Effect of Cross-Linking Time on the Thermal and Mechanical Properties and Pervaporation Performance of Poly(Vinyl Alcohol) Membrane Cross-Linked with Fumaric Acid Used for Dehydration of Isopropanol

Maryam Heydari,[1] Ahmad Moheb,[1] Mehran Ghiaci,[2] Mahmood Masoomi[1]

[1]Department of Chemical Engineering, Isfahan University of Technology, Isfahan 8415683111, Iran
[2]Department of Chemistry, Isfahan University of Technology, Isfahan 8415683111, Iran
Correspondence to: A. Moheb (E-mail: ahmad@cc.iut.ac.ir)

ABSTRACT: Cross-linked poly (vinyl alcohol) membranes were prepared using fumaric acid as the cross-linking agent and were used for the pervaporation separation of water/isopropanol mixtures. Cross-linking process was carried out at 150°C at three different times of 10, 30, and 60 min. The membranes were characterized by different known methods of FT-IR, TGA, XRD as well as tensile test. The effects of cross-linking time on the thermal and mechanical properties of the membranes and also their pervaporation performance were investigated. Formation of more ester groups by increasing the cross-linking time was confirmed by the FT-IR results. TGA analyses showed that thermal stability of the membranes is improved by prolonging the duration of cross-linking process. This was due to the formation of more compact structure in the membranes. The XRD results revealed that the crystalline regions of the membranes were relatively diminished with an increase in the cross-linking time. No specific trend was observed for the variation of tensile strength at break with the cross-linking time. The PVA membrane cross-linked for 60 min showed high selectivity of 1492 for water permeation for the feed mixture containing 10 wt % water. The temperature dependency of the permeation flux was investigated using Arrhenius relationship, and the activation energy values were calculated for total permeation (E_p), water (E_{pw}), and IPA (E_{pIPA}) fluxes. Lower value of E_{pw} in comparison with E_{pIPA} supported excellent dehydration performance of the cross-linked membranes. Despite large increase in activation energy of water with prolonged cross-linking time, the selectivity was improved. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

INTRODUCTION

Pervaporation (PV) is an emerging and promising membrane-based process which is widely used for separation of liquid-phase mixtures. This clean, cost effective, and energy-saving process is a proper mean to separate the components of close boiling point and azeotropic mixtures where distillation processes encounter difficulties.[1] Also, PV is usually carried out at ambient temperature and therefore is useful for separating thermal-sensitive components.[2–4] PV processes could be recognized from other membrane separation processes with a phase change occurring for the separated species while transferring across the membrane. The performance of PV is highly affected by the membrane type and its characteristics. Polymeric membranes are extensively used in PV processes because of their intrinsic characteristics. In comparison to the zeolite membranes, they are easy to fabricate and therefore more economic.[5] Hydrophilic polymeric membranes are widely used in PV for separation of

azeotropic mixtures and dehydration of alcohols and other organics in various industrial processes.[6–8] Among different polymeric materials, poly (vinyl alcohol) (PVA) is a suitable and attractive polymer for making hydrophilic membranes. PVA is used by many researchers due to its good film-forming property[9] and good mechanical, thermal, and chemical resistances.[10–12] PVA is a semicrystalline polymer with a large number of polar hydroxyl groups that can make strong hydrogen bonds between polymer chains.[13] While using a PVA membrane for dehydration of an organic solution, swelling of the membrane occurs due to strong interaction between water molecules and hydroxyl groups in PVA. This characteristic strongly influences the membrane selectivity.[14] Also, poor stability of the PVA membranes in aqueous solutions strongly affects the mechanical properties of the membrane. To overcome the above-mentioned problems, it is necessary to make proper modifications on the membrane structure.[15] Some different modification methods

