Original Article

Sago/PVA blend membranes for the recovery of ethyl acetate from water


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Abstract Sago starch is a relatively new polymeric material for development of a hydrophilic membrane for dehydration of alcohol/water. In this study sago based membranes were developed through casting technique for the dehydration of ethyl acetate at azeotropic conditions via pervaporation. Sago was blended with polyvinyl alcohol (PVA) to produce blended sago–PVA membranes with improved physical and chemical properties. The membranes were cross-linked using three different approaches; firstly, using glutaraldehyde, secondly using thermal treatment (80°C) and thirdly by using both glutaraldehyde and thermal treatment. The effects of various cross-linking methods on the intrinsic properties of hydrophilic polymer membrane were investigated. The membranes were characterized using Fourier transform infrared (FTIR), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). The effect of operating conditions such as feed temperature and concentration on the separation factor and flux was discussed. Sago starch polymer shows very high performance and very good stability after polymer blending and cross-linking, which is promising for use in industrial applications.

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1. Introduction

Pervaporation 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 (Xia et al., 2011; Ghazali et al., 1997; Zhang et al., 2009a). Two main advantages of pervaporation are no pollution and high production efficiency (Zhang et al., 2009b; Huang and Yeom, 1991). All chemical and pharmaceutical industries are presently expressing incredible interest in new technologies that offer low energy consumption, high separation efficiency and are eco-friendly in nature (Rachipudi et al., 2011; Hyder...
Pervaporation has several applications such as the recovery of water from organic mixtures with, similar boiling point and dehydration (Huang and Yeom, 1991; Hasanog˘lu et al., 2005; Liu et al., 2011). Ethyl acetate is an important solvent, widely used in various manufacturing processes such as the production of drugs in the pharmaceutical industry. It was also used in the chemical industry for manufacturing cleaning fluids, inks, coated paper and perfume (Yongquan et al., 2012; Yuan et al., 2011). The recovery of ethyl acetate from water is complex and expensive since the separation of azetrope and water uses a distillation column which requires an entrainer that must be removed (Wu et al., 2012). 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. However high separation factor and permeation flux depend on the membrane material and operating conditions such as feed temperature and concentration (Zhao et al., 2009). Table 1 summarizes the effect of different materials for recovery of ethyl acetate and water mixture. In general hydrophilic polymer materials with O–H groups are usually preferred membrane materials. Extensive research has been done to develop membranes by blending for dehydration of alcohol/water mixtures such as chitosan, polyvinyl alcohol, and cellulose. However high separation factor and permeation flux depend on the membrane material and operating conditions such as feed temperature and concentration (Zhao et al., 2009). Table 1 summarizes the effect of different materials for recovery of ethyl acetate and water mixture. In general hydrophilic polymer materials with O–H groups are usually preferred membrane materials. Extensive research has been done to develop membranes by blending for dehydration of alcohol/water mixtures such as chitosan, polyvinyl alcohol, and cellulose. However high separation factor and permeation flux depend on the membrane material and operating conditions such as feed temperature and concentration (Zhao et al., 2009). Table 1 summarizes the effect of different materials for recovery of ethyl acetate and water mixture. In general hydrophilic polymer materials with O–H groups are usually preferred membrane materials. Extensive research has been done to develop membranes by blending for dehydration of alcohol/water mixtures such as chitosan, polyvinyl alcohol, and cellulose. However high separation factor and permeation flux depend on the membrane material and operating conditions such as feed temperature and concentration (Zhao et al., 2009). Table 1 summarizes the effect of different materials for recovery of ethyl acetate and water mixture.

Table 1 Comparison between different materials on the separation of ethyl acetate/water mixture.

