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# SEPARATION OF ETHYL ACETATE FROM WATER MIXTURE USING SAGO/POLY (VINYL ALCOHOL) BLENDED MEMBRANES: EFFECT OF SAGO BLENDED RATIOS

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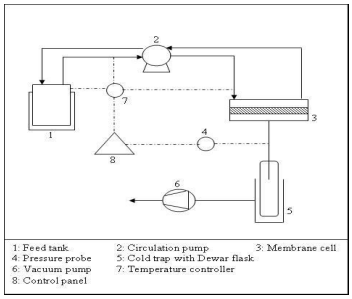
## Graphical abstract




Pervaporation

## Abstract

Relatively new Sago/PVA blended membranes were prepared by solution casting technique. Homogenous sago/PVA membranes were prepared with different ratio of sago content in the membrane. The blended membranes were characterized using Fourier Transform Infrared Spectroscopy (FTIR), contact angle measurements, and degree of swelling (DS). The blended membranes were tested for pervaporation of ethyl acetate-water mixture at a range of 1-4wt% of water in the solution. The effects of feed temperature and concentration were investigated. The permeation flux increased around 30% with sago content in the blend membranes from 3wt% to 7wt% at 60°C. However, the separation factor decreased from 433 to 387 for same membrane.

*Keywords*: Sago, membrane, pervaporation, blended

## Abstrak

Secara relatifnya membran Sagu/PVA baru yang disebatikan telah disediakan melalui teknik penuangan larutan. Membran Sagu/PVA homogen telah disediakan dengan kandungan sagu yang berlainan kadar di dalam membran. Membran-membran yang disebatikan telah dicirikan menggunakan Fourier Transform Infrared Spectroscopy (FTIR), pengukuran-pengukuran sudut hubungan, dan Darjah Gelembung (DS). Membran-membran sebatian telah diuji bagi penelapsejatan campuran etil asetat-air pada julat di antara 1-4wt% air dalam larutan. Kesan daripada suhu bagi proses pembentukan hablur dan pati telah dikaji. Fluks peresapan telah meningkat kira-kira 30% dengan peningkatan di dalam kandungan sagu dalam membran-membran sebatian daripada 3wt% sehingga 7wt% pada 60°C. Bagaimanapun faktor pengasingan telah menurun daripada 433 kepada 387 untuk membran yang sama.

*Kata kunci*: Sagu, membran, penelapsejatan

## 1.0 INTRODUCTION

Alcohol/water mixtures are difficult to separate via normal distillation and extraction [1-3]. Pervaporation process can separate azeotropes, close-boiling mixtures, and thermally sensitive compounds, and removing species present in low concentrations [4-9]. Polymers are the main membrane materials for pervaporation because of their excellent permselectivity and high processability. Hydrophilic polymers are the main material for dehydration of alcohol-water mixture such as chitosan, cellulose, polyvinyl chloride, and polyvinyl alcohol have been used in many researches to prepare a good membrane. A good membrane should have a high separation factor and permeation flux [9-11]. Various modification techniques are employed to increase the separation performance of the membranes such as cross-linking and blended with other polymers [12, 13].

During the early stages of membrane research, recovery of ethyl acetate from water by pervaporation process has received substantial attention. Ethyl acetate is an important solvent, and has extensive application such as printing ink, paint, and perfume [14, 15]. Pharmaceutical and chemical industries are using large amounts of solvents such as ethyl acetate and may end up as waste streams. The uses of ethyl acetate have been increasing yearly. In 2001, the global use of ethyl acetate was 200,000 tons; by 2008 the amount of ethyl acetate used exceeded 1000,000 tons [14]. The production of ethyl acetate is usually by estrification of acetic acid and ethanol and the product water and ethyl acetate, and large amount of ethyl acetate end up as a waste stream form chemical and pharmaceutical industries [16]. Recovery of ethyl acetate by normal distillation is very difficult especially at azeotrpoic point at 8.5 wt % or less, and also required entrainer materials that have to be removed [17].

