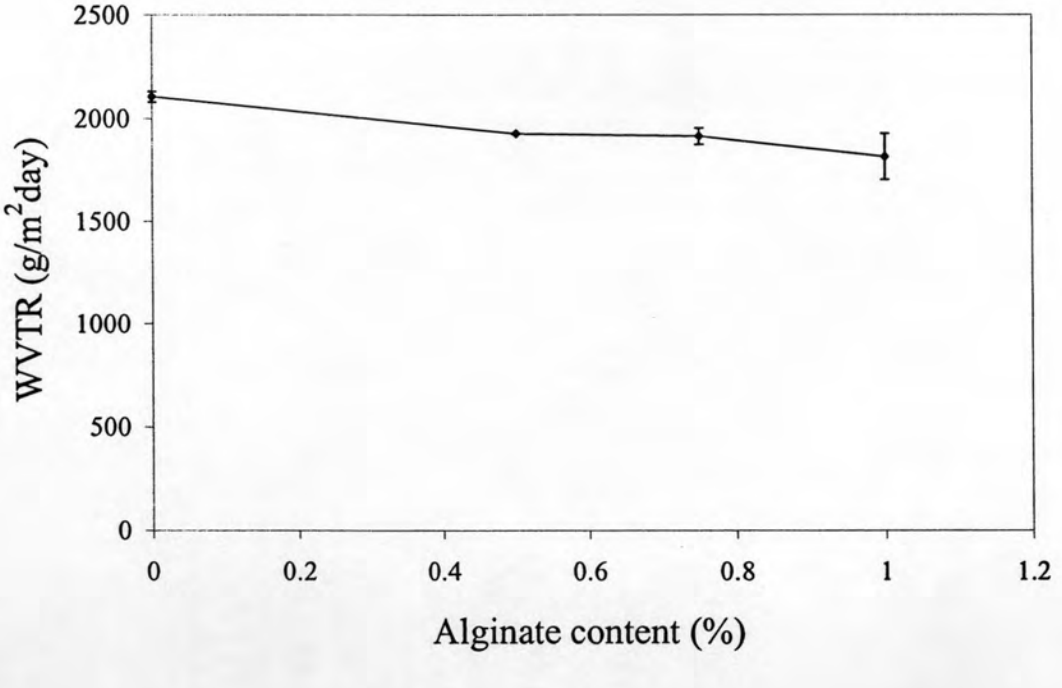


Figure 5.9 The water vapor transmission rate of the BC-alginate membranes as a function of alginate content in culture medium.

From the previous result, the degree of swelling increased with increasing alginate content. On the other hand, the water vapor transmission rate (WVTR) slightly decreased when increasing alginate content as can be seen from Figure 5.9. Owing to the denser structure of the films when increasing alginate content, water vapor should be more difficult to diffuse though the denser membrane. Therefore, the WVTR in the BCA membrane was decreased even though the degree of swelling (sorption) increased.

5.1.7 Oxygen permeability test (OTR)

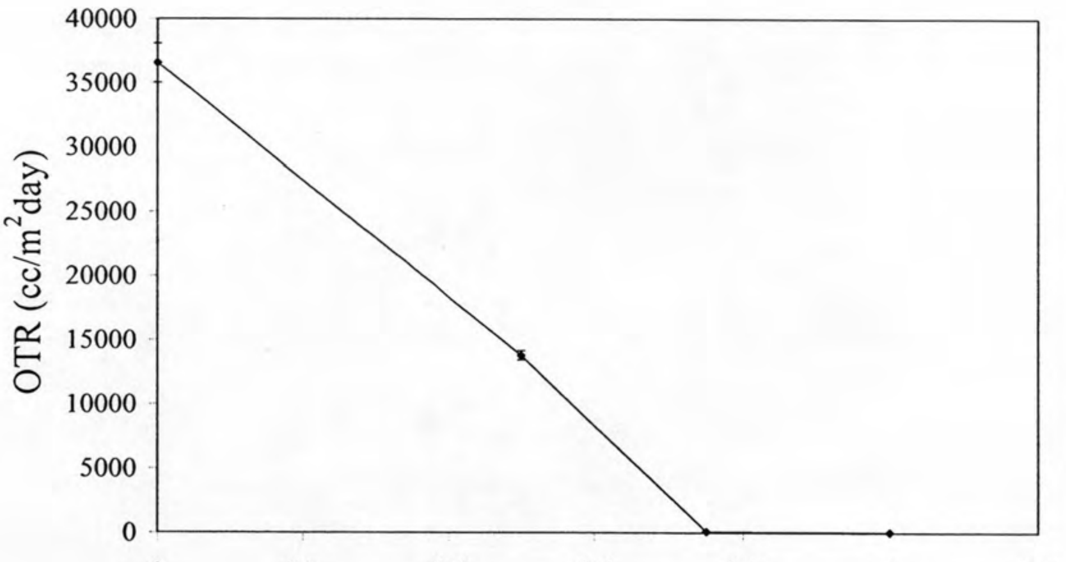


Figure 5.10 The oxygen transmission rate of the BC-alginate membranes as a function of alginate content in culture medium.

Figure 5.10 showed the results of the oxygen transmission rate (OTR) of the BC and BCA membranes. As alginate content increased, the OTR was highly decreased. The similar reason as it was reported previously on the WVTR test could explain this phenomenon. Besides that, it was observed that the OTR decreased in a larger amount in comparison to the WVTR. Since oxygen molecule was larger than water molecule, the denser and hydrophilic structure could cause a greater reduction in diffusivity through the membrane. With the supplement of 0.75-1.0% alginate in the culture medium, the OTR of BCA membrane was less than 110 cc/m^{2}day.