<table>
<thead>
<tr>
<th>Water content in the feed</th>
<th>Temperature °C</th>
<th>Membrane material</th>
<th>Crosslinking</th>
<th>Flux J/(kg/m²·h)</th>
<th>Separation factor a</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1–2.5) wt.%</td>
<td>30–60</td>
<td>Polyvinyl alcohol</td>
<td>Yes</td>
<td>(0.0001–0.0065)</td>
<td>(10⁻¹–10⁻⁴)</td>
<td>Salt et al. (2005)</td>
</tr>
<tr>
<td>5.1 wt.%</td>
<td>60</td>
<td>PVA/ceramic composite</td>
<td>No</td>
<td>1.45 * 10⁻⁴</td>
<td>129</td>
<td>Xia et al. (2011)</td>
</tr>
<tr>
<td>9 wt.%</td>
<td>35</td>
<td>Chitosan/poly (vinyl pyrrolidone)</td>
<td>No</td>
<td>0.953</td>
<td>746</td>
<td>Zhang et al. (2009a)</td>
</tr>
<tr>
<td>97 wt.%</td>
<td>30–50</td>
<td>Poly(vinylidene fluoride-co-hexafluoropropene)</td>
<td>No</td>
<td>0.2–2</td>
<td>100</td>
<td>Tian and Jiang (2008)</td>
</tr>
<tr>
<td>95 wt.%</td>
<td>60</td>
<td>Commercial NaA zeolite</td>
<td>No</td>
<td>2.65</td>
<td>200–500</td>
<td>Shah et al. (2000)</td>
</tr>
<tr>
<td>4 wt.%</td>
<td>60</td>
<td>Sago/PVA</td>
<td>No</td>
<td>0.3</td>
<td>9000</td>
<td>This work</td>
</tr>
</tbody>
</table>

The sago starch as main raw material was donated by Ng Kia Heng Sago Industries Sdn Bhd, Batu Pahat, Johor; Hydrolyzed polyvinyl alcohol (86,000 MWt) 99–100% purity, Ethyl acetate (99% purity) and glutaraldehyde were purchased from New Jersey, USA. The sulfuric acid (99% purity) was obtained from Thailand, while acetone (C₃H₆O) was obtained from QReC Chemicals (Asia) Sdn Bhd and deionized water. The chemicals were analytical grade and were used without further purification. Water was deionized in the laboratory before used.

2.2. Preparation of sago/PVA membranes

Sago starch (3 wt.%) and (10 wt.%) of PVA were dissolved in hot water at 90 °C to make a homogenous solution for 3 and 6 h respectively and separately. Subsequently the sago solution and PVA was mixed [50 wt.%, 50 wt.%] and stirred at 70 °C for 24 h. The solution was kept in the oven for 24 h before casting. The solution was cast onto a glass plate and dried in ambient air for 72 h. The membrane was then cross-linked to achieve good selectivity and high permeation flux by first chemically immersing the membrane in a chemical solution containing 0.5 wt.% sulfuric acid (H₂SO₄), 2.5 wt.% glutaraldehyde, 48 wt.% acetone and deionized water for 30 min. All films were immersed at room temperature. The films were removed and washed continuously with distilled water and immersed in distilled water for 7 h at room temperature to remove residual H₂SO₄. The membrane was then removed from distilled water and dried at room temperature for 24 h. The second cross-linking stage was carried out via heat treatment by casting the film onto a glass plate followed by immediate placement of it in an oven at 70 °C for 4 h. On completion the membrane was removed from the oven and the film peeled off the glass. The third crosslinking involved chemical and thermal treatment, in which the membranes were first treated by chemical solution for 30 min and washed using distilled water and were further heat treated in an oven at 70 °C for 4 h. All sago/PVA membranes were subsequently tested for stability and separation performance by pervaporation using ethyl acetate–water mixture (water content in the feed 1–4 wt.% at azetrotic point).
2.3. Characterization

2.3.1. Thermal analysis

The membrane samples were characterized using Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA). DSC thermal analysis was carried out using Differential Scanning Calorimetry (Model TA Instruments model DSC 2920). The analysis was carried out by heating 6–8 mg in an aluminum crucible from 0 to 200 °C at a heating rate of 10 °C/min using nitrogen gas (N₂) as a sweeping gas. The resulting DSC scans were corrected for baseline. Thermogravimetric analysis (TGA) was carried out using a simultaneous DSC–TGA analyzer (TA Instruments, model SDT 2960) by heating samples from 30 to 200 °C at a heating rate of 10 °C/min.

2.3.2. FTIR spectroscopy

FTIR spectroscopy was used to determine the chemical composition of each membrane film before and after crosslinking. The absorption spectra were recorded from 4000 to 400 cm⁻¹. The four samples analyzed were labeled pristine normal (N), chemical (CH), thermal treatment (TH) and chemical + thermal treatment (CH + TH).

