CHAPTER IV

Preparation of Bacterial Cellulose Membranes from Nata De Coco with and without Silver Ions for CO_2/CH_4 Separation

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Abstract

Carbon dioxide removal from natural gas is an important process because the existence of carbon dioxide in natural gas contributes to pipeline corrosion, reduces the heating value, and takes up volume in the pipeline. In this study, bacterial cellulose was chosen for the gas separation membrane due to the unique structure and prominent properties of bacterial cellulose. Moreover, bacterial cellulose can be obtained simply by culturing the bacteria so called "Acetobacter xylinum" through fermentation of coconut juice which is available abundantly in Thailand. Bacterial cellulose membranes with and without silver ions were prepared to investigate the effect of silver ions on the CO_2/CH_4 separation performance. Bacterial cellulose membranes without silver ions were prepared by varying the weight ratios of dried Nata de coco to water. SEM micrographs and gas pycnometer measurements were shown the effect of the addition of water. The gas separation measurements showed that bacterial cellulose membrane with the weight ratio of 1:10 achieved the highest CO_2/CH_4 selectivity and thus it was chosen for further studying the gas separation performance by impregnating with $AgNO_3$ solutions. The 1.0M Ag^+-BC membrane showed the highest CH_4/CO_2 selectivity. The increasing of $AgNO_3$ concentrations could improve the selectivity.

Keywords: Bacterial cellulose membrane, Nata de coco, CO_2/CH_4 separation, silver ions

1. Introduction

The coconut trees are mostly grown in Thailand, thereby we obtained a lot of coconut juice for food products. One of the most famous food products from coconut water is Nata de coco, which is well known as dessert, produced by fermentation of coconut water with a culture of Acetobacter xylinum. Glucose in coconut juice is converted into bacterial cellulose that is metabolized by Acetobacter xylinum. The main component of Nata de coco is bacterial cellulose [1]. Bacterial cellulose is one of the most attractive biological based materials and a nano-biomaterial which provides many unique properties [2]. It has also a wide variety of potential applications.

Among many applications of bacterial cellulose, a selective membrane is an interesting application. Bacterial cellulose has been introduced to use as a membrane because of its superior mechanical properties, high resistance to chemical corrosion, biodegradability, ease of tailorability and economical processing [3]. Consequently, bacterial cellulose is chosen for this work as a hydrophilic membrane for CO_2/CH_4 separation.

Due to the increasing of demand for the use of natural gas as the principal feedstock for the chemical industry [4], the purification of natural gas is also an important process. Generally, the compositions of natural gas include methane, other light hydrocarbons, such as ethane and propane, and heavier hydrocarbons. In addition, carbon dioxide, hydrogen sulfide, helium and nitrogen at varying concentrations can be contained in natural gas as well. Therefore, the separation of CO_2 from natural gas is an important industrial process because at higher concentrations, it contributes to pipeline corrosion, etc. In this work, membrane technology will be used for CO_2 separation because of the various advantages of membrane separation technology.

2. Materials and Methods

2.1 Materials and Chemicals

Nata de coco was provided by Mrs. Boonyuan Thongampai, Thailand. Sodium hydroxide (NaOH) was purchased from LABSCAN ASIA CO., Ltd., Thailand and Silver nitrate ($AgNO_3$) was purchased from VR BIOSCIENCE CO., Ltd., Thailand. All chemicals were used as received without any further treatment.

2.2 Measurements

2.2.1 Thermogravimetric/Differential Thermal Analyzer (TG/DTA)

Thermal gravimetric analysis were performed using Perkin Elmer Pyris Diamon TG/DTA instrument in a nitrogen atmosphere (flow rate 10 ml/min). The sample was heated from 50°C to 110°C, then were hold at 110°C for 30 min and heated from 110°C to 450°C at a heating rate of 10°C/min.

2.2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetric experiments were carried out by using a Differential Scanning Calorimeter (DSC 822, Metler Toledo) in a nitrogen atmosphere (flow rate 20 ml/min). A 4-8 mg of sample was placed in a tightly sealed aluminum pan. The sample was subjected to run against an empty pan as a reference at a heating rate of 10°C/min in the temperature range 0°C –300 °C.

2.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of bacterial cellulose membranes were characterized by the Spectrum one FTIR (Perkin Elmer). Each sample was analyzed to determine the structural characteristics in the range of 515-4000 cm^{-1} at room temperature by using a Universal ATR Sampling Accessory. Moreover, the sample impregnated with silver ions was further investigated the reaction with CO_2 by soaking the sample into the CO_2 contained bottle overnight and then this sample was analyzed by FTIR (Universal ATR Sampling Accessory) technique.

2.2.4 Scanning Electron Microscopy (SEM-EDX)

The morphologies of the samples were studied using Scanning Electron Microscope (SEM, JEOL, JSM-5410LV). Prior to analysis, the samples were cracked in liquid nitrogen into the small pieces and sputtered coated with a thin layer

of gold under vacuum, then examined at 35x and 100x magnifications for every samples and at 500x and 3,500x magnifications for the samples impregnated with silver ions, of which the last magnification was used for the sample without silver ions as well in order to improve that these membranes do not show the presence of silver nitrate in bacterial cellulose fibers. Additionally, the chemical compositions on the surface of membranes can be proved by the EDX mode (EDX, Oxford ISIS series300). Two regions of surface area of the membranes were randomly chosen for analyzing.

2.2.5 X-ray Diffraction (XRD) Analysis

The crystalline structure of bacterial cellulose membrane was investigated by the XRD pattern which was recorded by X-ray diffractometer (XRD, Rigaku) equipped with filter Cu K_β radiation at a scanning rate of 8°/min ranging from 10° to 80° (2Θ angle).

2.2.6 Gas Pycnometer (Ultrapycnometer 1000)

Gas pycnometer (Ultrapycnometer 1000) was used for determination of the average true density of the membranes at each ratio of dried Nata de coco to water.

2.3 Gas Separation Study

All of bacterial cellulose membranes with and without silver ions were tested in a single gas (carbon dioxide or methane) measurement. Carbon dioxide (CO_2) and methane (CH_4) gas were of high purity and used as received. The experiments were performed for two hours at room temperature and the pressure difference between the feed and the permeating sides (ΔP) was maintained at 20 psi. The area of the membrane in contact with the gas was 0.5024 cm^2. The gas separation unit for this study is schematically shown in figure 2.1. The equilibrium state was obtained by measuring the constant permeate rate. When it reached the steady–state, individual gas flow rate was measured by a gas flow meter. The obtained data were used to calculate the gas permeance and selectivity [5].

The permeance of the permeated gas can be determined by the following equation:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \, x \, 14.7x10^6}{(A)x(\Delta P)x76} \qquad (2.1)$$

Where $(\frac{P}{\delta})_i$ = permeance of gas "i" (GPU),

P = permeability of gas 'i' (10^{-10} cm^3 (STP) cm/cm^2 s cm Hg)

(1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm Hg = 7.5×10^{-18} m^2 s^{-1} Pa^{-1}),

δ = thickness of membrane (μm),

Q_i = volumetric flow rate of gas 'i' (cm^3/sec),

A = membrane area (cm^2), and

ΔP = pressure difference between the feed side and the permeating side (psi).

The ideal separation factor (Gas selectivity, $S_{A/B}$) for component A and B is defined according to the following equation [5]:

$$S_{A/B} = \frac{P_A}{P_B} \qquad (2.2)$$

Where P_A = the permeance of component A, and

P_B = the permeance of component B.

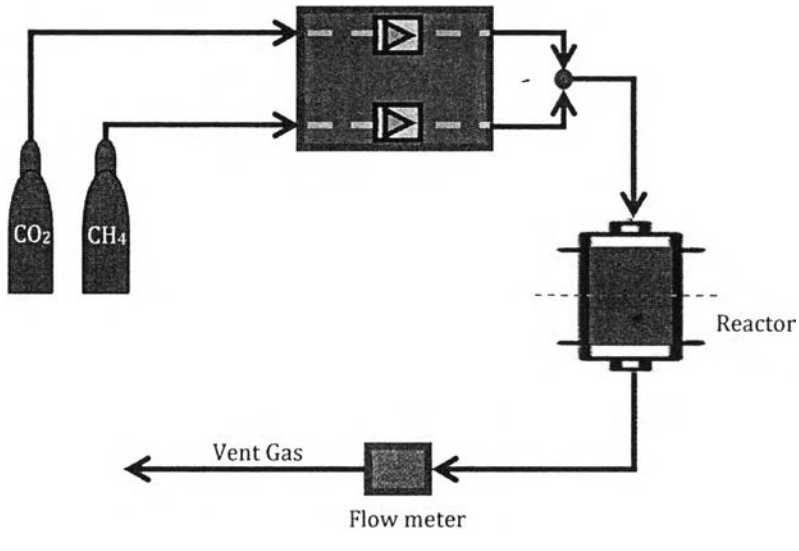

Figure 2.1 The unit of separation study.