5.2 Pervaporation results

In pervaporation experiments, membrane performance was studied in terms of flux and selectivity. The BC-alginate membranes prepared in this study, were hydrophilic in nature and hence, were water selective. The effect of alginate content, feed concentration, temperature, membrane thickness and permeate pressure were studied.

5.2.1 The effect of alginate content

Figure 5.11 (a) and (b) showed the influences of alginate content in membranes on pervaporation performances at 40 μm of membrane thickness, 10 mmHg, 30°C and azeotropic feed composition. It was found that as alginate content increased, the flux decreased in the similar way as it was observed previously on the WVTR result. However, the selectivity increased when increasing alginate content. Since the BCA membrane had greater affinity towards water than ethanol and it was higher hydrophilic when increasing alginate content. Therefore, the selectivity of the membrane increased with increasing alginate content.

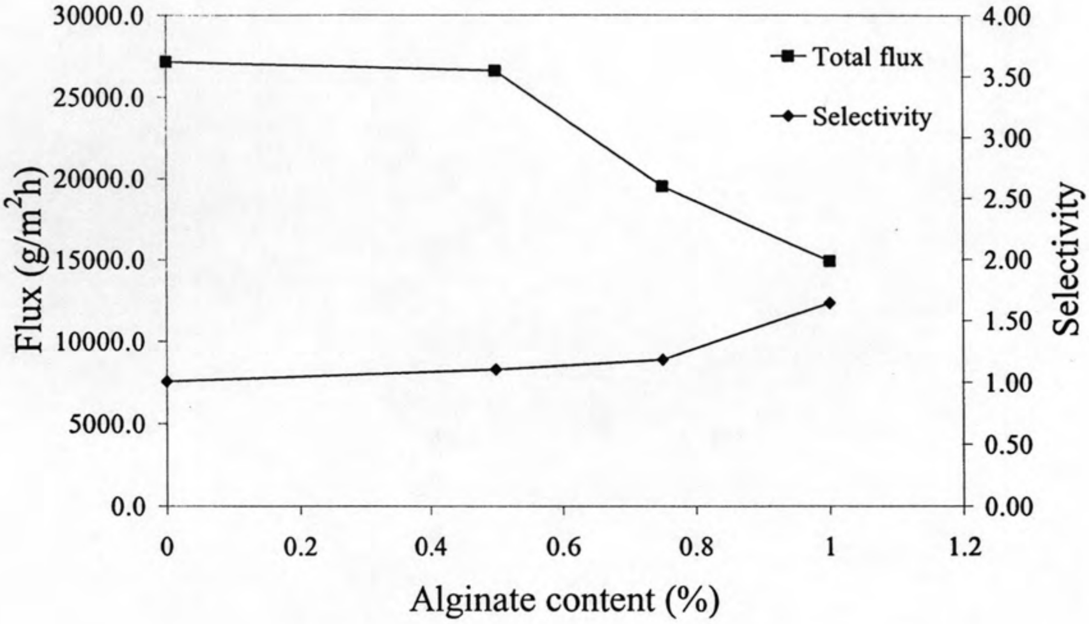


Figure 5.11 (a) The effect of alginate content on total flux and selectivity.

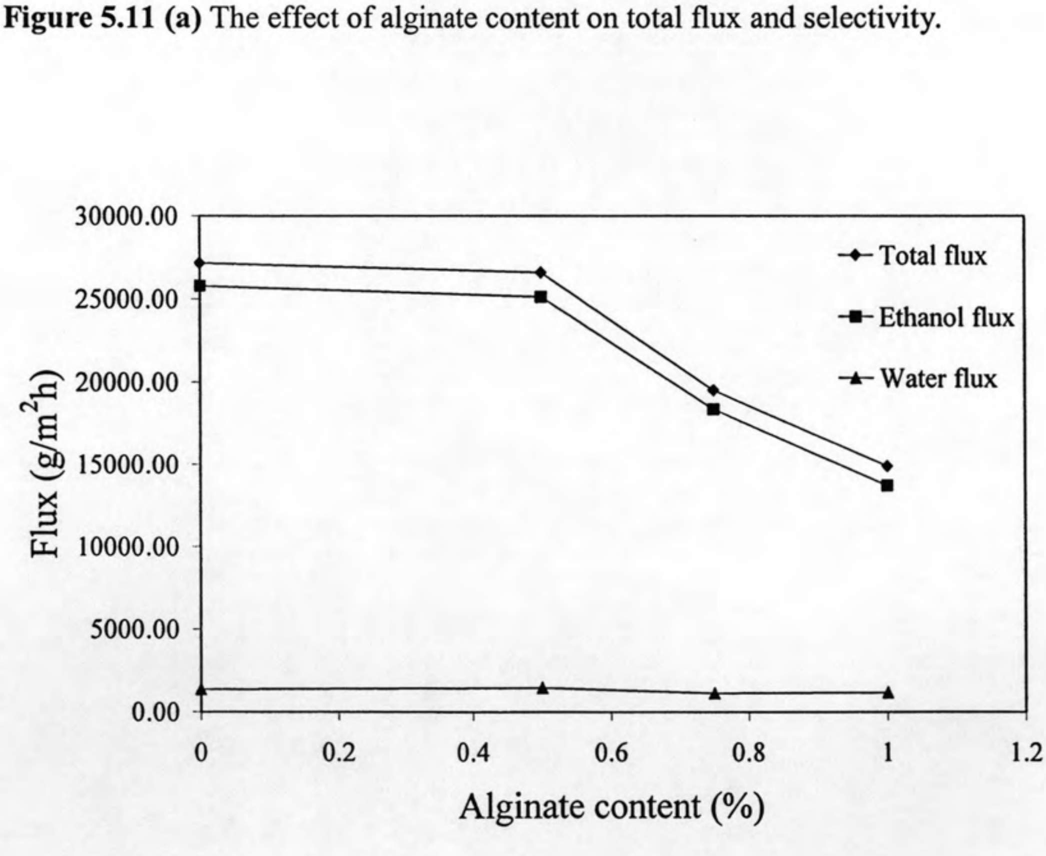


Figure 5.11 (b) The effect of alginate content on total flux, ethanol flux and water flux.