2.3.3. Scanning electron microscopy (SEM)

Sago/PVA blend membranes were examined using scanning electron microscopy. The sago/PVA cross-linked membrane specimens were initially dried under vacuum at room temperature for 24 h. Then the specimens were fractured in liquid nitrogen to prevent spoiling of the sago/PVA membranes polymer structures. After that, the prepared samples were mounted onto top of metal aluminum stub and sputter-coated with gold prior to the macroscopic observation.

2.4. Pervaporation

The pervaporation of ethyl acetate–water mixture was tested using the apparatus which is described in Fig. 1. The membrane was placed in the cell without any supporting device to remove water from the solution using a membrane to separate the solution and permeate. The effective membrane area for pervaporation was 78 cm². The vacuum pressure was kept below 3 mm Hg while the experiments were carried out at temperatures between 30 and 60 °C. The concentration of ethyl acetate in the feed was 1–4 wt.%. The permeate was collected in an icecooled collector. The composition of the permeate was analyzed using a refractometric index to determine the concentration (in%) of ethyl acetate in the water. The errors inherent in the pervaporation measurements are less than 1.0%. The total permeate flux (J) was calculated from the following equation:

\[ \text{Permeation flux} (J) = \frac{w}{A \times \Delta t} \]  

(1)

where \( w \) refers to the amount of the permeate (g), \( A \) refers to the effective area (m²) of the membrane used in the pervaporation and (\( \Delta t \)) is the time (h).

The separation factor \( \alpha \) was calculated from the values of the weight fractions of water and ethanol in the permeate, \( X_w \) and \( X_{eth} \), and in the feed, \( x_w \) and \( x_{eth} \). As written in Eq. (2)

\[ \alpha = \frac{Y_w / Y_{eth}}{X_w / X_{eth}} \]  

(2)

3. Results and discussion

3.1. Membrane characterization

3.1.1. DSC

The results showed that the structure of sago starch and polyvinyl alcohol was modified after crosslinking. For sago starch material, helical structures which are subsequently crystallized were observed. In contrast the polyvinyl alcohol revealed a semi-crystalline structure after cross-linking. Differential scanning calorimetry can be used to detect changes in the melting temperature (\( T_m \)) of cross-linked membrane material. The DSC curve of sago/PVA membrane is presented in Fig. 2. A melting endothermic peak was observed at 96 °C for chemical cross-linked membrane, whereas the melting endothermic peak for normal membrane can be seen at 60 °C. For thermal cross-linked membrane and (CH + TH) cross-linked membrane the melting endothermic peak was observed at 208 °C and 90 °C respectively. Finally, it can be seen that the melting temperature of the membranes investigated increased after cross-linking.

3.1.2. Thermal stability TGA

The thermal stability of pure sago starch/PVA and its cross-linking membranes was investigated using TGA analysis under nitrogen flow. The resulting thermograms are shown in Figs. 3. From the thermograms, it is clear that all membranes exhibited three consecutive weight loss steps. In pure sago starch/PVA membrane as shown in Fig. 3a, the first weight loss of 20% occurred at temperatures ranging between 60 °C and 250 °C. The second weight loss of pure sago starch/PVA membrane was 6% which occurred between 250 °C and 300 °C, corresponding to physically absorbed water molecules. It is generally accepted that absorbed water molecules exist in a bound state rather than in a free molecular state (Shao et al., 2003; Guan et al., 2006). However the water molecules may be
bound directly to the polymer chain through hydrogen bonds. For the chemical crosslinking membrane presented in Fig. 3b, the first weight loss was 22% which occurred at temperatures between 50 °C and 300 °C. Compared to the non-cross-linked membrane the weight loss for the chemical crosslinking membrane increased although at a higher temperature, 300 °C, which may be due to desorption of the physically absorbed water molecules in the membrane. The second weight loss for the chemical cross-linked membrane was 80% at temperatures ranging between 300 °C and 450 °C which corresponds to the decomposition of sago starch and polyvinyl alcohol. Fig. 3c presents the TGA curves for the thermally treated membrane. The first weight loss for the sample, 19.87%, occurred between 60 °C and 200 °C, due to the loss of

Figure 2  DSC curve of effect of different crosslinking on sago/PVA blend membrane, (N = noncrosslinking, CH = chemical crosslinking, TH = thermal crosslinking, CH + TH = chemical + thermal crosslinking).

