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Chemical Cross-linking of Sago/PVA Blend Membrane for Pervaporation Separation of Water from Ethyl Acetate Mixture

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Abstract –*Sago/PVA blend membranes were prepared by solution method for the pervaporation separation of water-ethyl acetate mixture. The membranes were cross-linked with glutaraldehyde (GA). Chemical cross-linked was prepared by immersing the membrane at room temperature for 30 min in chemical solutions containing different content of GA, sulfuric acid and acetone. IR spectroscopy was used to characterize the cross-linking reaction between the hydroxyl group of sago/PVA and the aldehyde group of GA. The membranes were also characterized using scanning electron micrographs (SEM) and degree of swelling (DS). The pervaporation separation of water-ethyl acetate mixture was performed over a range of 1-4 wt% of water in the feed at feed temperature varying from 30°C to 60°C to examine the separation performance of the sago/PVA membranes.*

Keywords: Sago starch, Pervaporation, Ethyl acetate, Polyvinyl alcohol, Composite Membrane

1.0 INTRODUCTION

Pervaporation (PV) is a membrane separation process that has been studied intensively to separate alcohol/water mixture such as ethanol/water, iso-propanol/water and ethyl acetate/water [1-3]. Two main advantages of pervaporation are no pollution and high production efficiency [4, 5]. The recovery of ethyl acetate from water by pervaporation process has received more attention over the years. Ethyl acetate is an important solvent and widely used in various manufacturing processes such as the production of drugs in the pharmaceutical industry. It is also used in the chemical industry for manufacturing cleaning fluids, inks, coated paper and perfume [6,7]. Ethyl acetate is produced by the esterification of acetic acid and ethanol with water as waste product [8]. In addition, a large amount of ethyl acetate is produced as waste from chemical and pharmaceutical industry processes [6]. The recovery of ethyl acetate from water is complex and expensive since the separation of azeotrope, and water uses a distillation column that requires an entrainer that must be removed [9-12]. 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 [13-15]. However, high separation factor and permeation flux highly depends on the membrane material and operating conditions such as feed temperature and concentration. In general, hydrophilic polymer materials with O-H groups are usually preferred as membrane materials. Extensive research has been carried out to develop

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environmentally friendly, starch-based polymers for renewable energy applications. Sago starch is evidently a hydrophilic polymer, which is an interesting material to develop for water removal from alcohol. In this study, an azeotrope forming mixture of ethyl acetate-water was separated using sago/PVA membrane. The effects of different operating conditions on the separation are discussed in this work.

2.0 MATERIALS

Sago starch as the main raw material was donated by Ng Kia Heng Sago Industries Sdn Bhd, Batu Pahat, Johor. Mean while, hydrolyzed polyvinyl alcohol (86,000 MWt) of 99-100% purity, ethyl acetate (99% purity), N, N-dimethlyformide (DMF) and glutaraldehyde were purchased from New Jersey USA. Sulfuric acid (99% purity) and acetone (C_3H_6O) were obtained from QReC Chemicals (Asia) Sdn Bhd and deionized water. The chemicals were of analytical grade and used without further purification. Water was deionized in the lab before used.

3.0 METHODS

3.1 Membrane preparation

The preparation of sago membrane was started by dissolving 3wt% and 10wt% of sago and PVA respectively in hot water for 4 h at 90°C. Sago and PVA were mixed by 50wt% for each material and stirred for 24 h at 70°C. The membrane was casted onto glass plate and dried in ambient air for 72 h. After that, the membrane chemical cross-linked was prepared by immersing the membrane in a chemical solution containing 0.5wt% sulfuric acid (H_2SO_4), 2.5wt% glutaraldehyde, 48wt% acetone and deionized water for 30 min. All films were immersed at room temperature. The films were removed and washed continuously and immersed in distilled water for 7 h and then dried at room temperature.