5.2.2 The effect of feed concentration

The effect of ethanol content in feed using the 1%alginate BCA membrane, 40 μm of membrane thickness, 10 mmHg and 30°C of temperature was showed in Figure 5.12 (a) and (b). It was found that when ethanol content in the feed under 80% (v/v), the flux increased when decreasing the ethanol content (increasing water content) while selectivity decreased. This phenomenon might be due to swelling effect of water. As the water content in feed increased, the membrane swelled and the polymer chains become more flexible, allowing more ethanol molecules passed through, thus increasing flux while decreasing selectivity (Dubey et al., 2002). When the content of ethanol exceeded 80% (v/v), the flux and selectivity decreased when increasing the ethanol content, a reversal in the phenomenon of selectivity might be attributed to flow coupling between water and ethanol.

From this result, it found that the selectivity of BCA membrane at excess 80% (v/v) did not follow the typical trade-off phenomenon which has been widely used to explain the low flux and high selectivity in pervaporation experiments. The similar result was reported in the study of pervaporation of aqueous ethanol mixtures through alginate/chitosan composite membrane (Huang et al., 2000). They suggested that this phenomenon was not necessarily found for all kind of membrane but generally observed for membrane which polar interaction is not so strong.

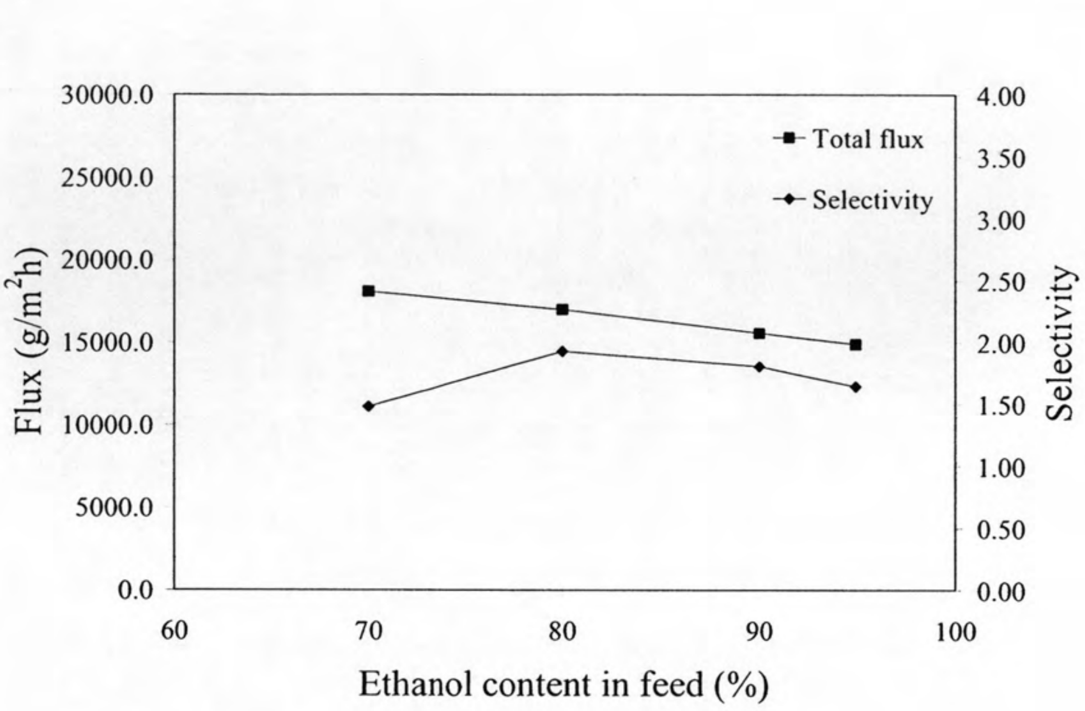


Figure 5.12 (a) The effect of ethanol content in feed on total flux and selectivity.