such as cross-linking, blending with other polymers, and incorporating of fillers into the PVA matrix have been used by researchers to reduce the swelling effect and improve the PVA membrane properties.[16–18] Of these methods, cross-linking of the polymer seems to be most attractive and is widely attended by the researchers. Cross-linking of the polymer changes the ratio of crystalline to amorphous regions in the polymer matrix and in most cases cross-linking reduces this ratio. Also, by cross-linking the chain flexibility of the side groups in the polymer matrix is reduced which in turn prevents the swelling effect and resulting reduction in the separation factor of the membrane. Some publications have reported the insolubilization of PVA by cross-linking. PVA can be cross-linked by several chemicals such as citric acid, adipic acid, maleic acid and glyoxal,[19] malic acid,[20] and amic acid.[21] Xio et al. cross-linked PVA with trimesoyl chloride.[22] Glutaraldehyde also is widely used for cross-linking of PVA.[12] Sulfur–succinic acid is another cross-linking agent which has been used by Felipe et al.[23] In these works, mostly the effect of cross-linking agent type has been the main subject of the work. However, during cross-linking of the polymeric membranes, some other different parameters have significant effects on the properties of the synthesized membranes.[24] One of the most important effects is the duration of cross-linking. Cross-linking duration strongly affects the degree of the cross-linking of the membrane.[15] Because of the reduction of OH groups during the cross-linking and changes in the crystallinity regions and hydrophilicity of polymer, duration of the cross-linking process affects the mechanical and thermal stability as well as membrane performance which is evaluated by means of pervaporation tests. The effect of cross-linking time on the separation properties of the PVA membrane was studied by Kusumocahyo et al. In their work, PVA was cross-linked by glutaraldehyde, and the synthesized membrane was used to study the water permselectivity in the pervaporation of acetic acid–water mixture.[15] In another work, Praptowidodo investigated the effect of cross-linking time of PVA by glutaraldehyde, and the performance of the synthesized membranes was evaluated in the pervaporation dehydration of ethanol.[24] In the last two cases, the researchers' works were only focused on the effect of cross-linking time on the PV performance and no attempts was made to investigate the effects of cross-linking time on the mechanical and thermal properties of the membranes.

Among different chemicals with the ability of reaction with hydroxyl groups of PVA, dicarboxylic acids such as malic acid, maleic acid, and fumaric acid can be considered as proper candidates for cross-linking of PVA for making PV membranes. This is due to relatively high polarity of these acids due to their carboxylic groups which leads to strong interaction with water through hydrogen bounding. Also, low price of dicarboxylic acids make them very suitable for using them as cross-linking agents.[25] PVA membranes cross-linked by malic acid, maleic acid, and fumaric acid were used by Guan et al. for dehydration of ethanol. Their results showed that the highest separation factor was achieved by the membrane cross-linked by fumaric acid. It was due to unique structure of this acid which can pack the polymer chains more effectively in comparison with other

acids used in their work for cross-linking.[25] However, in that work cross-linking of the membranes were done at a constant time and the effect of time on the membrane properties and PV performance were not investigated.

Isopropanol (IPA) is known as a foam inhibitor, deicing agent, and important solvent for lacquers and inks.[26] IPA is widely used in the semiconductor, medicinal, and petroleum industries.[27] IPA forms an azeotropic mixture with water at 14.7 wt % water concentration, which makes their separation by azeotropic distillation a difficult and high energy consuming task. To solve this problem, PV has proven to be a promising and successful tool.[28–32]

To the authors' knowledge, application of the PVA membranes cross-linked by fumaric acid for dehydration of IPA has not been investigated by other researchers. Also, as mentioned before there is no significant published paper on an exclusive study on the effect of cross-linking time of PVA membranes on the membrane properties. In the present work, self-supported cross-linked PVA membranes were prepared by using fumaric acid as the cross-linking agent. The main aim of the work was to study the effect of the cross-linking duration on the mechanical and thermal stability of the PVA membranes. Also, the membrane separation properties in terms of flux and selectivity were studied in dehydration of isopropanol by PV. For this purpose, the cross-linking was conducted at 150°C for three different times of 10, 30, and 60 min. Each cross-linked membrane was characterized by different methods for its mechanical and thermal properties. Then the synthesized membranes were used in a laboratory scale PV set-up for dehydration of IPA and the effects of feed concentration and operating temperature on the membranes' PV performance were investigated. Also, activation energy of permeability was calculated to investigate the effect of separation process temperature on the membrane performance.

EXPERIMENTAL PROCEDURE

Materials
PVA (M.W. 7200 and degree of hydrolysis of ≥98%) and fumaric acid (purity ≥99%) were purchased from Merck. Very low conductivity (0.05 μS cm^{-1}) deionized water was used as the solvent for PVA. All chemicals were used without further treatment and purification.