Figure 3a  TGA for noncrosslinking sago/PVA membrane.
absorbed water. The second weight loss was 83% observed between 200 °C and 400 °C, which may due to corresponding structural decomposition of sago/PVA. For the chemical and thermal cross-linked membrane, the first weight loss was 12.17% which occurred between temperatures of 50 °C and 280 °C, due to physical change in the polymer after dehydra-

Figure 3b   TGA for chemical crosslinking membrane.

Figure 3c   TGA for thermal crosslinking membrane.
tion. The second weight loss was 87% which occurred between 300 °C and 450 °C as presented in Fig. 3d. In comparison with the initial membrane chemical + thermal cross-linked membrane displayed better stability. In general pervaporation operating temperature was less than 100 °C, which shows all membranes meet the thermal stability requirement.

3.1.3. FTIR

The FTIR spectrum of pristine sago/PVA and its effect on cross-linked membranes is presented in Fig. 4. The absorption peak for normal sago/PVA membrane was observed from 3830 to 3865 cm$^{-1}$ corresponding to the hydroxyl (–OH) group. For the cross-linked membranes, CH, TH and CH + TH, a
decrease in absorbance was found at $\sim 3750 \text{ cm}^{-1}$ as compared to the non-cross-linked sago/PVA membrane. Correspondingly, there is an increase in absorbance at $\sim 1800 \text{ cm}^{-1}$. The hydroxyl groups in the poly (vinyl alcohol) and sago starch also have several hydroxyl groups on the starch chain which react with the aldehyde group during the chemical crosslinking. The products of the chemical reaction between poly (vinyl alcohol) and glutaraldehyde are acetal groups or ether linkages and esters due to sago starch in the polymer network. For the cross-linked membranes (TH and CH + TH), the increase in the absorbance peak at $\sim 1800 \text{ cm}^{-1}$ is probably due to $-\text{COC}$ groups. At CH + TH cross-linked film, the membrane contains several $-\text{OH}$ groups, and as the cross-linking reaction duration was only 30 min, the aldehyde could not be completely reacted. FTIR showed that the intrinsic properties of cross-linked membranes have changed compared to non-cross-linked membrane. In conclusion, the decrease of (-OH) group in the membrane leads to decrease in the permeation flux.

3.1.4. Scanning electron microscopy (SEM)

The surface morphology of cross-linked and non-cross-linked sago/PVA blend membranes was studied using scanning electron microscopy and the results are presented in Fig. 5. As we can be clear from the photographs it is clear that the membranes are considered as dense membranes in this study. It is known that the non-cross-linked polymer surface is smoother than the cross-linked membrane. From the figures, it can be clearly observed that the chemical cross-linked membrane is rougher than other membranes and that the normal membrane is smoother. All these membranes were tested for separation of ethyl acetate from water. The non-cross-linked membrane shows high separation and permeation flux compared to cross-link due to surface roughness of the membranes. Furthermore, high membrane roughnesses of membrane surface made hardness of dissolving of water onto the membrane surface while the smoothest membrane had a superior ability to dissolve water onto the top of the membrane surface.