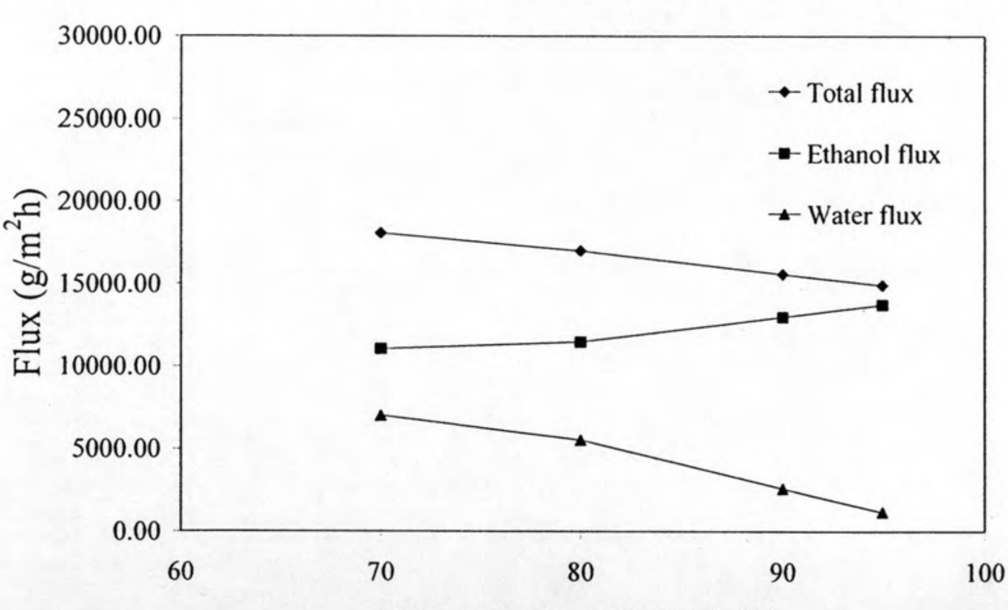


Figure 5.12 (b) The effect of ethanol content in feed on total flux, ethanol flux and water flux.

5.2.3 The effect of temperature

The influences of feed temperature on pervaporation performances using the 1%alginate BCA membrane and 40 μm of membrane thickness were given in Figure 5.13 (a) to (f). As expected, when temperature was increased, the total permeation flux slightly increased, while the selectivity decreased. Jiratananon et al., (2002) suggested that 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. In addition, the polymer chains were more flexible at higher temperature and caused larger available free volume of polymer matrix for diffusion. Therefore, the selectivity decreased with increasing temperature. The similar formation was previously reported in the studied pervaporation of bacterial cellulose membrane (Dubey et al., 2005 and Pandey et al., 2005).

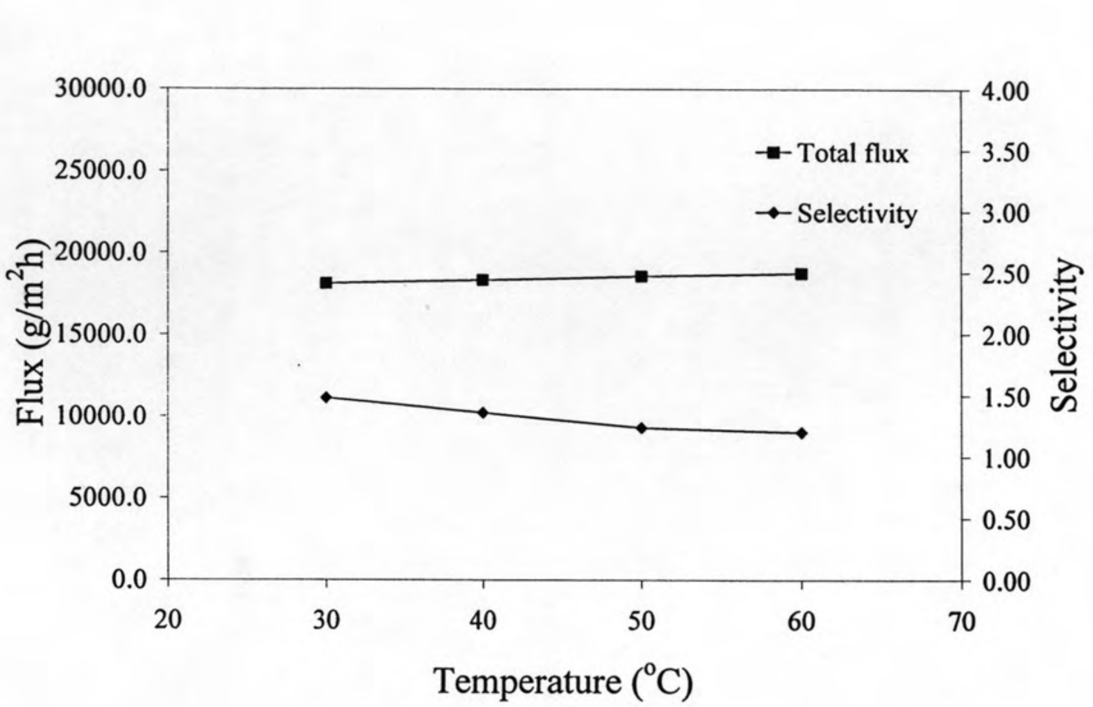


Figure 5.13 (a) The effect of temperature on total flux and selectivity at 70% ethanol in feed.