3.2 Characterization of the membrane

The membrane was characterized by degree of swelling (DS) and scanning electron micrographs. The swelling degree was calculated using the following equation (1):

$$\text{Degree of swelling } (\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

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

Penerbit Akademia Baru

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4.0 RESULTS AND DISCUSSION

4.1 Characterizations of the membrane

4.1.1 IR spectra analysis

Cross-linked of sago/PVA membranes is an effective method to decrease the degree of swelling of the membrane polymer. Fig. 1(a), (b) and (c) presents the IR spectra of the sago/PVA membranes cross-linked using different GA solution content in the reaction solution. As can be observed, there is a decrease in the absorption peak at 3000-4000 for 2.5wt% GA, 5wt% GA and 10wt% GA.As the GA content increases, the absorption peaks increase due to the reaction between hydroxyl group (-OH) of sago/PVA and aldehyde group (-CH=O) of GA. Correspondingly, two additional absorption peaks appeared at 980 and 1260cm^{-1}, which arise from the formed acetal group (-C-O-C-O) and ether group (-C-O-C) in the polymer network, respectively [6].

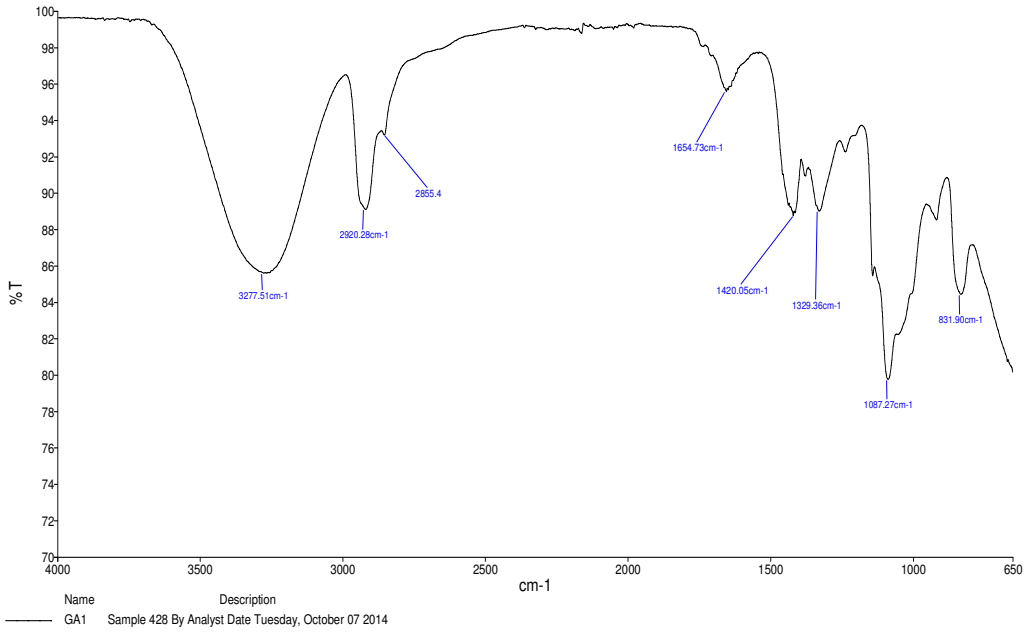

Figure 1 (a): IR spectra of sago/PVA membrane cross-linked with 2.5wt% GA.

4.1.2 Membrane morphology and effect of GA content on the degree of swelling

The surface morphology of cross-linked and non-cross-linked of sago/PVA bend membranes has been studied using scanning electron microscopy and the results are presented in Fig. 2 and Fig. 3. It is clear that the membranes are considered as dense membranes in this study. From Fig. 2, it is clearly observed that the surface of chemical cross-linked membrane is rougher compared to non-cross-linked membrane. Fig. 4 shows the effect of the degree of swelling on the cross-linked membrane. It can be observed that the increase in the GA solution content decreases the degree of swelling from 50% at 2wt% of GA to 20% at 10wt% of GA due to the presence of hydroxyl group in sago and PVA reacts with aldehyde group during the cross-linking reaction.