2.3 Experimental

2.3.1 Purification of Coconut Gel (Nata De Coco)

Nata de coco was cut into the small pieces and soaked in boiled water for fifteen minutes with continuous stirring, followed by soaking and continuous stirring in 0.1 M NaOH at 80°C until its color was clear. The alkaline solution was changed every two hours. After that Nata de coco was washed several times with distilled water until the pH of water became neutral [6]. This purified gel was stored in distilled water prior to use.

2.3.2 Preparation of Bacterial Cellulose Membranes

The purified Nata de coco was blended by the blender and separated water out. Afterward, it was dried in an oven for 6 hours and then blended it again to obtain bacterial cellulose powder. The various amounts of water, which are 7, 10, 13, 15, 17 and 20 ml, were added into 1 g of the bacterial cellulose powder for each condition and the samples were stirred until the powder was swollen enough to be continuous matrix membranes. The samples were then freeze-dried by a freeze-dryer to finally obtain bacterial cellulose membranes.

2.3.3 Preparation of Bacterial Cellulose Membranes with Silver Ions

Certain amount of water, which is 9 ml, was added into 1 g of the bacterial cellulose powder and stirred until the powder was swollen enough to be continuous matrix membranes. Various concentrations of silver nitrate solution (1 ml), (0.1M, 0.5M and 1.0M) were added into the swollen samples. After that the samples were then freeze-dried by the freeze-dryer to obtain bacterial cellulose membranes with silver ions.

3. Results and Discussion

3.1 Thermal Properties of Bacterial Cellulose Membranes

The thermal stability of dried bacterial cellulose membrane was investigated with TGA. Figure 3.1 shows the TGA curve of bacterial cellulose membrane. As shown in TGA thermogram, the maximum rate of weight loss is at the temperature of approximate 330°C. It can be attributed to the decomposition of bacterial cellulose which falls in the range of 240°C - 345°C. Since bacterial cellulose contains the crystalline and amorphous phases which will be discussed by XRD technique, the wide temperature of degradation was found. This result was similar to Yang *et al* [7] and also Surma-Ślusarska *et al* [8]. Moreover, the TGA curve showed one step of degradation that confirmed the purity of Nata de coco which was used for this work.

In addition, the DSC thermogram also shows the thermal behavior of bacterial cellulose membrane in figure 3.2. The endothermic peak indicating the melting peak of the crystalline structure in bacterial cellulose membrane is about 140°C. Carreño Pineda *et al* [9] illustrated the DSC thermogram of bacterial cellulose membranes as well. Although, the melting temperatures of bacterial cellulose membranes from their work have significant variations (127°C-164°C) that depend on the culture and purification conditions, the melting point value obtained from our work was still in the range of their work.

3.2 Chemical Structure of Bacterial Cellulose Membranes with and without Silver Ions

The chemical structure of bacterial cellulose membranes with and without silver ions was revealed using ATR-FTIR technique. The FTIR spectra of bacterial cellulose membrane from Nata de coco without silver ions and silver ions-impregnated bacterial cellulose membrane show various distinguished peaks as shown in figure 3.3 (a) and (b), respectively. Table 3.1 concludes the significant peaks showed from FTIR spectra. These results also correspond to the result reported by Pecoraro *et al* [10] and

Halib *et al* [1] which can be claimed that these membranes, included the membrane which contains silver on bacterial cellulose matrix, show the characteristic of bacterial cellulose. In case of the membrane with silver ions, only small peaks shifted were observed in comparison with bacterial cellulose spectrum. We suppose that there are too much weaker interactions between silver ions and bacterial cellulose chains because bacterial cellulose structure is 3-dimensional structure, hence it allows quest molecules to penetrate in its network and, probably, the silver ions are such guest molecules so we could obtain bacterial cellulose-silver membranes which was described by Jinga *et al* [11].

Additionally, after bacterial cellulose was impregnated with silver ions, the infrared spectra of a sample exhibits the peak of silver nitrate at 1299 cm^{-1} [12], [13], [14] as shown in figure 3.3 (b). In case of silver ions-impregnated bacterial cellulose membrane that was soaked in CO_2 overnight before ATR-FTIR testing, the FTIR spectra is demonstrated in figure 3.3 (c). As can be observed, it shows the significant peaks of 1299 cm^{-1} shifted to 1308 cm^{-1} which refer to the interaction of silver ion with CO_2. Due to the increasing of polarity, the peak shifted to the higher of wavenumber.

3.3 Crystalline Structure of Bacterial Cellulose Membrane

Figure 3.4 shows the X-ray diffraction (XRD) pattern of the bacterial cellulose membrane. The existence of the broad diffraction peaks at 2Θ values 14.4, 16.8 and 22.6 corresponds to the cellulose I crystallographic planes $10\bar{1}$, $10\bar{1}$ and 002, respectively [15]. Thus, the XRD spectrum confirmed the crystalline structure and also the amorphous phase of bacterial cellulose membrane.

3.4 Characterizations of Bacterial Cellulose Impregnated with Silver Nitrate Solutions

The elemental compositions of the membrane's surfaces were determined by the SEM-EDX instrument. Figure 3.5 and 3.6 shows the energy dispersive X-ray analysis (EDX) spectra of bacterial cellulose membrane without silver ions and

bacterial cellulose membrane impregnated with 0.1M silver nitrate solution, respectively. However, in figure 3.6, it can be observed the peaks of silver that confirmed the presence of silver ions on the surface which is complemented with the FTIR analysis. Additionally, Majeed Khan *et al* [16] and Sarkar *et al* [17] reported the binding energies of silver at the similar positions with this spectrum.

The EDX analysis also revealed the amount of each element on the surface of the membranes in table 3.2, in addition, table 3.3 shows the concentration of silver ions on the surface in the Molar unit. In case of silver ions-impregnated bacterial cellulose membranes, when the concentration of $AgNO_3$ solutions increased, the amount of silver ions on the surface of the membranes also increased as shown in table 3.1 and 3.2. However, the amount of silver ions (Molar unit) for all of membranes were lower than the added concentrations (Molar unit) of $AgNO_3$ solutions into the membranes. This was probably owing to the error in the preparation step. When we used too small amount of $AgNO_3$ solution, the amount of silver ions on the surface of the membrane was much more different from the beginning solution concentration.

3.5 Density of Bacterial Cellulose Membranes without Silver Ions

Gas pycnometer analysis was performed to find the average true density of bacterial cellulose membranes at each weight ratio of dried Nata de coco to water. The results are shown in table 3.4. It was found that when the amount of water increased, the average true density of the membranes decreased which will be further discussed.

3.6 Morphology of Bacterial Cellulose Membranes with and without Silver Ions

The morphological features of the two types of prepared bacterial cellulose membranes with or without silver ions are illustrated in figure 3.8 and figure 3.7, respectively. These figures reveal the distinctive three-dimensional network with entangled of cellulose fibers as reported by Hu *et al* [18]. Moreover, the effect of varying the content of water added into the dried Nata de coco to be the membranes

was compared in figure 3.7 (a-l) exhibiting the differences in the densification of bacterial cellulose fibers. It can be noticed that the higher content of water, the larger size of voids were found in the membranes which confirmed by the results from gas pycnometer measurement. The denser structure can be obtained when the weight ratio of 1:7, 1:10 and 1:13 as shown in figure 3.7 (a-f). As can be compared from overall figures, the membrane with 1:7 weight ratio was the densest as agree with gas pycnometer experiment result, but actually its texture was still not smooth, so it was difficult to cut into the continuous membrane since it was easily to be broken into pieces. However, the smooth texture could be obtained from the weight ratio of 1:10 to 1:20. It can be observed that the amount of added water in the preparation step could have an effect to the structure of the final membrane product. Therefore, we chose the membrane with 1:10 weight ratio to further study the effect of adding silver ions into this membrane.