3.2. Pervaporation results

3.2.1. Effect of feed temperature

Temperature is an important parameter in pervaporation as it affects the sorption and diffusion rates (Moheb Shahrestani et al., 2013). Fig. 6a, shows the effect of feed temperatures on pervaporation of ethyl acetate and water for all membranes in the range of 30–60 $^\circ$C. Conventionally, an increase in feed temperature results in an increase in the permeation flux and a decrease in separation factor. From Fig. 6a we can observe that the permeation flux of the normal membrane (without cross-linking), increased from 0.4 (kg/m h) at 30 $^\circ$C to 4.9 (kg/m h) at 60 $^\circ$C. This can be explained by increased mobility
and hydrophilicity of the polymer chains and free volume expansion. However, the non-cross-linked membrane showed a higher flux than the chemical + thermal cross-linked with permeation flux 0.162 (kg/m h) at 30 °C, an increase of 0.132 kg compared to chemical cross-linked membrane at the same feed temperature. The permeation flux at 60 °C was 0.549 (kg/m h). The increase in flux for non-crosslinked membrane can be explained by the structure of the membrane, which is more hydrophilic without cross-linking. In addition, the thermally treated membrane showed good stability and higher flux compared to chemical cross-linked membrane and chemical + thermal crosslinking membrane. Furthermore, the permeation flux increased with increasing temperatures, although a decrease in flux at 50 °C was observed for all other membranes. The permeation flux for thermal treatment membrane was 0.217 (kg/m h) at 30 °C, but increased to 1.192 (kg/m h) at 60 °C. Non-cross-linked membrane has shown the highest permeation flux compared to other crosslinking membranes. The permeation flux was 0.148 (kg/m h) at 30 °C, which is lower than chemical + thermal and heat treatment membrane at this temperature, but the flux was maximum at 60 °C, which was 4.967 (kg/m h). Fig. 6b shows the effect of feed temperature on the separation factor for all membranes. The best separation factor was for chemical cross-linked membrane as shown in the figure compared to other membranes that have cross-linking. The separation factor was 9000 at 60 °C for chemical cross-linked membrane due to decrease in the degree of swelling after cross-linked, while the separation factors were 1960, 1760 and 400 for heat treatment, chemical + thermal and non-cross-linked membranes respectively.

The result demonstrated that the various cross-linking of sago/PVA membrane led to variation in the membrane performance. As an illustration, the value of permeation flux for non-cross-linked membrane was high compared to other membranes due to changes in the intrinsic properties of the membrane polymer as explained in the membrane morphology and also due to the surface of this membrane which was more hydrophilic and smooth compared to other membranes. The maximum observed were for non-cross-linking which was around (4960 (g/m² h)) and the lowest was for chemical cross-linking. Moreover, all cross-linked membranes show good stability during pervaporation of ethyl acetate–water mixture (Albo et al., 2014).

3.2.2. Effect of feed concentration

The effect of water content on the permeation flux is shown in Fig. 7. All four different membranes were carried out at different feed concentrations at 30 °C. As seen from Fig. 7, with an increase in the water content in the feed from 1 to 4 wt.% for all membranes, the permeation flux increased. It can be seen that the ethyl acetate decreased in the feed solution when the water content in the permeate increased. This is due to two reasons. First, water transport increases when water content increases in the feed, resulting in a corresponding increase in the total permeation flux. Secondly, higher water content makes membranes swell thereby increasing the flexibility and network of polymers. However an increase in water content lowers membrane selectivity preventing ethyl acetate and water from permeating the membrane (Hyder et al., 2006). On the other hand, there is a difference in the permeation flux in each membrane. As seen in Fig. 7, at 1 wt.% water content in the feed, the lowest permeation flux was for chemical + thermal cross-linking membrane, and the highest was for non-cross-linking membrane. At 4 wt.% water the permeation flux for chemical + thermal cross-linking membrane was higher than normal and thermal membranes. Generally speaking, when the water content increased in the feed, the degree of membrane swelling will increase as well. Moreover, when water content increased the interaction of both water and ethyl acetate with the membrane becoming more intensive, this could increase the transport speed of the permeation molecules.

4. Conclusion

Pervaporation of ethyl acetate–water mixture through Sago/PVA blend membranes was conducted. The effect of various cross-linking on the separation of ethyl acetate–water and the effect of feed temperature and feed concentration on the permeation flux and separation factor were investigated. Sago/PVA membranes were cross-linked in three different ways. First chemically; second thermal cross-linked and third one was chemical + thermal cross-linked. FTIR, DSC and TGA were used to determine the intrinsic properties of sago/PVA blend membranes. FTIR measurements of sago/PVA membrane showed that the hydroxyl polymer group decreased with chemical cross-linked membrane. The decrease of hydroxyl groups for chemical cross-linked membrane was due to the formation of an acetal linking group after cross-linking reaction, and as a result, the membranes are less hydrophilic. DSC showed an increase in the melting temperature for all membranes after cross-linking reaction. The pervaporation
experiment showed that the non-cross-linked membrane gives high permeation flux (4960 g/m² h) at 60 °C due to the surface of the membrane is highly hydrophilic and smooth compared to other membrane. The highest separation factor was for chemical cross-linked membrane (9000) at same feed temperature 60 °C compared to other cross-linked membranes. Finally, all cross-linked membranes showed excellent stability during the pervaporation work.

Acknowledgments

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References