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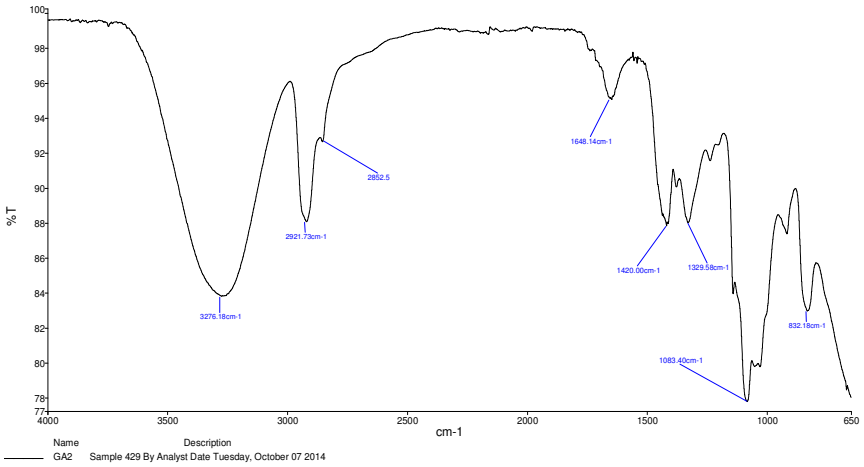

Figure 1 (b): IR spectra of sago/PVA membrane cross-linked with 5wt% GA.

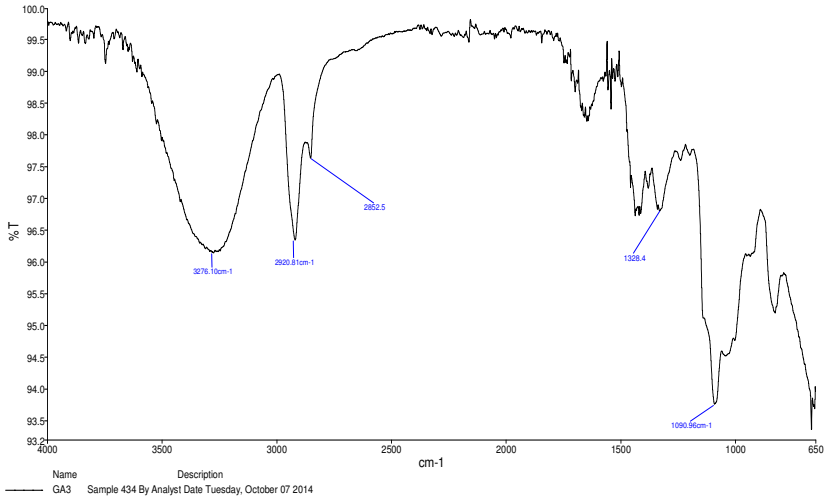

Figure 1 (c): IR spectra of sago/PVA membrane cross-linked with 10wt% GA.

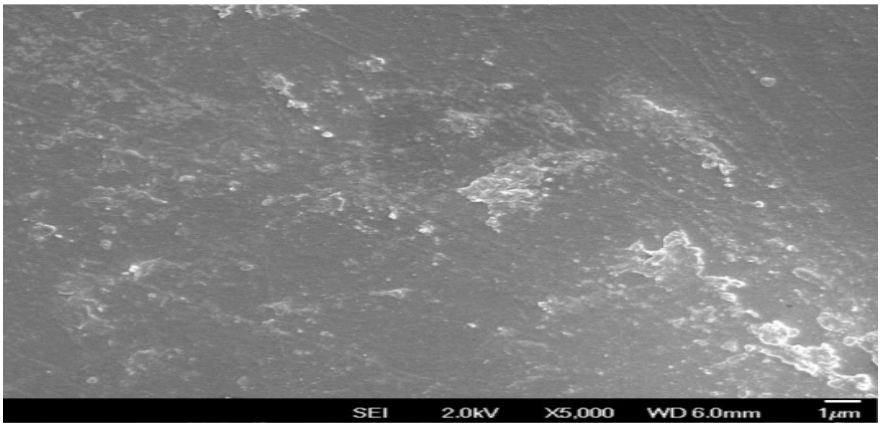

Figure 2: SEM of chemical cross-linked membrane.