Figure 3.8 (a-l) demonstrate the effect of adding silver ions into bacterial cellulose membranes (weight ratio of dried Nata de coco: water =1:10) with varying concentration of silver ions. Figure 3.8 (d), (h) and (l) shows that silver was incorporated into bacterial cellulose fibers. In case of these membranes, not only the voids size were smaller than the ones that were absent of silver ions, but the membrane structure were also stiffer. It was indicated that the presence of silver ions could improve the structure of bacterial cellulose membrane by decreasing the void size within the membrane. As shown in figure 3.8 (a-l), we can notice that when the silver ions concentration increased, the void size decreased accordingly.

Additionally, bacterial cellulose membranes without silver ions can be proved by the SEM micrograph in figure 3.9 where it does not show the presence of silver within these membranes.

3.7 Gas Separation Study

The gas separation experiments were carried out by flowing a single gas (CO_2 or CH_4) through bacterial cellulose membranes in the separation unit at room temperature and ΔP = 20 psi. The CO_2 and CH_4 permeance of bacterial cellulose membranes without silver ions at every weight ratio are shown in figure 3.10 where it

can be observed that the CO_2 permeance through bacterial cellulose membrane was lower than the CH_4 permeance because CO_2 molecules could react with the polar groups [19] within bacterial cellulose membrane (such as hydrophilic hydroxyl groups) resulted in lower flux, on the other hand, the CH_4 molecules could not react with these polar groups, thus these molecules were able to pass easily through the membrane resulted in higher flux. In addition, the kinetic diameter of CO_2 molecule is smaller than the CH_4 molecule, hence, CO_2 molecule had more complex pathway to exit the membrane than the CH_4 molecule caused the lower flux of CO_2 than the CH_4 [5]. However, the densification of bacterial cellulose membrane also affects the permeance value as can be seen from figure 3.10 as well. As above-mention, the membrane with the weight ratio of 1:7 had the highest density and the other weight ratios had lower density in descending order. When the densification of bacterial cellulose membrane decreased, the permeance value increased due to the larger size of voids in the membrane were presented. Thus, we found that the highest of CO_2 and CH_4 flux through these membranes was obtained from the weight ratio of 1:20 because the largest void size were presented.

Additionally, the CO_2 and CH_4 flux through these membranes in every conditions was higher than the previous study by Nicharat *et al* [5] and Treeratdilokkul et al [20] as shown in table 3.5.

The CH_4/CO_2 selectivity of bacterial cellulose membranes at different weight ratio of dried Nata de coco to water are demonstrated in figure 3.11 where it can be seen that the highest selectivity value was obtained from the membrane with the weight ratio of 1:10 probably due to the smaller void size within this membrane and the higher membrane densification. When the CO_2 molecule passed through this membrane, the chance of reaction between CO_2 with polar groups within this membrane was more than the membrane that had larger void size because some CO_2 molecules could passed easier through the larger voids by no reaction as same as CH_4 molecules. This reason lead to the highest selectivity could be achieved from 1:10 ratio. In contrast, the weight ratio of 1:7 achieved the lowest selectivity value probably due to the texture of this membrane as above-mention in the morphological features. Consequently, we used the 1:10 weight ratio for impregnating silver nitrate solutions into the membrane and comparing gas separation performance with the ones without

silver ions. However, the CH_4/CO_2 selectivity of the membranes prepared from different weight ratios of Nata de coco to water was in the range of 1.24-1.50. When we compared with the membranes prepared from the previous work of Nicharat *et al* [5] and Treeratdilokkul *et al* [20] as presented in table 3.5, the membranes from our work had slightly lower selectivity than their membranes. This was due to our membrane exhibited much higher permeance for both CO_2 and CH_4 than their membranes.

Figure 3.12 represents the effects of the presence of silver ions in bacterial cellulose membranes (weight ratio of 1:10) to the CO_2 and CH_4 permeance values. As can be observed in this figure, not only the permeance of CO_2 was lower than that of CH_4 which was the same result as bacterial cellulose membrane without silver ions, but also the CO_2 flux through these membranes was lower than that of the membranes without silver ions noticeably. This was due to the л-complexation reactions between silver ions and double bonds of CO_2 molecules resulting in lower CO_2 permeance [5], [21] which was confirmed by FTIR spectra. Furthermore, we found that when the concentration of silver ions increased, the CO_2 and CH_4 flux decreased. Since the presence of silver ions could reduce the void size within bacterial cellulose membranes as can be seen in the SEM images (figure 6.8) and caused the membranes to become more rigid.

Figure 3.13 shows the CH_4/CO_2 selectivity of bacterial cellulose membranes incorporated with silver ions that increased with an increasing of $AgNO_3$ solutions concentrations (0.1M, 0.5M and 1.0M $AgNO_3$) which is similar to the previous report of Nicharat *et al* [5] since the л-complexation reaction between silver ions and double bonds of CO_2 molecules had an effect on the significant lower permeance of CO_2, on the other hand, it had a slightly effect on the lower CH_4 permeance, thus the CH_4 flux was still high resulting in the higher CH_4/CO_2 selectivity. We can conclude that the 1.0M Ag^+-BC membrane showed the highest CH_4/CO_2 selectivity when compared with other membranes.

4. Conclusion

Bacterial cellulose membranes from Nata de coco with and without silver ions were prepared for CO_2/CH_4 separation study, the membranes without silver ions were prepared by varying the weight ratios of dried Nata de coco to water. The densification of these membranes decreased when the amount of water increased. From gas separation measurements revealed that the CO_2 permeance through bacterial cellulose membrane was lower than the CH_4 permeance and the 1:10 weight ratio of dried Nata de coco to water achieved the highest CH_4/CO_2 selectivity which was 1.50, thus it was chosen for further studying the gas separation performance by impregnating with $AgNO_3$ solutions. From all of the results, the 1.0M Ag+-BC membrane obtained the highest CH_4/CO_2 selectivity. Moreover, we found that the increasing of $AgNO_3$ solutions concentrations could improve the separation selectivity.

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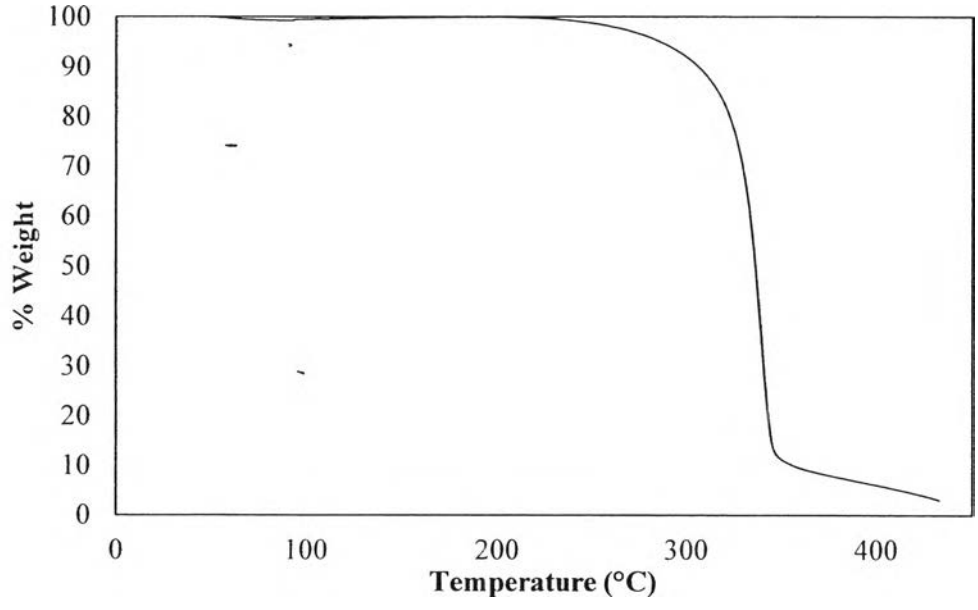


Figure 3.1 TGA thermogram of bacterial cellulose membrane.