Membrane Preparation
To prepare a 10 wt % homogeneous PVA solution, 4.5 g of PVA was dissolved in 40.5 g deionized water with the aid of refluxing while heated at 90°C for at least 6 h. After preparing the solution, a specific amount of fumaric acid (0.03 moles per each vinyl alcohol repeating unit) was added to the PVA solution and the mixture was stirred at 50°C overnight. Then the solution was cooled, filtered, and finally degassed by applying vacuum. To prepare the membrane film, the clear and degassed solution was cast on a flat glass plate by using a casting knife. The cast film was kept at room temperature in a dust-free atmosphere for 24 h. Then, the dried membrane was peeled from the glass plate surface and heated in a vacuum oven at 150°C for adjusted times for occurring the reaction between PVA and fumaric acid and cross-linking of the PVA membrane, shown by
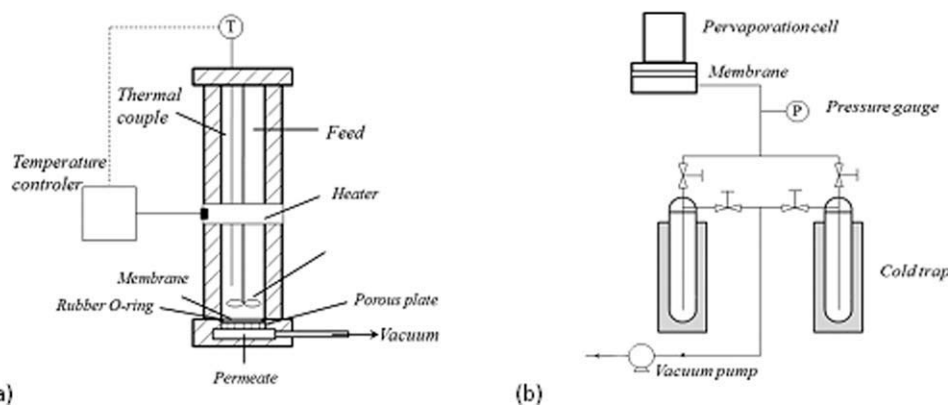
Figure 1. Schematic of the experimental pervaporation system: (a) pervaporation cell, (b) pervaporation set-up.

Scheme 1. The reaction time was adjusted at three different levels of 10, 30, and 60 min and the resulting self-supported membranes were designated as PVA-10, PVA-30, and PVA-60, respectively. At least two samples were synthesized for each type. The thickness of the membranes was found about 50 ± 3 μm (measuring with a micrometer). Also, plain PVA membranes without cross-linking, named PVA-0, were made to compare the effect of cross-linking time on the mechanical and thermal properties of the membranes.
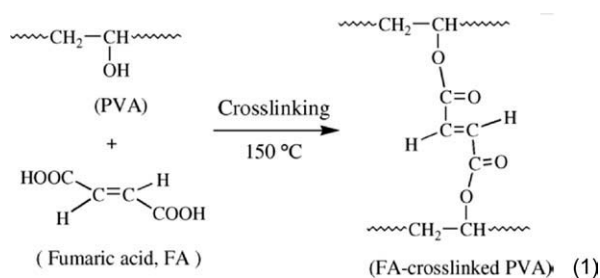
Membrane Characterization

Fourier Transform Infrared (FTIR) Spectroscopy. FT-IR spectroscopy was used to confirm the chemical reaction between PVA and fumaric acid. For this purpose, all samples were scanned by a Bruker-Tensor 27 FT-IR spectrophotometer. The wave number varied between 400 and 4000 cm^{-1}.

Thermal Gravimetric Analysis (TGA). A BAHR-STA503 analyzer was used to determine the thermal stability of the synthesized membranes. The analyses were carried out under N_2 atmosphere with temperature variation in the range from 50 to 650°C at heating rate of 10°C min^{-1}.

X-Ray Diffraction (XRD). The XRD patterns of the samples were obtained by using a Bruker X-ray diffractometer (model D8 Advance, Germany) to investigate the crystalline structure of membranes before and after cross-linking. The diffraction angle (2θ) was varied from 5 to 80.

Tensile Stability. The tensile strength and percent elongation at break were determined for all the samples by using a Universal Testing Machine (UTM) (Zwick, Model 1446-60, Germany). For this test, the samples were prepared according to ASTM-D882

standard (used for plastic sheets with a thickness less than 1.0 mm). The length and width of samples were 14.5 and 1 cm, respectively. The films were stretched at a cross head speed of 10 mm min^{-1}.