Many different natural and synthetic polymeric materials have been used to develop membranes by blending for dehydration of alcohol/water mixtures such as chitosan, polyvinyl alcohol and cellulose. Blending is an easy method to adjust membrane structure and properties, which will combines excellent properties of the PVA and CA membranes to produce the blended membranes with the optimal microstructure and hydrophilicity. However, high separation factor and permeation flux highly depend on the membrane material and operating conditions such as feed temperature and concentration. In general, hydrophilic polymer materials with O-H groups are usually the preferred membrane materials. Extensive research has been carried out to develop environmentally benign friendly, starch-based polymers for renewable energy applications. Sago starch is evidently a hydrophilic polymer, which is an interesting material to develop to remove water from alcohol.

There has been no research on the use of sago starch, and effect of blended ratio with another polymer for dehydration of alcohol-water mixture. In this study, an azeotrope forming mixture of ethyl acetate-water was separated using sago/PVA membrane. Sago/PVA membranes were prepared with different sago blended ration with PVA and characterized using Fourier transform infrared (FT-IR) spectroscopy, degree of swelling and contact angle measurements. The effects of feed temperatures and feed concentration on the separation factor and permeation flux were investigated. Sago membrane showed good result for purification of ethyl acetate from water and will attract more attention in the future in this area.

## 2.0 EXPERIMENTAL

### 2.1 Material

The sago starch used in this study was obtained from Malaysia; polyvinyl alcohol (PVA) (MW 85000) 99-100% purity was purchased from New Jersey USA. Ethyl acetate was supplied by Rinting. Water was deionized and distilled before use.

### 2.2 Membrane Preparation

The polymer membranes were prepared by solution casting technique. The polyvinyl alcohol solution was prepared by dissolving 10wt% of PVA in hot water at 90°C, and stirred for 6 hours to form a homogenous solution. The sago starch was prepared by dissolving 3wt%, 5wt% and7wt% in hot water at 90°C for 5 hours separately. The solutions were filtered using a filter paper and a vacuum pump. The solutions were carefully mixed at ratio PVA-S: 10-3, 10-5, and 10-7 respectively. The mixtures stirred for 24 hours to make homogenous solutions. After that, the solutions were kept in the oven for 24 hours. Then the solutions were casted onto a glass plate to dry for 72 hours at room temperature. The dried membranes were peeled off from the glass plate. After that, the membranes were washed by deionized water for several times. Finally, the membranes were fully dried under ambient condition and ready for use.

### 2.3 Pervaporation

Prepared membranes were teste for pervaporation separation of ethyl acetate–water mixture on a setup shown in Figure 1. Homogenous sago/PVA membranes are placed in the pervaporation cell in a stainless steel plate between the solution in the feed and the permeate side without any supporting device to remove water from the solution by transport limitation to the surface of the membrane or gradient concentration. The effective surface area of the membrane for the pervaporation was 78 $cm^2$. The membrane thickness was 60 μm. The refractometric index test was used to analyze the composition of ethyl acetate and water in the permeate side after collecting it in the permeate collector. The downstream pressure was controlled by using vacuum

pressure levels and was kept below 3 mmHg. The experiments were conducted at different concentrations of 1wt%, 2wt%, 3wt% and 4wt% water in the feed and the feed temperatures of 30, 40, 50 and 60°C.

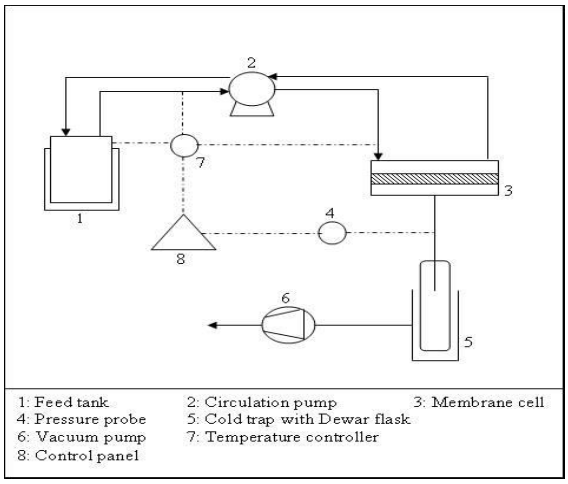



**Figure 1** Schematic diagram of pervaporation process

### 2.4 Membrane Characterization

#### 2.4.1 Fourier Transform Infrared (FT-IR) Spectroscopy

The cross-linked reaction of Sago/PVA membranes was confirmed by FTIR analysis. The FTIR spectra of blended membranes were scanned using Perkin Eimer Precisely Spectrum one. The absorption spectra were recorded from 4000-400 $cm^{-1}$.