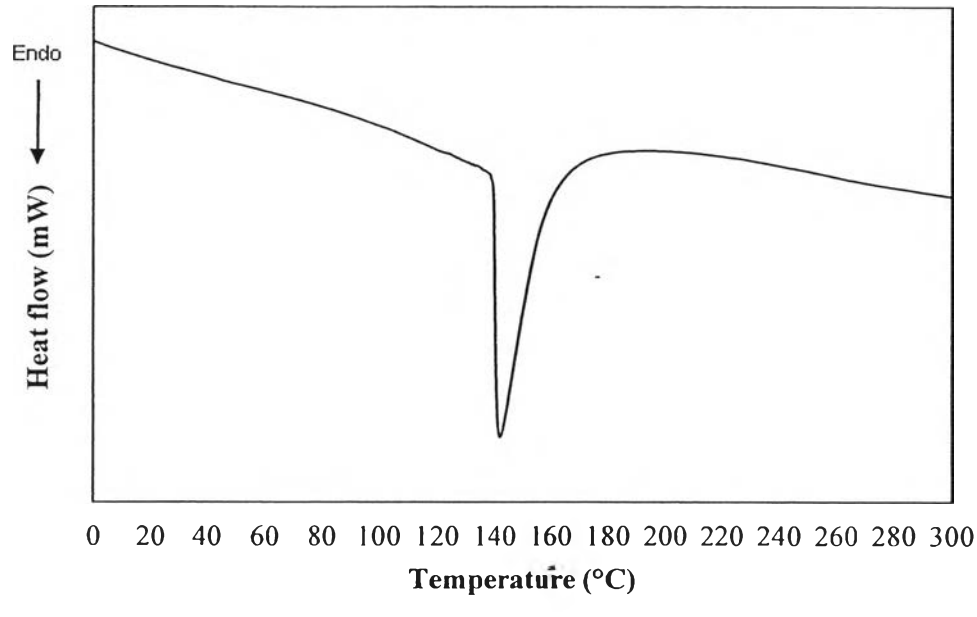


Figure 3.2 DSC thermogram of bacterial cellulose membrane.

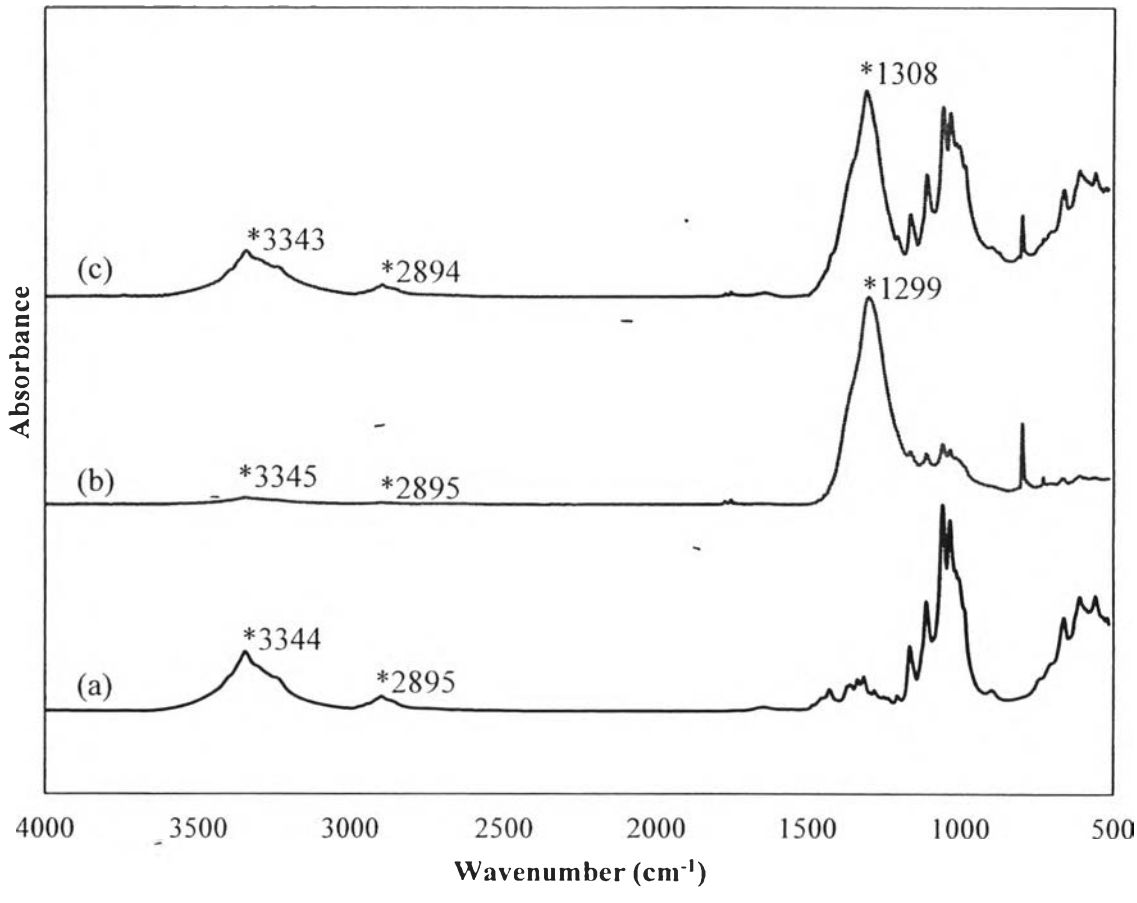


Figure 3.3 FTIR spectra of (a) pure bacterial cellulose membrane (b) bacterial cellulose membrane with silver ions and (c) bacterial cellulose membrane with silver ions which was soaked in CO_2 overnight before testing.

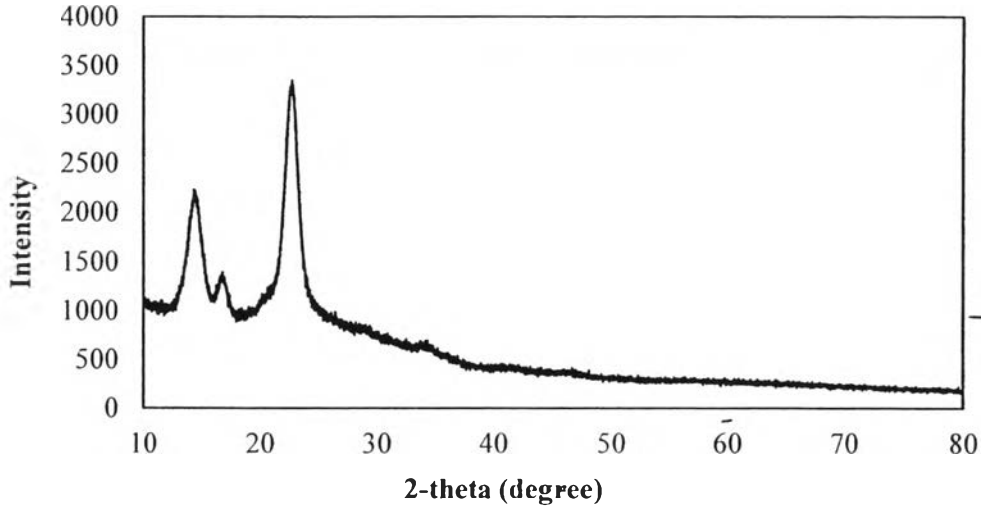


Figure 3.4 XRD pattern of bacterial cellulose membrane.

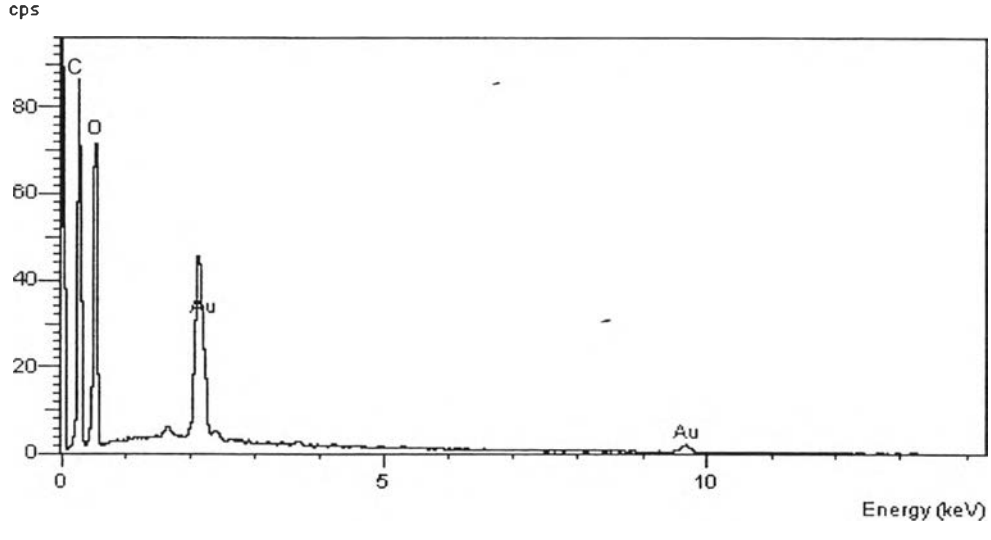


Figure 3.5 EDX spectra of bacterial cellulose membrane without silver ions.