Scanning Electron Microscopy (SEM). The surface and cross section morphology of the pure PVA and cross-linked PVA membranes were examined using a scanning electron microscopy (Philips XL30). Before SEM imaging, all the membranes were broken in liquid nitrogen and then vacuumed dried. Finally, the samples were coated with a thin layer of sputtered gold before imaging.

Degree of Swelling. Each cross-linked sample with dimensions of 2.5×2.5 cm was weighed with a laboratory balance (Kern, model PLS 360-3) with accuracy of 0.001 g and immersed in deionized water at 30°C for 48 h to make sure that membrane is in its equilibrium state. Then, the membrane was taken out of the water and surface water was carefully removed with a clean tissue. The swollen membrane was again weighed and the degree of swelling was calculated by eq. 2:

$$DS(\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

where W_s and W_d are the weights of swollen and dry samples in gram, respectively. Also, the relative water content of the swollen membranes was calculated using the following equation:

$$Hw = \frac{\text{The weight of water}}{\text{The weight the swollen membrane}} \qquad (3)$$

For the PV experiments done on IP/water, the degree of swelling was determined by using the feed solution instead of pure water.

Pervaporation Experiments. Pervaporation experiments were carried out in a 500-ml stainless steel cell shown in Figure 1. The membrane with the effective surface area of 19.6 cm^2 was placed at the bottom of the cell on stainless steel mesh as the membrane support. A rubber O-ring was used between the membrane and the cell to prevent any leakage. To keep the homogeneity of the feed solution, the cell was equipped with a mechanical stirrer powered by a DC motor. Also, the feed temperature was adjusted at three different levels of 40, 50, and

60°C by using a temperature controller and an external electrical heating coil. Prior to each experiment, the membranes were equilibrated with the feed solution for 2 h. The water concentration in the feed mixture varied between 10, 20, 30, and 40 wt %. To have a constant concentration feed during the experiments, 500 ml of the feed solution was fed to the cell on top of the membrane and it was continuously stirred throughout the experiments. A low pressure vacuum pump (Vacuubrand, MD1, GMBH, Germany) was used to provide the necessary vacuum and the permeated vapor was trapped and condensed in a cryogenic cold trap at −45°C. The condensed permeate was weighed by a balance (Kern, model PLS 360-3) with an accuracy of 0.001 g.

The permeation flux, J (kg m^{-2} h^{-1}) was calculated using the following equation:

$$J = \frac{W}{A.t} \tag{4}$$

where W (kg), A (m^2), and t (h) are the weight of condensed permeate, the effective area of the membrane, and the duration of permeation collection, respectively.

The feed and permeate samples were analyzed for their water and IPA content by HPLC (Jasco, Germany) equipped with an Amino HPX-87 H (300 × 7.8 mm) column. RI detector (operated at 40°C) was used for alcohol detection. Oven temperature for HPLC was adjusted at 60°C and the sample injection volume was 20 μL.

The selectivity (α) of the membrane for water permeation was calculated using the following equation:

$$\alpha = \left(\frac{y_A}{1 - y_A} \right) \left(\frac{1 - x_A}{x_A} \right) \tag{5}$$

where x_A and y_A are the weight fractions of water in the feed and permeate samples, respectively.

RESULTS AND DISCUSSION

The results obtained in this work are presented in two parts. In the first part, the results of membrane characterization are presented and discussed. The results of PV experiments and related issues such as permeation flux and separation factor are discussed in the second part.

Membrane Characterization
FTIR Results. The FT-IR spectra of plain and cross-linked PVA membranes are shown in Figure 2. The spectra for the cross-linked membranes (graphs b–d) show some absorption bands which are stronger than the similar ones for the plain PVA membrane, as seen in graph (a). Two of these bands are seen at 1710 and 1141 cm^{-1} which are related to (—CO—O—) and (C—O) stretching bands in the ester groups, respectively. On the other hand, the absorption bands at 1085 and 3200 cm^{-1} are attributed to the ether band (C—O—C) and hydroxyl group (O—H) of bond water molecules in PVA network, respectively. The existence of bands for ester and ether groups confirms that the reaction between fumaric acid and PVA has occurred. As
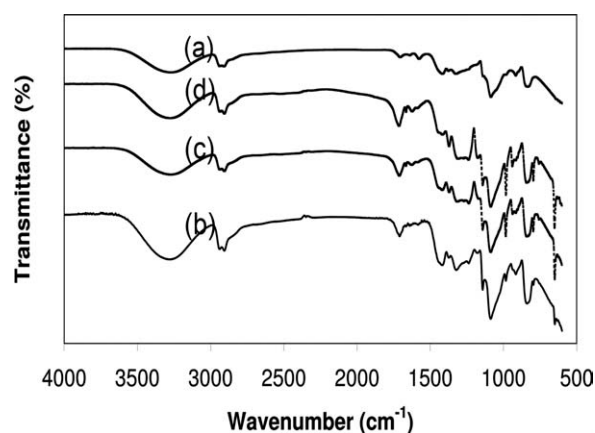
Figure 2. The FTIR spectra of (a) PVA-0, (b) PVA-10, (c) PVA-30, and (d) PVA-60.