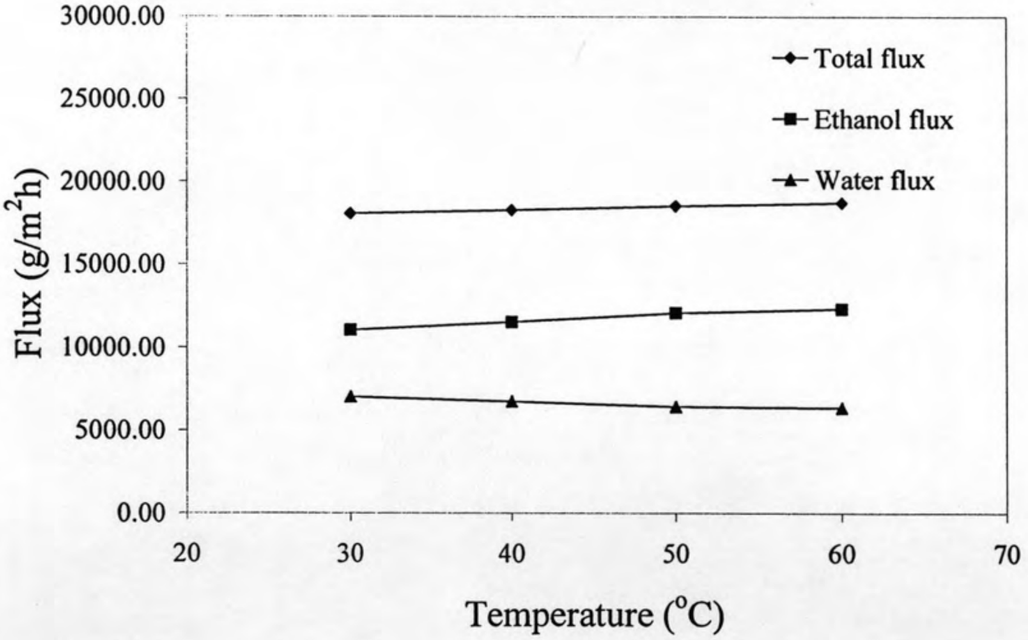


Figure 5.13 (b) The effect of temperature on total flux, ethanol flux and water flux at 70% ethanol in feed.

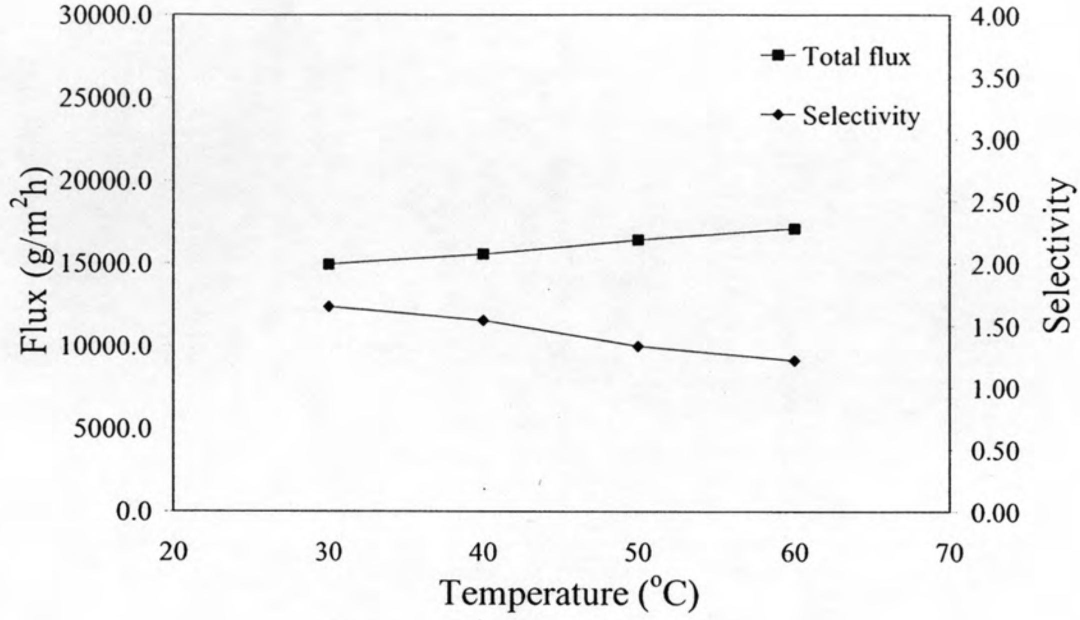


Figure 5.13 (c) The effect of temperature on total flux and selectivity at 90% ethanol in feed.

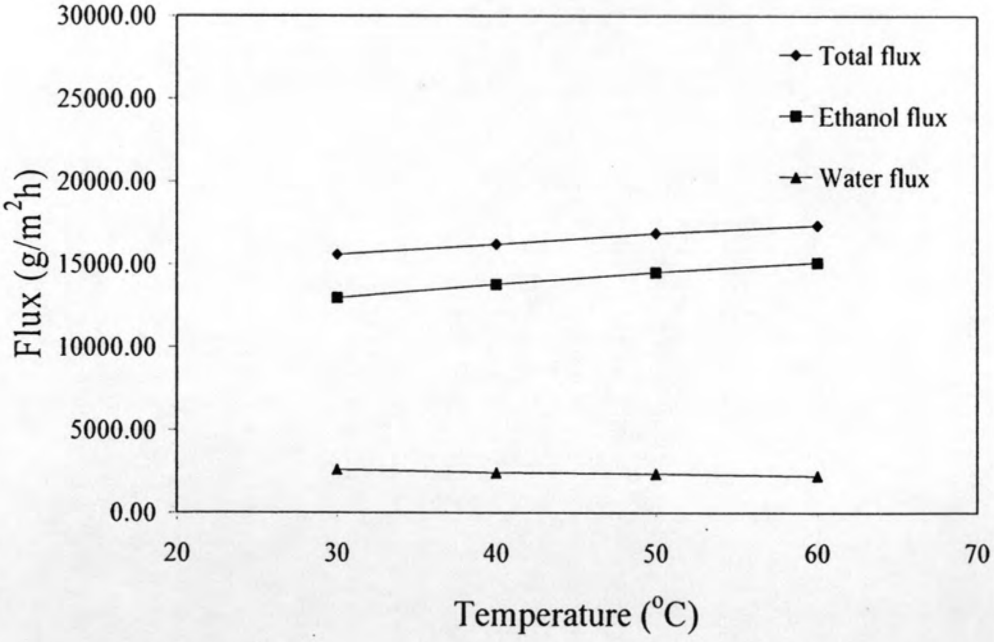


Figure 5.13 (d) The effect of temperature on total flux, ethanol flux and water flux at 90% ethanol in feed.