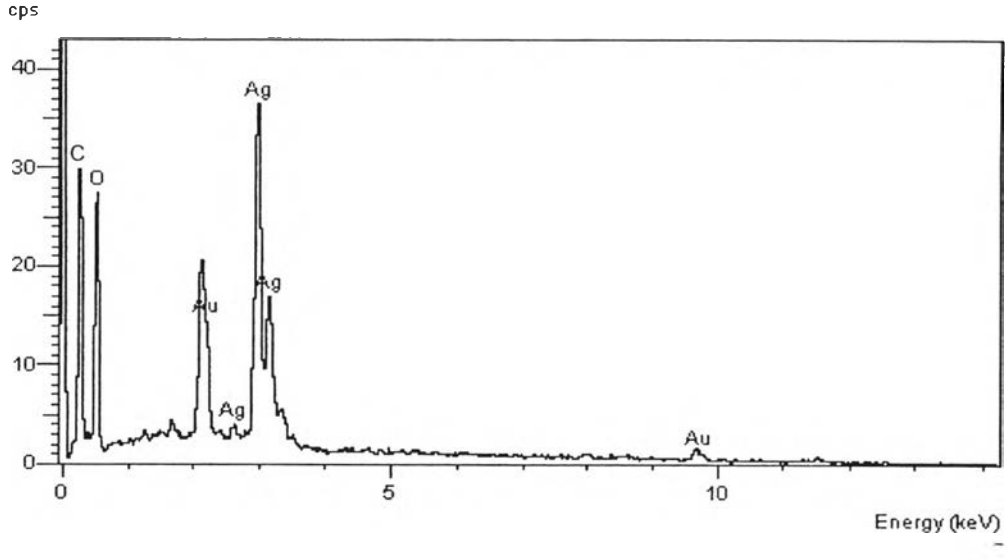
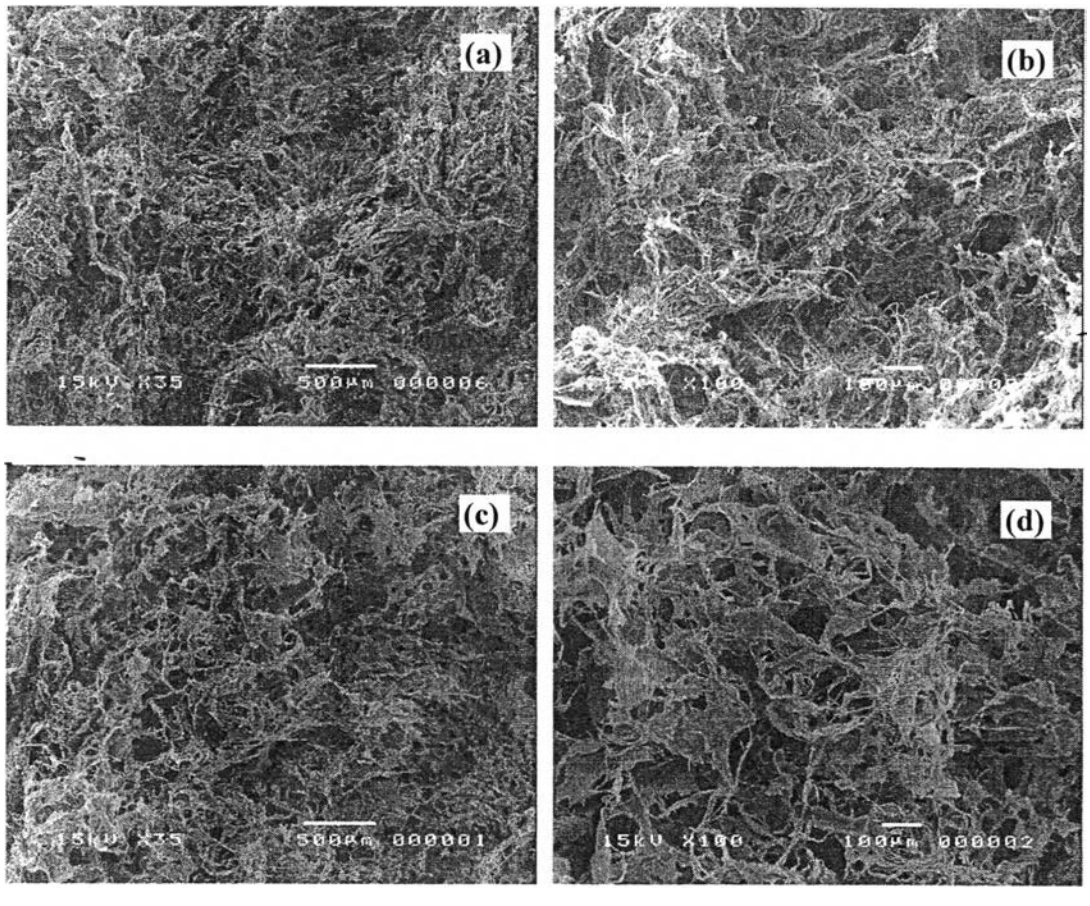
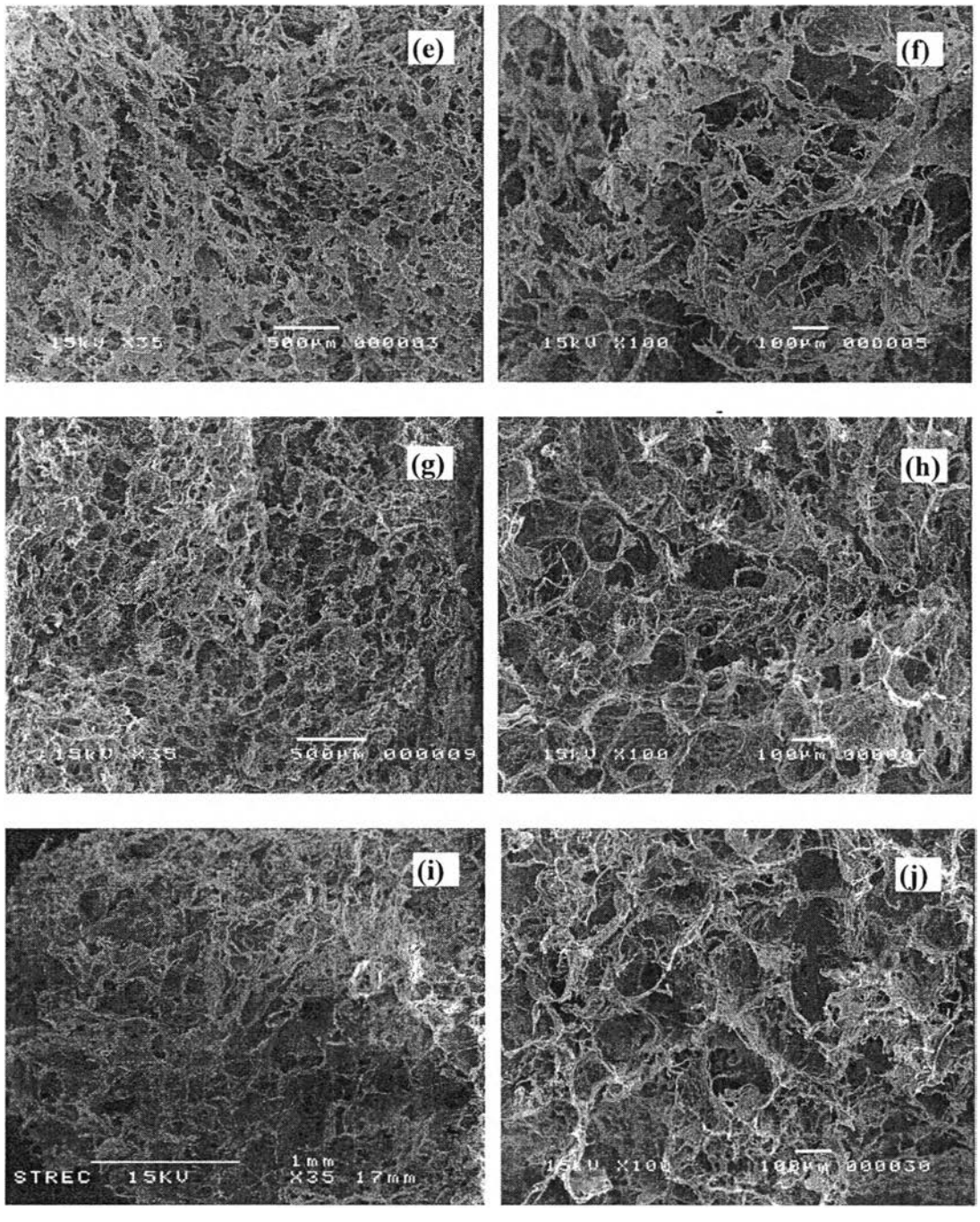