seen in Figure 2, the intensity of the bands owing to ester and ether groups has increased with the increase in the time of cross-linking. This effect is an evidence of more reactions taking place between hydroxyl groups of PVA and carbonyl groups of fumaric acid when longer time is given for the cross-linking step. By the reaction between PVA and fumaric acid, the hydroxyl groups of PVA diminish and are replaced by the ester groups. On the other hand, water is a by-product of reaction between PVA and fumaric acid. By increasing the degree of cross-linking with an increase in the time of cross-linking, hydrophilicity of the membrane is reduced and hence the total water content of the PVA matrix is decreased.[33] This can be better understood by comparing the absorbance (%) of the (O—H) band at 3200 cm^{-1}, given in Table I, for the PVA membranes cross-linked for 10 and 30 min. However, it is noticeable that by further increasing the cross-linking time from 30 to 60 min, the absorbance increases. This is probably due to the fact that by further increasing the time, more esterification reactions occur and subsequently the number of water molecules produced by the reaction is increased. In addition, by increasing the cross-linking time, the polymer matrix becomes more compact which makes it difficult for water molecules to exit from the membrane network.

Thermal Analyses. TGA plots for the plain PVA and cross-linked PVA membranes are shown in Figure 3. Also, Figure 4 shows the results of differential gravimetric analysis (DTG).

TGA and DTG curves indicate that the weight loss occurs in three stages for all the samples. The first stage, seen between 50 and 150°C, was related to loss of the bound water molecules. In this stage, the weight loss of membranes was negligible compared to other stages. Since the amount of bound water produced during the cross-linking was higher for the membrane cross-linked for 10 min (see Table I), this sample showed the highest weight loss at this stage. The weight losses at 150°C are reported in Table I, confirming the results of FT-IR analyses. The second stage weight loss was due to decomposition of the side chains of PVA. This occurred in the ranges of 218–412 and 218–360°C for the cross-linked and the plain PVA membranes, respectively. According to the DTG curves at the second stage

Table I. Characterization Data of the Different Membranes Synthesized with Different Cross-Linking Time

The time of cross-linking (min)	0	10	30	60
Membrane name	PVA-0	PVA-10	PVA-30	PVA-60
FTIR analysis				
Absorbance of the (O—H) band at 3200 cm^{-1} (%)		7	5	6
DTG analysis				
Weight loss at 150°C	1.2%	3%	0.3%	0.9%
Total weight loss at second stage	72.27%	57.74%	52.2%	50.08%
XRD analysis				
The area under crystalline peak	5059.3	2234.1	2151.7	978.7
The total area	5100.4	3543.2	3828.9	2402.0
X_c (%)	99	63	56	40
Swelling measurement				
Degree of swelling (%)		86.3	70.6	43.2
H_w		0.48	0.4	0.3

for the cross-linked membranes, the variation of weight at first happened slowly and suddenly increased at 300°C. T_{max} was 367°C in this region. Contrary to the cross-linked membranes, for the untreated membrane this variation in the second stage was sharp and T_{max} was seen at 284°C. The total weight losses for the second stage are also reported in Table I. It is clear that the thermal stability of PVA membrane significantly enhances with cross-linking. The third stage of weight loss was in the range of 422–541 and 356–520°C for the cross-linked and untreated membranes, respectively. In this region, the polymer backbone was completely decomposed.