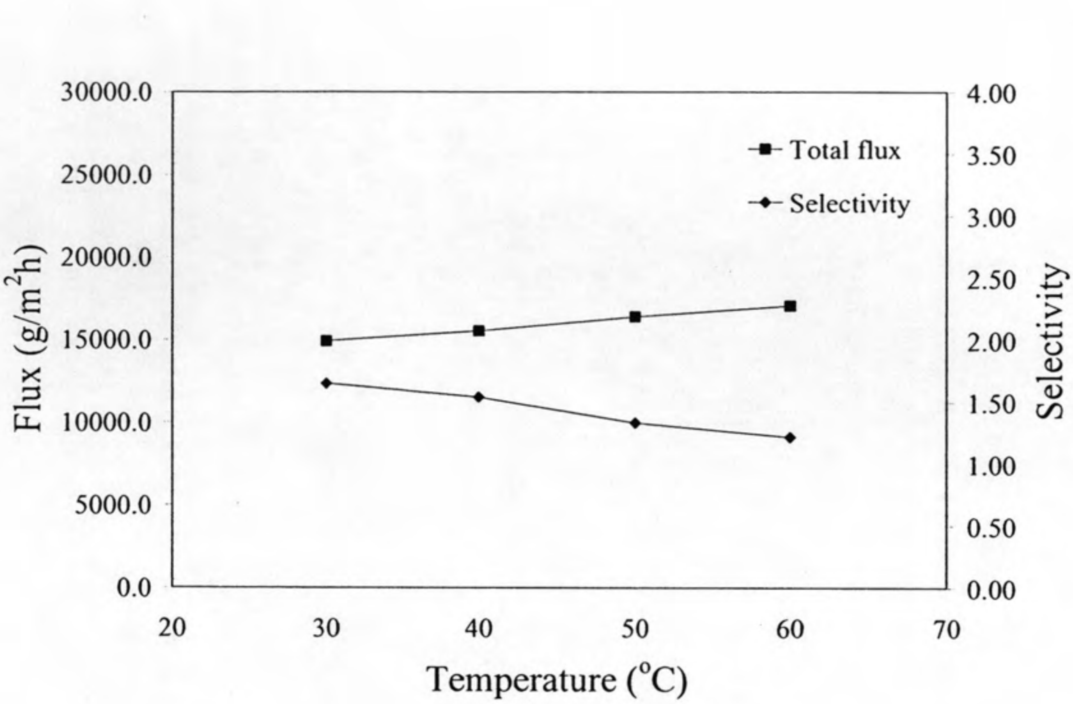


Figure 5.13 (e) The effect of temperature on total flux and selectivity at 95% ethanol in feed.

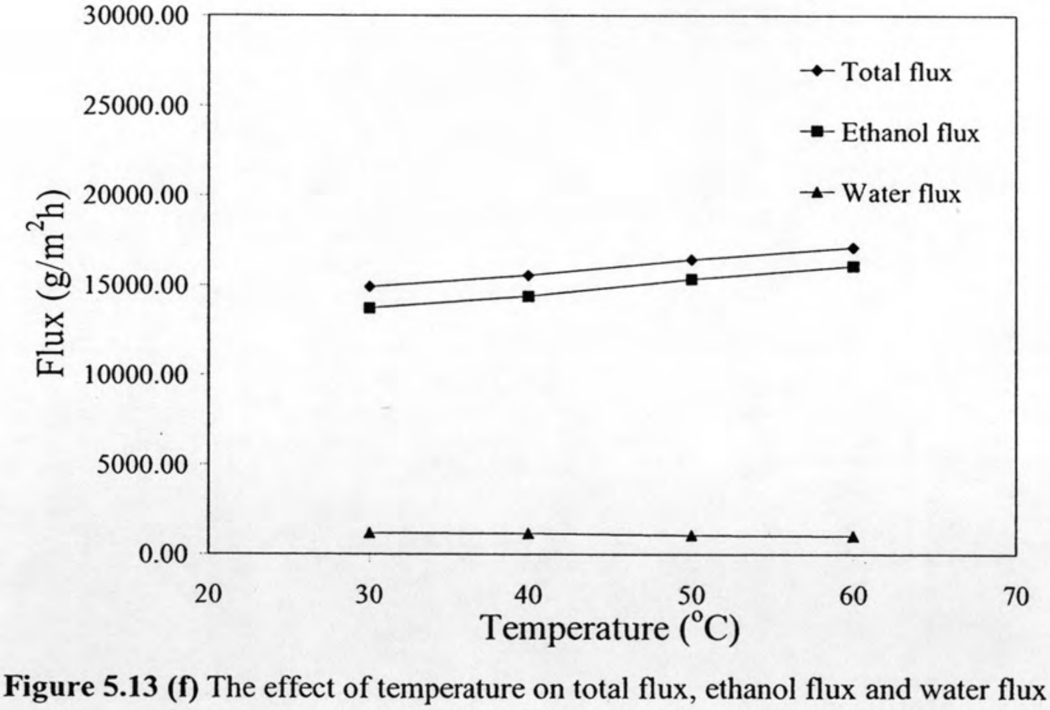


Figure 5.13 (f) The effect of temperature on total flux, ethanol flux and water flux at 95% ethanol in feed.