Figure 3.6 EDX spectra of bacterial cellulose membrane impregnated with 0.1 M silver nitrate solution.




(e)
15kV X35
500µm 000003
(f)
15kV X100
100µm 000005
(g)
15kV X35
500µm 000009
(h)
15kV X100
100µm 000007
(i)
STREC 15KV
1mm
X35 17mm
(j)
15kV X100
100µm 000030

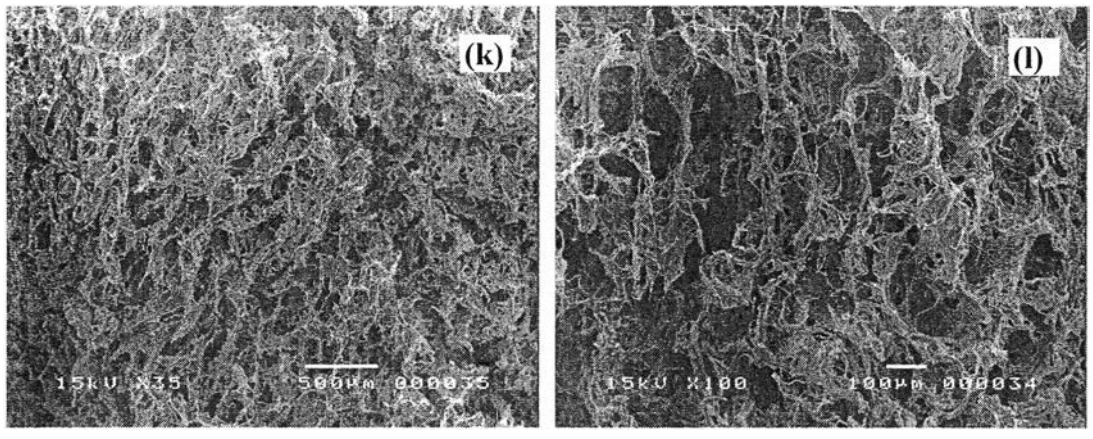
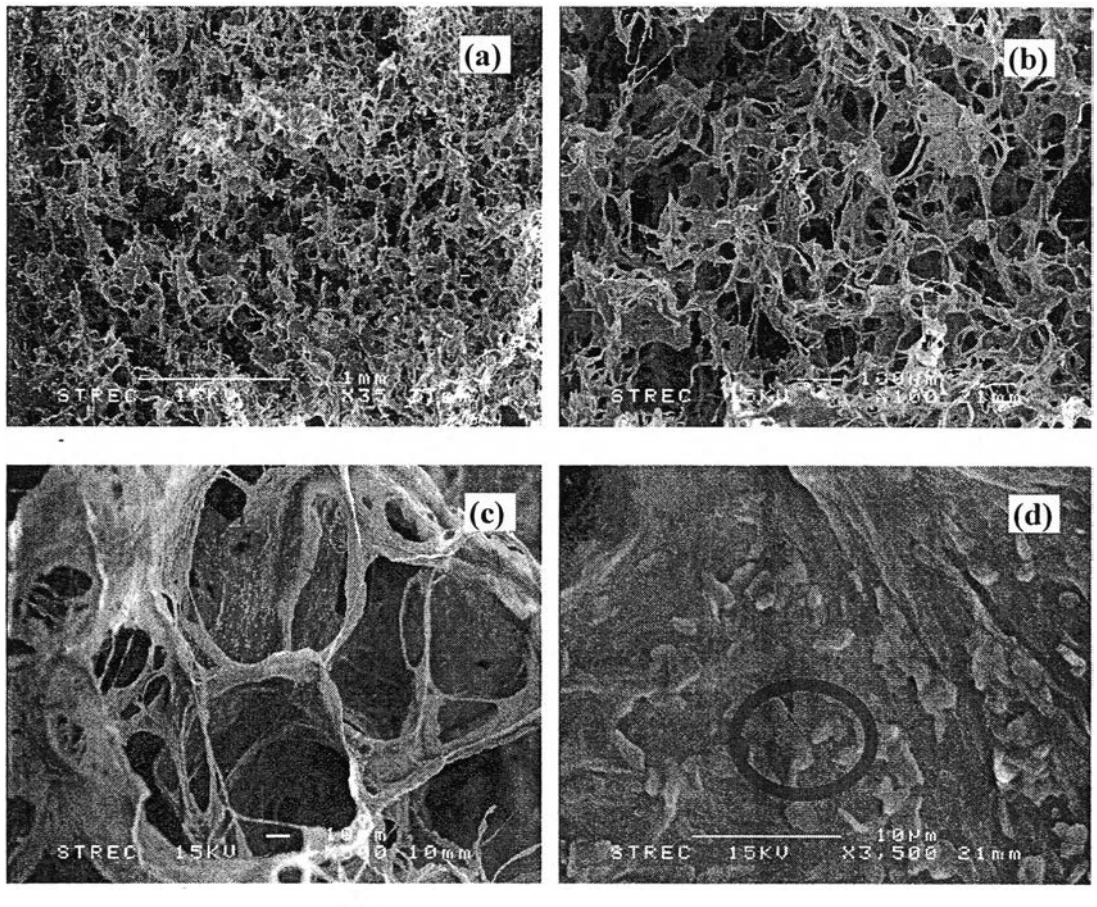
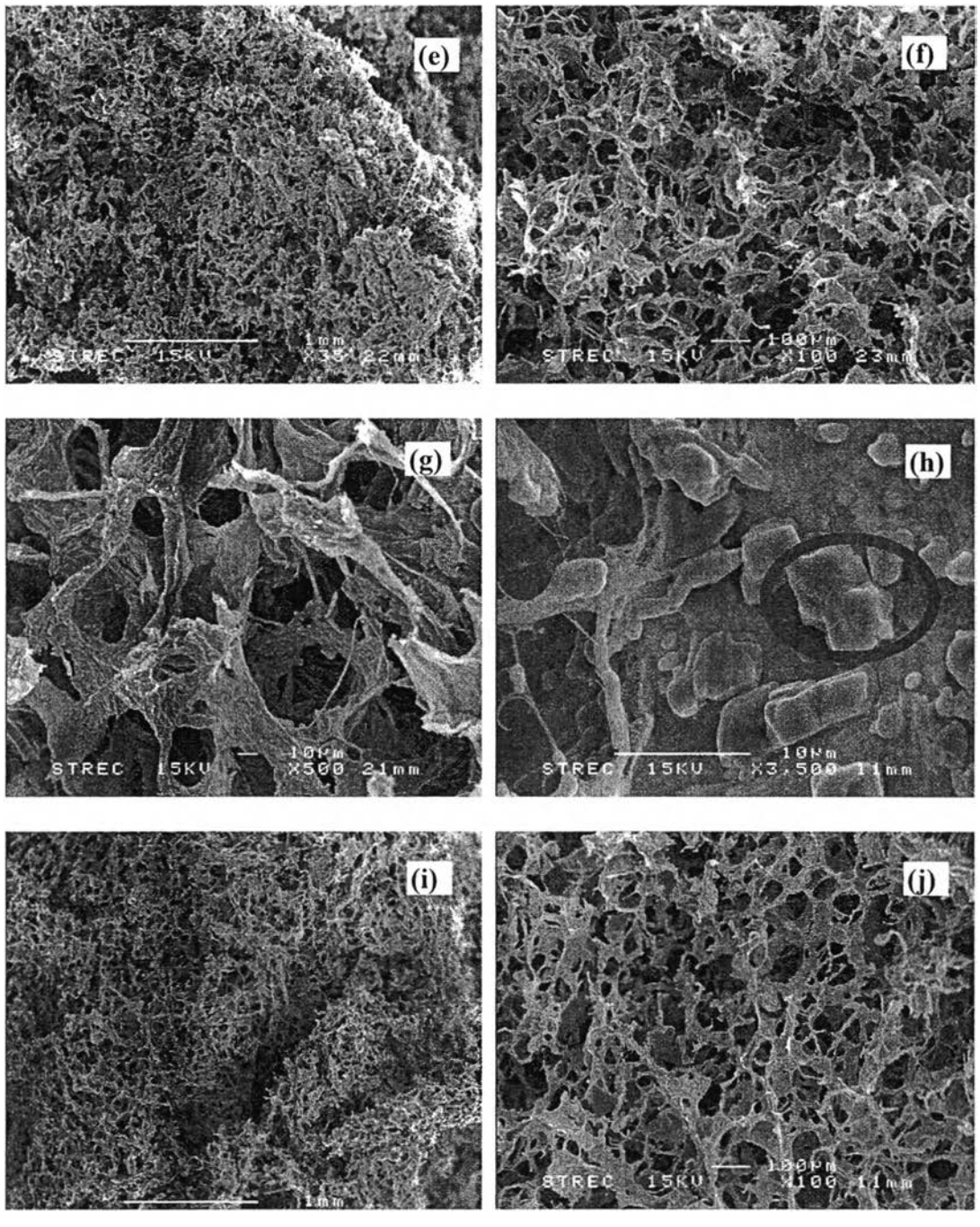