XRD Results. The XRD patterns of the PVA membranes before and after cross-linking for different times are shown in Figure 5. A sharp peak at 2θ = 20° is seen in this figure in the pattern of the untreated PVA, which is related to the semicrystalline structure of PVA due to the intermolecular hydrogen bonding. Also, Figure 5 reveals that the net area under the crystalline peak is reduced by increasing the time of cross-linking because of the

reaction between fumaric acid and hydroxyl groups in PVA. It means that the degree of crystallinity decreases with an increase in the degree of cross-linking. Therefore, the amorphous regions in the polymer increase which is generally in favor of mass transfer in the membrane.

The values for the net area under the crystalline peaks and total area for all the synthesized membranes are presented in Table I. Using the values of the area given in Table III, the percentage of crystallinity is calculated from the following equation:

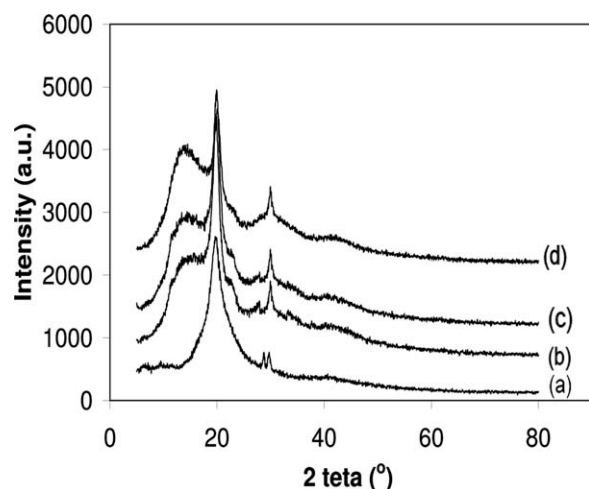$$X_c(\%) = \frac{A_c}{A_t} \times 100 \qquad (6)$$

where A_c is the area under the crystalline peak, and A_t is the total area. The results for X_c, which are given in Table I, depict that the percentage of crystallinity declines with an increase in the time of cross-linking.
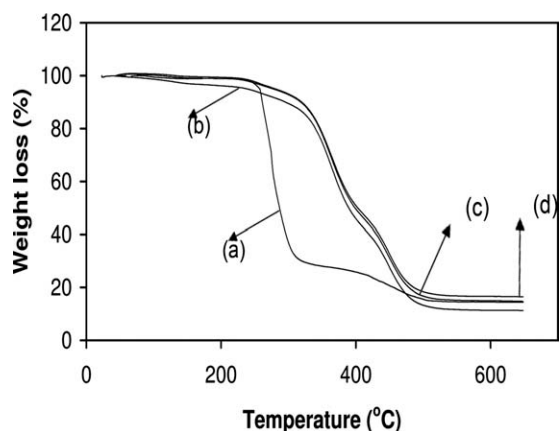
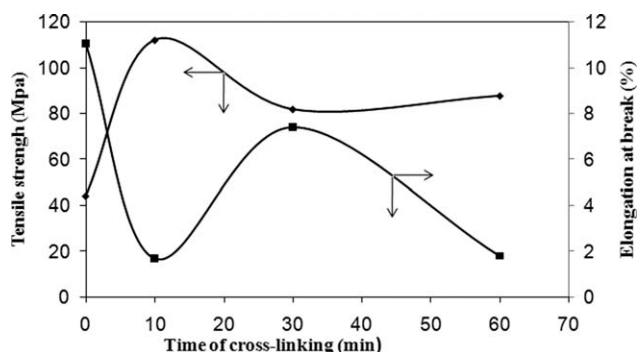**Figure 3.** The TGA plots of (a) PVA-0, (b) PVA-10, (c) PVA-30, and (d) PVA-60.
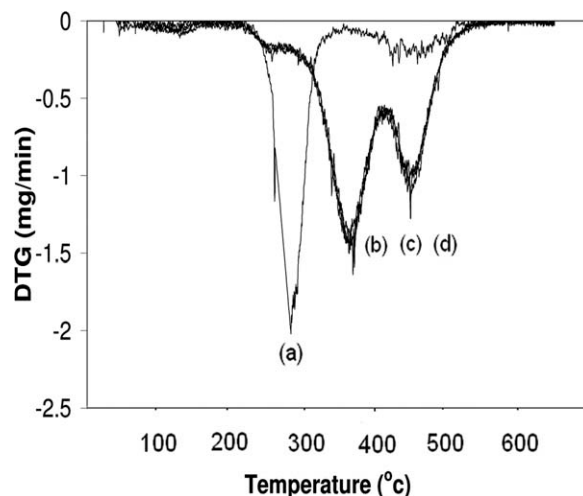
Figure 4. The DTG plots of (a) PVA-0, (b) PVA-10, (c) PVA-30, and (d) PVA-60.