5.2.4 The effect of permeate pressure

The permeate pressure was varied from 5 to 10 mmHg to study the permeation characteristics using the 1%alginate BCA membrane, 40 μm of membrane thickness and azeotropic feed composition. From Figure 5.14 (a), both total flux and selectivity decreased with increasing permeate pressure. This phenomenon was suggested by Jiratananon et al., (2002) that with the increase of permeate pressure, there was a reduction of driving force for transport of components. However, From Figure 5.14 (b), the decrease of water flux was larger than that of ethanol. Since the saturated vapor pressure of water was lower than that of ethanol, an increase of permeate pressure slowed down more evaporation of water. This result was similar to the previous reports in the studied pervaporation separation of ethanol-water mixtures through sodium alginate membranes (Kalyani et al., 2008) and Chitosan/alginate membrane (Kanti et al., 2004).

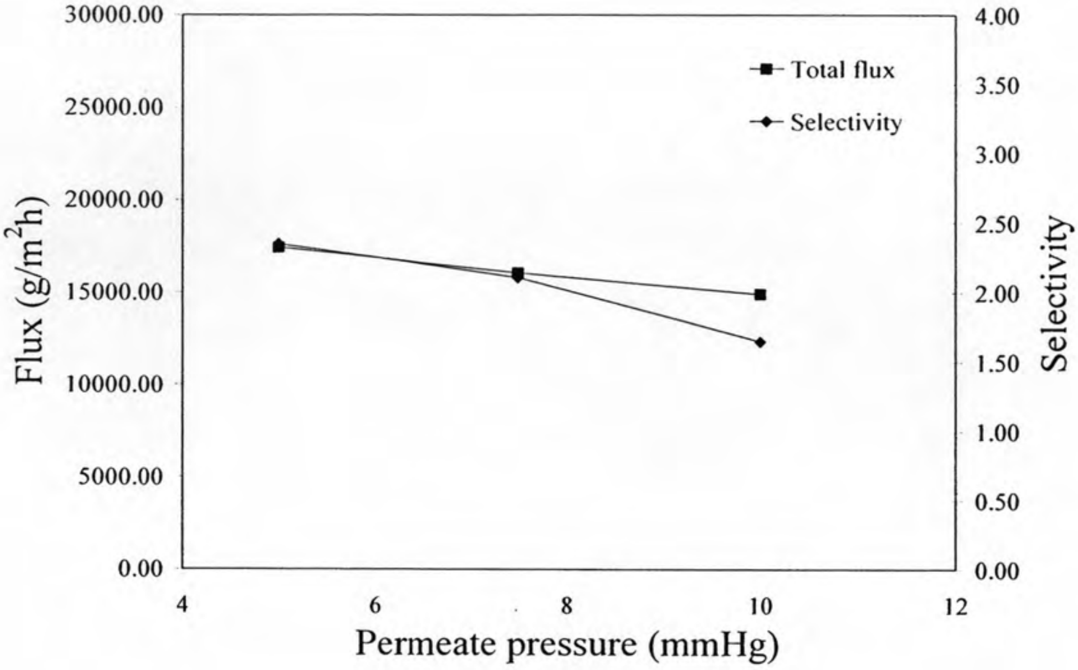


Figure 5.14 (a) The effect of permeate pressure on total flux and selectivity.

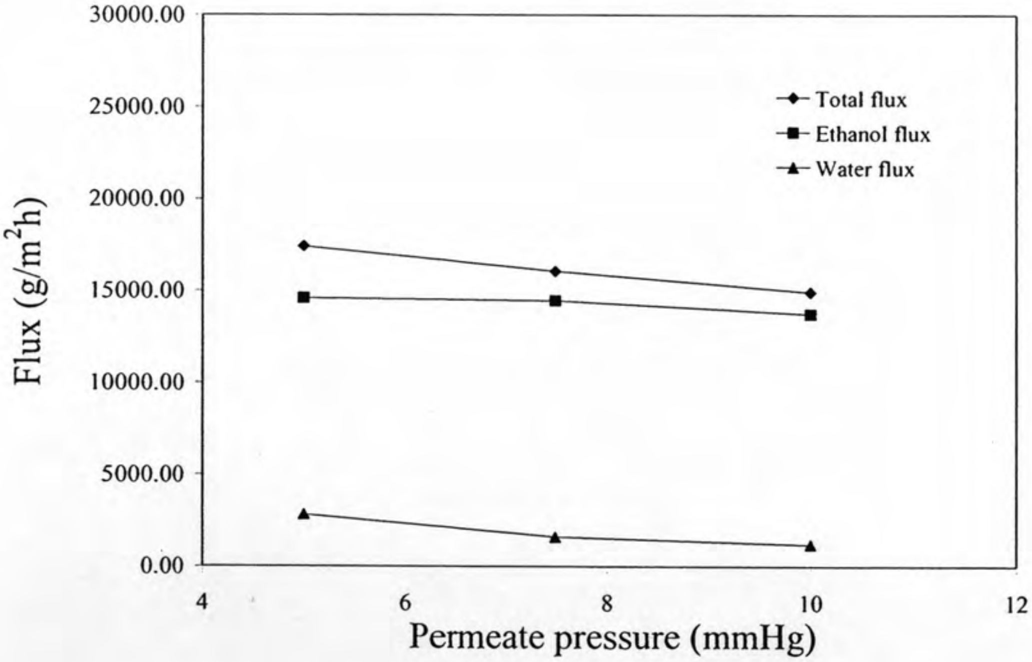


Figure 5.14 (b) The effect of permeate pressure on total flux, ethanol flux and water flux.