#### 2.4.2 Degree of swelling measurements (DS)

Swelling experimental was done by drying the membranes at 40°C under vacuum for 6 hours. Various ethyl acetate- water mixtures, containing 1 to 4wt% water were used to immerse the samples for 48 hours at ambient temperature. Constant weight experiments were used to confirm that the swelled membranes had reached equilibrium. The swollen membranes were blotted carefully with tissue paper to remove any surface solution, and the weight of the swollen membranes was measured by a mass balance. The swelling degree was calculated using the following equation:

$$\text{Degree of swelling (\%)} = (W_s - W_d)/W_d) * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where (Ws) is the weight of the swollen membrane and (Wd) is the weight of the membrane before immersed in the solution.

#### 2.4.3 Contact Angle Measurements

Blended membranes were analyzed by water contact angle using a Drop Shape Analyzer–DSA100. The dionized water was dropped onto the surface of the membranes at several sites and at different times and the average value of the result was calculated as water content angle.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Membrane Characterization

#### 3.1.1 Infrared Spectroscopy

Figure 2 Showed IR of bended membranes names 3wt%, 5wt% and 7wt% of sago. It's clear that, when the amount of sago increased the absorption peak decrease. For 3wt% of sago the absorption peak at 3540 $cm^{-1}$ relates to intermolecular hydrogen bonding and hydroxyl group –OH. The absorption peak of 5wt% and 7wt% of sage were 3400$cm^{-1}$ and 3300$cm^{-1}$ respectively.

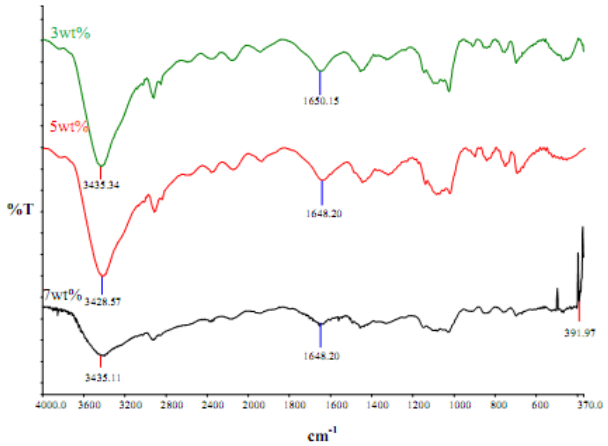



**Figure 2** FTIR spectra of blended sago membrane and blended ration

#### 3.1.2 Degree of Swelling

The effect of degree of swelling on the blended ratio membrane is illustrated in Figure 3. The degree of swelling on the blended membrane was plotted against sago content in the blended membrane. It is known that, the degree of swelling of the membrane depends on the composition and structure of the polymer membrane. The dry membranes were immersed in mixtures (1-4% water in ethyl acetate-water mixture). From Figure 3, the degree of swelling increased with increase of sago starch from 3wt% to 7wt%. 5 wt% of sago shows low degree of swelling compared to 3wt%. This may be because of increasing of hydroxyl group in the membrane. Moreover, the swelling increased with water content. At high water content and high starch content the degree of swelling was 65%, which is high for membrane that was used in pervaporation of ethyl acetate-water mixture. Figure 4 shows the effect of time and sago content on the degree of swelling of blended membrane. As we

can see, as the membrane take time in the solution mixture the degree of swelling increased from 20 hours to 80 hours for all membranes, after 80 hours in the mixture all membrane started to decrease in the swelling.