Figure 5. X-ray diffraction patterns for (a) PVA-0, (b) PVA-10, (c) PVA-30, and (d) PVA-60.

Figure 6. Variation of the tensile strength and percentage of elongation at break with the cross-linking time.

Mechanical Properties. The variation of tensile strength and percentage of elongation at break with cross-linking time for the treated and untreated membranes are illustrated in Figure 6. It is observed that the tensile strength at break for all the cross-linked membranes was higher than that of the plain membrane. However, the tensile strength at break for PVA-10 was larger than the values obtained for PVA-30 and PVA-60. This was due to less decrease in the number of hydroxyl groups in the polymer matrix and enhancement of the chains compatibility in PVA-10. The degree of cross-linking is one of the several factors which influence the stress values. Elimination of hydroxyl groups in PVA-30 and reduction of the degree of crystallinity were shown to be more than in PVA-10, which caused a decrease in tensile strength at break. Although PVA-60 had the lowest value for the degree of crystallinity, the compatibility between polymer chains in amorphous regions was high enough

to increase the tensile strength at break in comparison with PVA-30. As a result, no special trend can be seen for the variation of tensile strength at break with the cross-linking time. As expected, percentage of elongation at break (Figure 6) had reverse trend in comparison with tensile strength at break.

SEM Studies. Figure 7 illustrates the SEM micrographs of surface and cross section view of the pure and cross-linked PVA membranes synthesized in this work. The images show defect-free uniform and smooth structure for all samples. It seems that increasing the cross-linking time had no effect on the surface morphology of the membranes. On the other hand, the cross section micrographs show that increasing the cross-linking time led to a more compact and rougher structure of the polymer film.

Degree of Swelling. The results of the calculated degree of swelling and relative water content for the cross-linked membranes are reported in Table I. These results reveal that increasing the cross-linking time had a strong influence on the degree of swelling. For example, by increasing the cross-linking time

Table II. Pervaporation Dehydration Results for Water/Isopropanol Mixtures at 60°C for Different Membranes