5.2.5 The effect of membrane thickness

The effect of varying membrane thickness was studied by using synthesized membranes of different thickness. Membranes thickness of 40, 60 and 90 μm were prepared and subjected to pervaporation at azeotropic feed composition. Figure 5.15 (a) and (b) showed the effect of membrane thickness with other operating parameters kept constant using the 1%alginate BCA membrane, 10 mmHg, 30°C and azeotropic feed composition. The total flux and ethanol flux was decreased, whereas the water flux was slightly increased with the increase of membrane thickness. The selectivity, therefore, increased with increasing membrane thickness. Kanti et al., (2004) suggested that in pervaporation, diffusion was the rate determining step which decreased with increasing membrane thickness causing a subsequent reduction in flux. For selectivity, the upstream layer of membrane was swollen due to absorption of feed liquid and allowed unrestricted transport of feed components. In contrast, the downstream layer was virtually dry due to continuous evacuation in the permeate side; therefore, this layer formed the restrictive barrier which allowed only certain species to pass through. It was expected that thickness of the dry layer would increase with increase overall membrane thickness resulting increased selectivity.

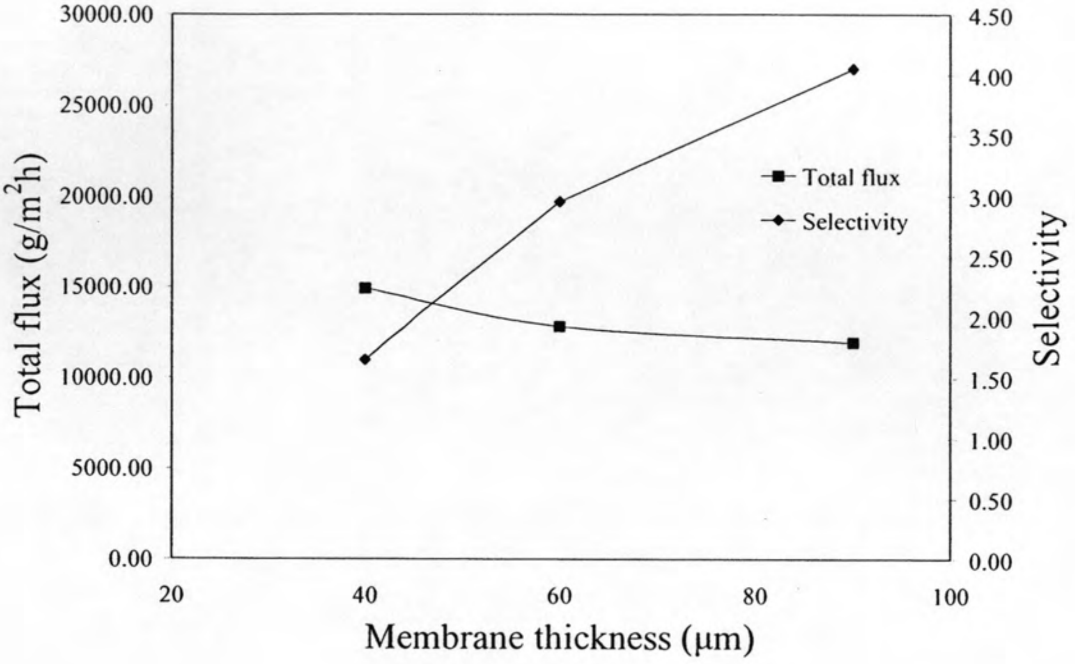


Figure 5.15 (a) The effect of membrane thickness on total flux and selectivity.

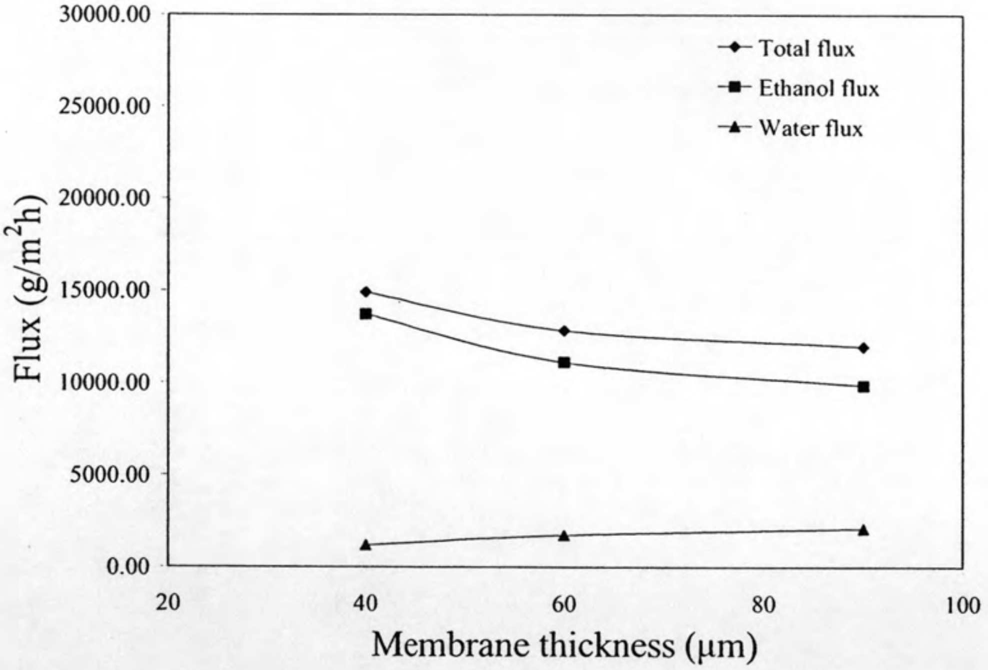


Figure 5.15 (b) The effect of membrane thickness on total flux, ethanol flux and water flux.