Figure 3.7 SEM micrographs of bacterial cellulose membranes at the weight ratio of 1:7 (dried Nata de coco: water) with a magnification of x35 (a) and x100 (b), 1:10 with a magnification of x35 (c) and x100 (d), 1:13 with a magnification of x35 (e) and x100 (f), 1:15 with a magnification of x35 (g) and x100 (h), 1:17 with a magnification of x35 (i) and x100 (j) and 1:20 with a magnification of x35 (k) and x100 (l).




(e)
STREC 15KV
(f)
STREC 15KV
(g)
STREC 15KV
(h)
STREC 15KV
(i)
(j)
STREC 15KV

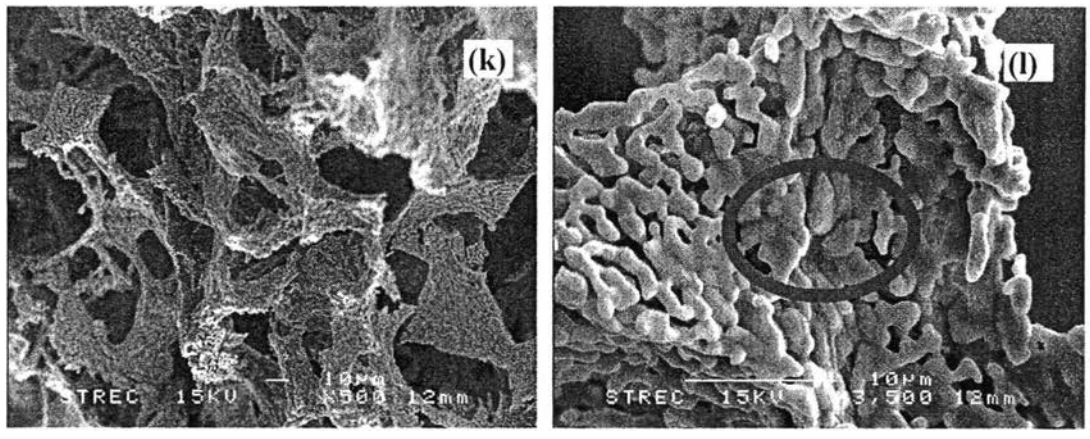


Figure 3.8 SEM micrographs of bacterial cellulose membranes impregnated with 0.1 M $AgNO_3$ with a magnification of x35 (a), x100 (b), x500 (c) and x3,500 (d), 0.5 M $AgNO_3$ with a magnification of x35 (e), x100 (f), x500 (g) and x3,500 (h) and 1.0 M $AgNO_3$ with a magnification of x35 (i), x100 (j), x500 (k) and x3,500 (l) at the weight ratio of 1:10 (dried Nata de coco: water).

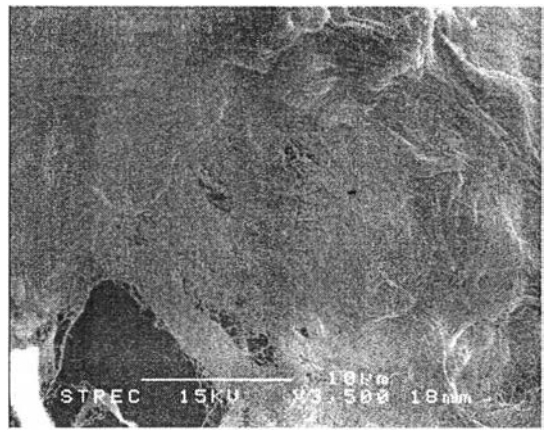


Figure 3.9 SEM micrograph of bacterial cellulose membrane without silver ions with a magnification of x3,500.

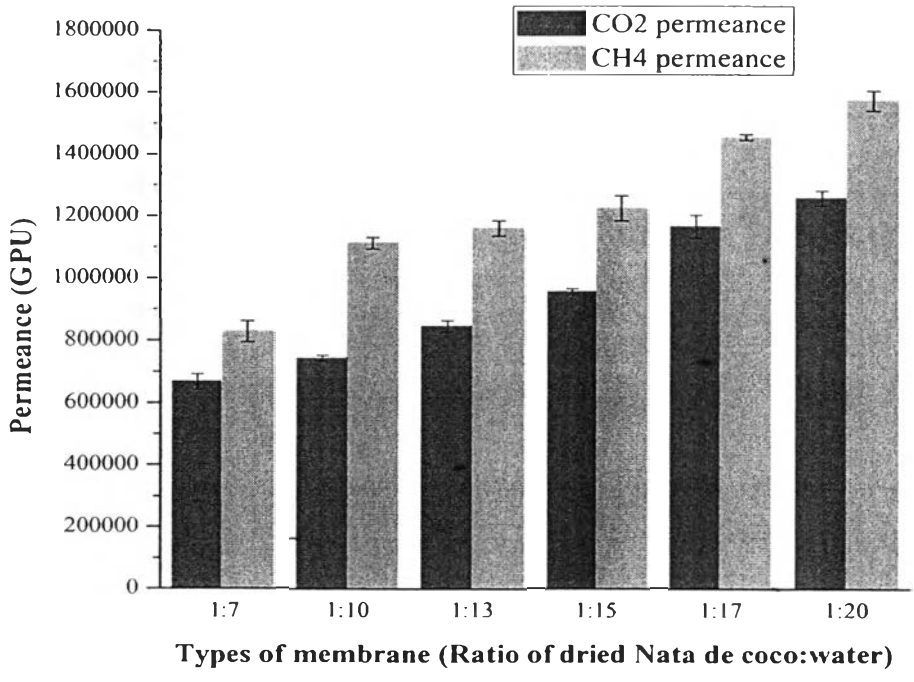


Figure 3.10 CO_2 and CH_4 permeance (GPU) of bacterial cellulose membranes.