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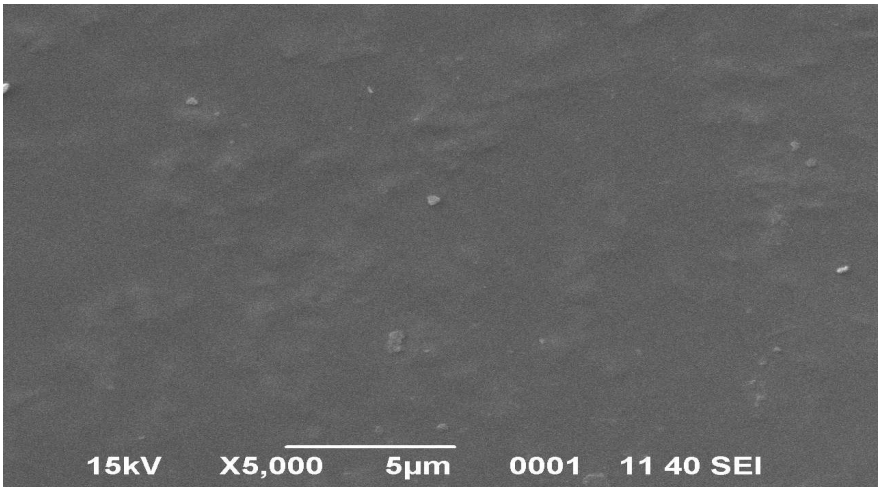

Figure 3: SEM of non-cross-linked membrane.

4.1.3 Effect of GA content on the permeation flux

Fig. 5shows the effect of GA content on the permeation flux. It is clear that the 5wt% GA has high permeation flux. At high GA content, the more hydrophilic groups are consumed the more hydrophobic groups are formed. These changes reduce the hydrophilicity of the membrane, and at low GA content, the hydrophilicity of the membrane is too high, which increases the membrane swelling, and consequently decreases the separation factor [3].

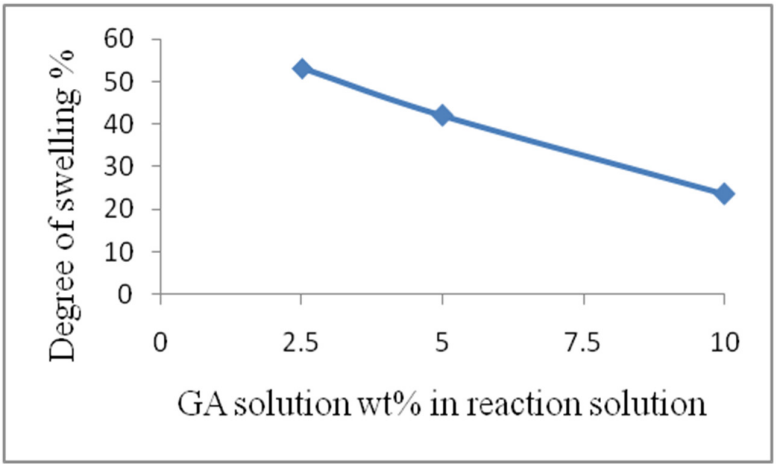

Figure 4: Effect of GA content on swelling.