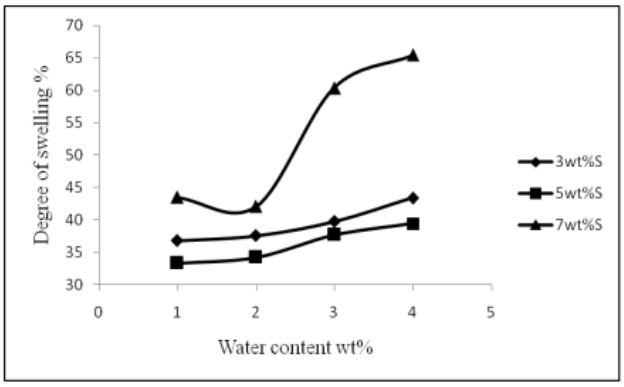



**Figure 3** Effect of degree of swelling on the blended ratio membranes (3wt%, 5wt% and 7wt% of sago)

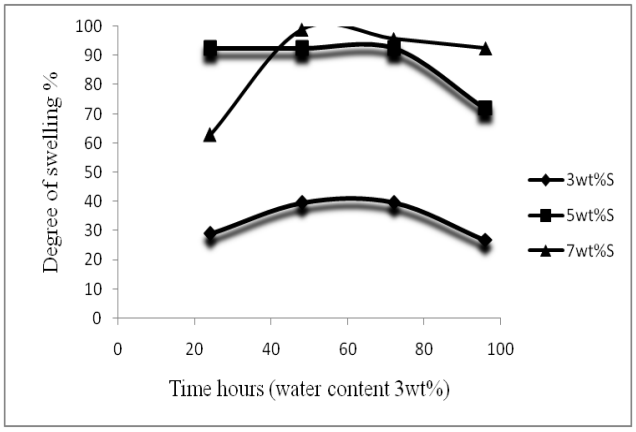


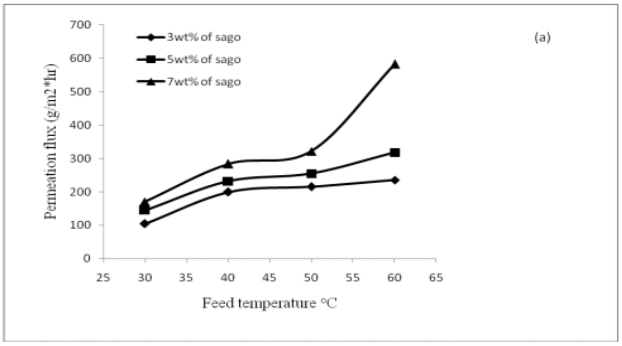

**Figure 4** Effect of time and sago content on the degree of swelling of blended membrane

### *3.1.3 Contact Angle Measurements*

The results of content angle measurements is summarized in Table 1, where the contact angle of sago/PVA membranes decreased with increase sago content in the blended membranes. This means that the membrane of high sago content has a high hydrophilicity, mainly due to more hydroxyl group in the membranes [18].

## 3.2 Effect of Feed Temperature

Feed temperature is an important parameter affecting the permeation flux and separation factor. Figure 5a shows the effect of feed temperature on the permeation flux for 3wt% of water in the feed. It is clear that, when feed temperature increased the permeation flux increases for all membranes. These phenomena can be demonstrated based on the solution diffusion model. When temperature increased, polymer chains have more free volume in the membrane, which increased in the diffusion in the membrane, as a result the permeation flux increased [19, 20]. Whereas, for separation factor, as feed temperature rises, the separation factor decreased exponentially, due to the increase in the free volume of the polymer membrane. Moreover, the increase in the sago starch from 3wt% to 7wt% escorted the increase in the permeation flux, because of the high hydrophilicity of the membrane as explained by the contact angle measurements. Figure 5b shows the effect of feed temperature on the separation factor, where the separation factor decreased by increasing the feed temperature for all membranes.