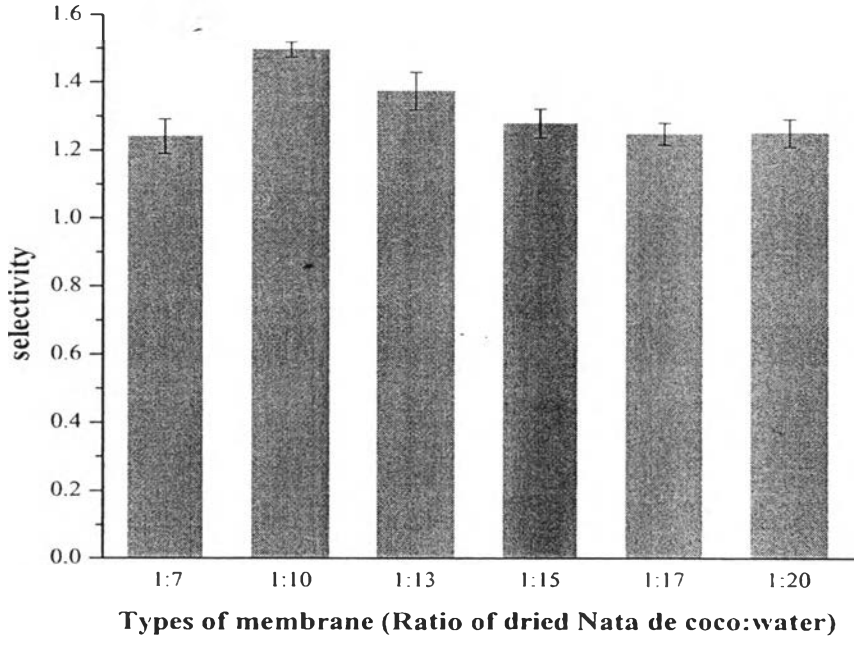


Figure 3.11 CH_4/CO_2 selectivity of bacterial cellulose membranes.

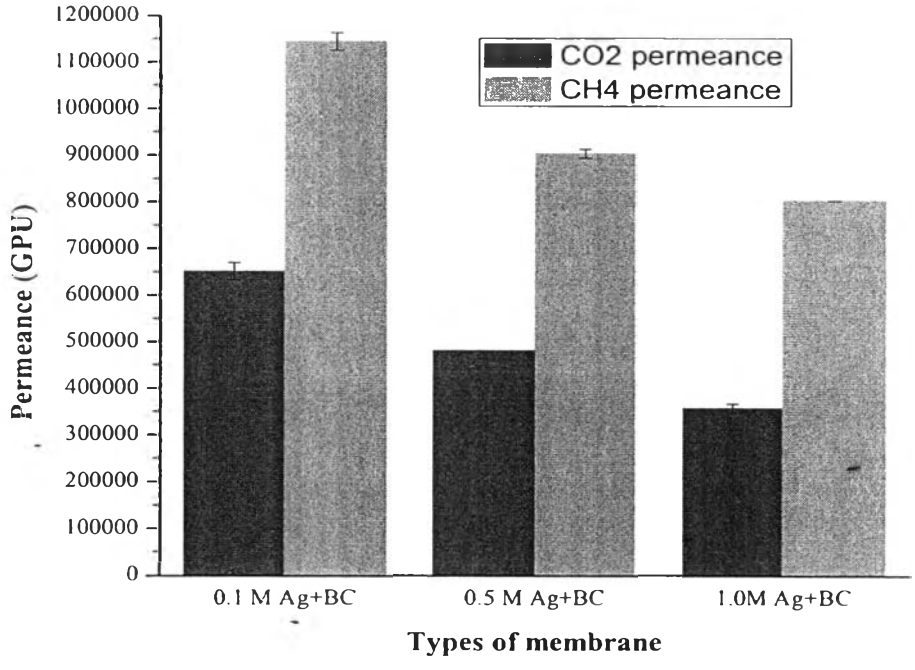


Figure 3.12 CO_2 and CH_4 permeance (GPU) of bacterial cellulose membranes (weight ratio of 1:10) incorporated with silver ions (0.1M, 0.5M and 1.0M $AgNO_3$).

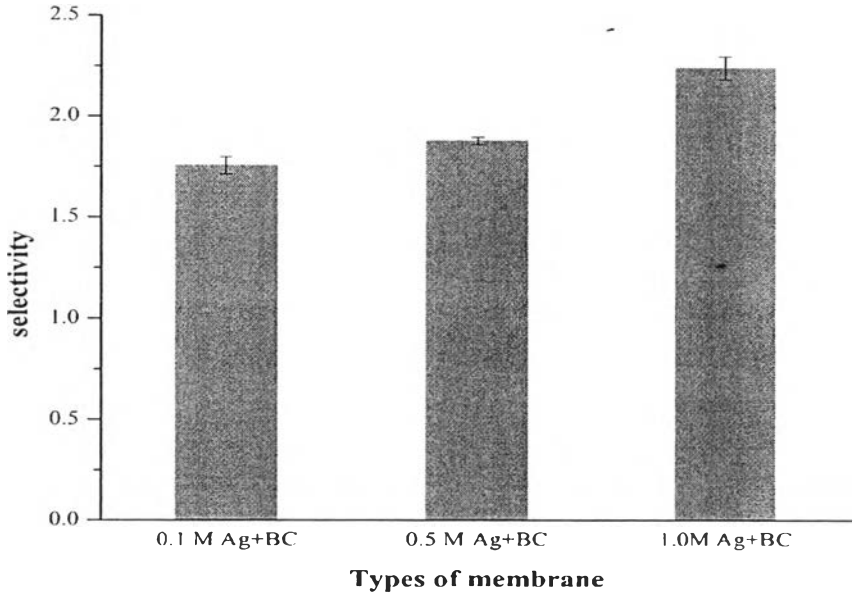


Figure 3.13 CH_4/CO_2 selectivity of bacterial cellulose membranes (weight ratio of 1:10) incorporated with silver nitrate solution (0.1M, 0.5M and 1.0M $AgNO_3$).

Table 3.1 FTIR peaks for each membrane

Range (cm^{-1}) [10]	**Functional groups**	**Significant peaks from each membrane**		
		BC	**Ag+-BC**	**Ag+-BC (soaked in CO_2 before test)**
3500-3300	O-H stretching	3344	3345	3343
3000-2870	CH and CH_2 stretching (CHOH; CH_2OH)	2895	2895	2894
1348	Silver nitrate	-	1299	1308
1430-1330	C-OH and C-H bending	1427	-	-
1200-1000	C-O-H stretching	1162	1162	1161
1150-1000	C-O-C stretching	1108	1109	1108
900-700	in plane bending vibration of CH_2 and CH	899	899	899
700-400	out of plane bending vibration of OH	664	671	663

Table 3.2 EDX measurements of the surfaces of bacterial cellulose membrane without silver ions (BC) and bacterial cellulose membranes impregnated with 0.1M (0.1M Ag^+-BC), 0.5M (0.5M Ag^+-BC) and 1.0M silver nitrate solution (1.0M Ag^+-BC)

Elements	**Atomic%**			
	BC	**0.1M Ag^+-BC**	**0.5M Ag^+-BC**	**1.0M Ag^+-BC**
C	40.92	24.31	14.14	6.84
O	59.08	49.86	40.21	31.16
Ag	-	25.84	45.65	62

Table 3.3 The amount of silver ions on the membrane's surfaces in the Molar unit

Types of membranes	0.1M Ag^+-BC	0.5M Ag^+-BC	1.0M Ag^+-BC
Ag (Molar)	0.041 ($\pm 1.41 \times 10^{-4}$)	0.360 ($\pm 1.22 \times 10^{-2}$)	0.977 ($\pm 1.19 \times 10^{-2}$)

Table 3.4 Average true density of bacterial cellulose membranes without silver ions measured by gas pycnometer

Types of membranes (Dried Nata de coco: water)	**Average true density (g/cm^3)**
BC 1:7	0.85
BC 1:10	0.71
BC 1:13	0.69
BC 1:15	0.61
BC 1:17	0.58
BC 1:20	0.54

Table 3.5 Membranes for CO_2/CH_4 separation study

Membrane	Conditions studies			CO_2 Permeability (GPU)	CH_4 Permeability (GPU)	CH_4/CO_2 Selectivity	References
	Temperature (°C)	Pressure ΔP (psi)	Area of the membrane in contact with the gas (cm^2)				
Activated carbon xerogel	25	20	1.13	55,275	9,301	3.79	[20]
Carbon membrane based polybenzoxazine xerogel	25	20	0.5024	~120,000	~190,000	~1.6	[5]
1.0CX-Ag membrane	25	20	0.5024	~52,000	200,000	~3.3	[5]
Pure bacterial cellulose membrane (weight ratio 1:10)	25	20	0.5024	743,252	1,112,205	1.50	this work
1.0M Ag^+-BC membrane	25	20	0.5024	358,258	802,071	2.24	this work