4.2 Pervaporation

4.2.1 Effect of feed temperature and concentration

At 5 wt% of GA solution content in the reaction solution, the membrane shows the highest permeation flux in the separation of ethyl acetate–water mixture as presented in Fig. 5 [16]. This membrane was used for the separation of ethyl acetate-water mixture over the range of

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1-4wt% of water in the solution and over the range of 30ºC-60ºC of feed temperature. As can be seen from Fig. 6 (A), the increase in feed temperature leads to the decrease in the separation factor.

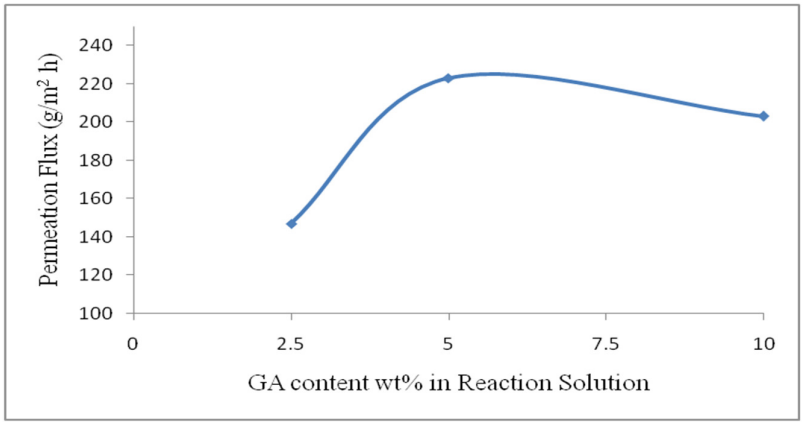

Figure 5: Effect of GA content on the permeation flux.

Fig. 6 (B) shows the effect of feed temperature on the permeation flux. It is clear that the total flux increased by increasing the feed temperature and concentration due to swelling behaviour of the membrane. Swollen membrane makes the polymer network more flexible for ethyl acetate molecules to transport to the permeate side and thereby lowering the separation factor as presented in Fig 6 (A). Moreover, with an increase in temperature, more energy is supplied to the transported solvent that can vaporize more easily on the permeate side [6].

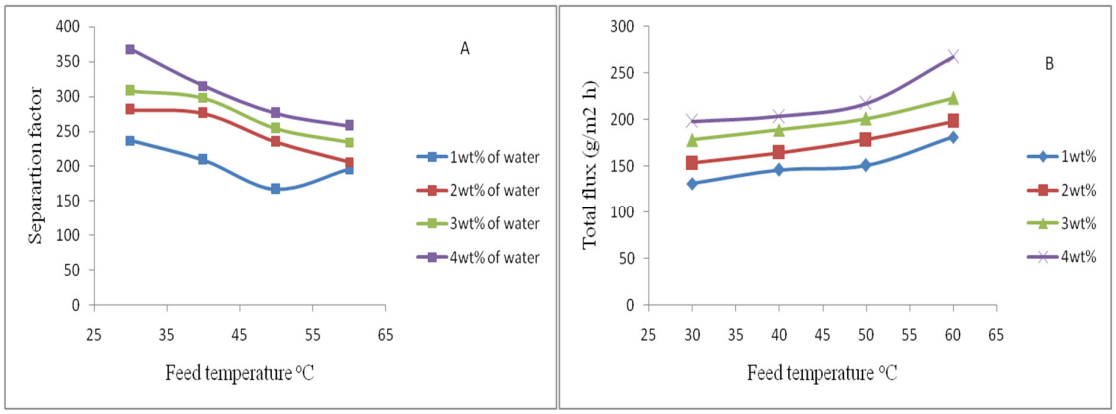

Figure 6 (A,B): Effect of feed temperature and concentration on the pervaporation of ethyl acetate-water

5.0 CONCLUSION

Sago/PVA blend membranes were prepared and tested for pervaporation of ethyl acetate-water mixture. The effects of feed temperature, feed concentration and glutaraldehyde cross-

linked were investigated and the membranes were characterized using SEM and degree of swelling. The membrane shows good separation factor and is very stable during the pervaporation process.

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