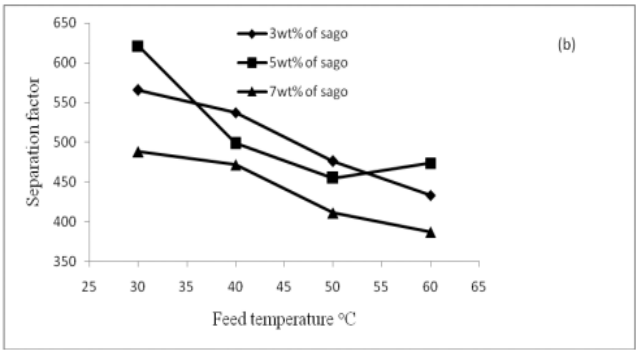




**Figure5 a, b** showed the effect of feed temperature on the permeation flux and separation factor

**Table 1** Contact angle of Sago/PVA membranes

| Sago content | Contact angle(°) |
|---|---|
| 3wt% | 86.4 |
| 5wt% | 75.11 |
| 7wt% | 50.34 |

### 3.3 Effect of Feed Composition

To scrutinize the effect of feed concentration on blended sago/PVA membranes, pervaporation of ethyl acetate-water mixture was performed from 1 wt% to 4 wt% of water in the mixture at 30°C, and did not show any unexpected phenomena on the separation factor and permeation flux [21, 22]. As we can see, increment in the water content in the feed leads to increase in the permeation flux from 1wt% to 4wt%. Furthermore, increasing the starch in the blended membrane resulted in the increment in the permeation flux as illustrated in Figure 6a. The effect of water content in the mixture on the separation factor is presented in Figure 6b. At higher water content in the solution, the membrane started to swell, resulting more free volume in the membrane that allowed both components to across the membrane, resulting the decrease in the separation factor [23]. Content angle measurements proved that the hydrophilicity of the membrane increase with sago starch content. As a result, the separation factor decreased with increase in the sago starch content in the membrane due to increasing hydrophilicity of the membrane, which makes membrane easy to swell.

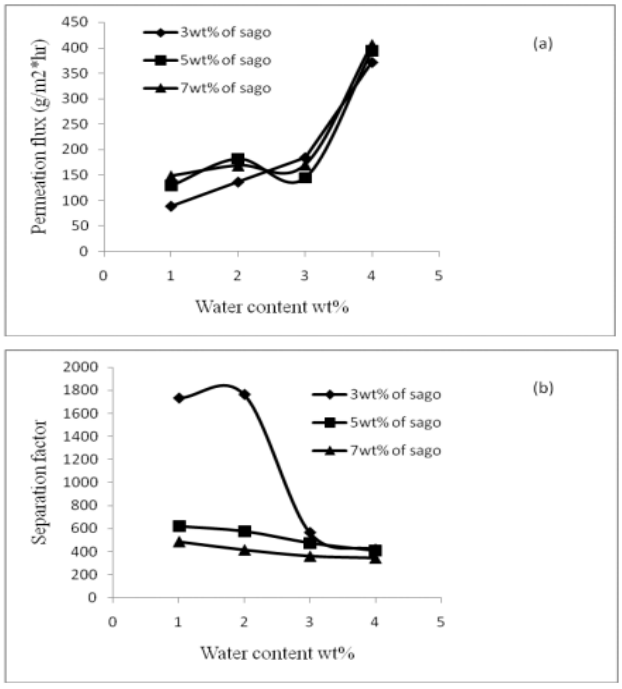



**Figure 6a, b** showed the effect of water content in the feed on the permeation flux and separation factor

## 4.0 CONCLUSION

Effect of sago content on the sago/PVA blended membranes was investigated. All the membranes were conducted for pervaporation of ethyl acetate-water mixture. The result showed that the increase of sago starch in the membranes leads to the increase in the permeation flux. Moreover, contact angle confirmed that in the blended membranes the hydrophilicity of the membrane increased with sago starch content. At 7wt% of sago in the blended membrane the flux was 582 g/m$^2$ .hr and the separation factor of 378, while the permeation flux and separation factor for 3wt% and 5wt% were 317 g/m2 .hr and 235 g/m$^2$ .hr with separation factor 473 and 433 respectively.

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