Feed water content (wt %)	Water flux (J_w) (kg (m² h)⁻¹)	Isopropanol flux (J_{IPA}) (kg (m² h)⁻¹)	Selectivity (α)
PVA-10			
10	0.1256 ± 8.792 e-3	0.0009 ± 6.300 e-5	1296
20	0.3465 ± 2.079 e-2	0.0035 ± 2.100 e-4	396
30	0.6645 ± 3.3225 e-2	0.0115 ± 5.75 e-4	134
40	1.0873 ± 4.349 e-2	0.0250 ± 1.00 e-3	65
PVA-30			
10	0.1014 ± 1.014 e-3	0.0007 ± 7.000 e-6	1398
20	0.2960 ± 1.180 e-2	0.0027 ± 1.080 e-4	440
30	0.5738 ± 1.721 e-2	0.0092 ± 2.760 e-4	145
40	0.9226 ± 3.69 e-2	0.0197 ± 7.880 e-4	70
PVA-60			
10	0.0818 ± 1.636 e-3	0.0005 ± 1.000 e-5	1492
20	0.2350 ± 7.050 e-3	0.0019 ± 5.700 e-5	489
30	0.4536 ± 1.814 e-2	0.0064 ± 2.560 e-4	164
40	0.7981 ± 3.190 e-2	0.0153 ± 6.120 e-4	78
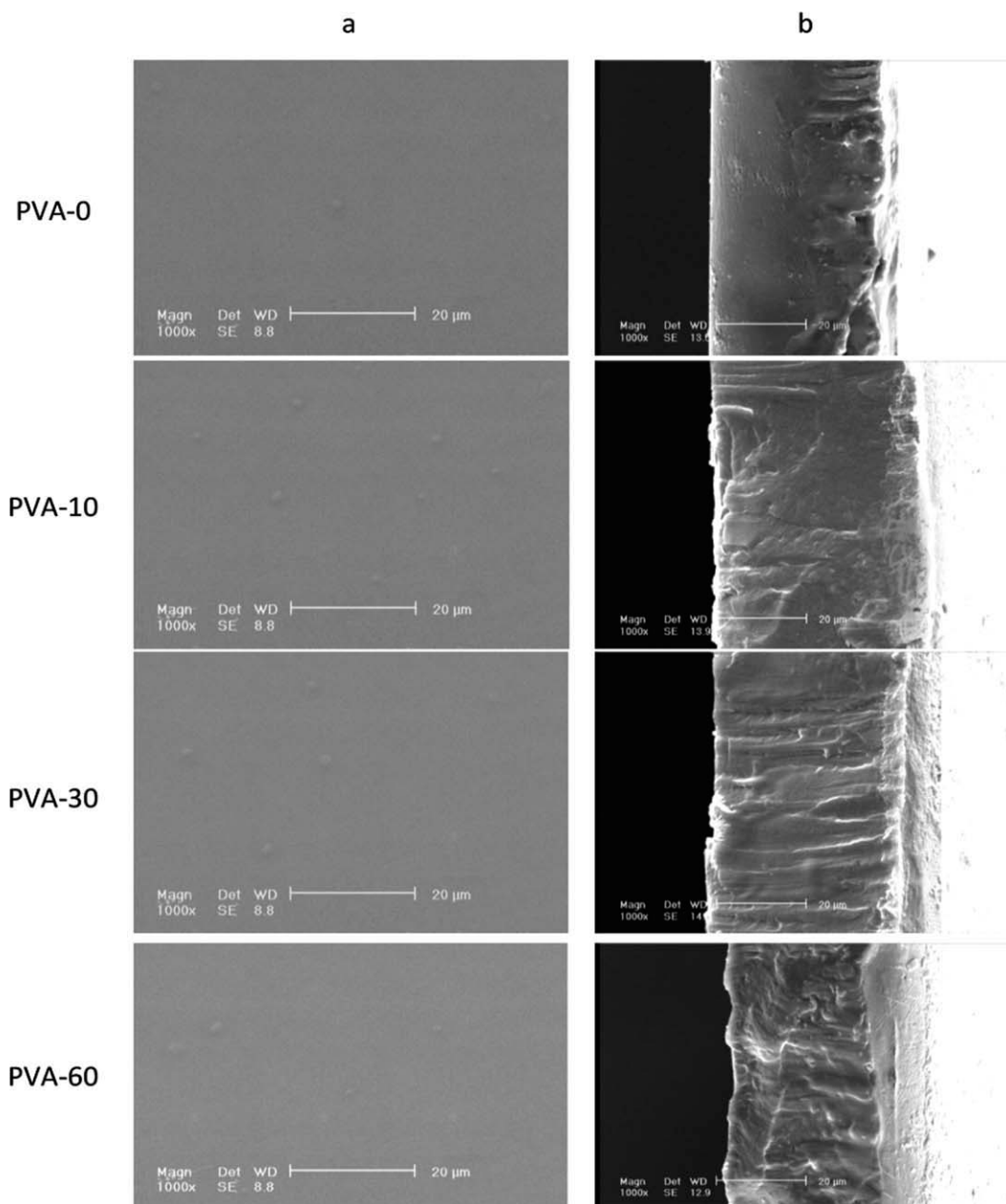
Figure 7. SEM micrographs of pure and cross-linked PVA membranes: (a) surface area and (b) cross section view.

from 10 to 60 min the degree of swelling has shown 50% reduction. This finding is in contrast to what can be expected by considering the results of XRD analyses for mass transfer improvement. As discussed in the XRD results, prolonging the cross-linking time enlarges the amorphous regions in the polymer matrix. This effect alone increases the mobility of the polymer chains which favors higher mass transfer through the membrane, including water penetration into the membrane and the resulting swelling. On the other hand, by increasing the time of cross-linking the degree of cross-linking in the amorphous regions increases, which in turn restricts the mobility of the polymer chains in these regions. Lower mobility of the polymer chains in the amorphous regions reduces the free volumes of the polymer. Unlike porous membranes, dense PVA membranes do not have physically visible pores. However, thermally induced motion of the chain segments forms penetrant-scale transient gaps in the polymer matrix, allowing penetrant species to diffuse through the membrane. These gaps are known as free volumes. The effect of cross-linking of PVA with fumaric acid on the free volume is somehow complicated. Reduction of inter-chain hydrogen bonding, due to reduced number of hydroxyl groups, leads to increase of free volumes. But inter-chain cross-linking as well as twisting of polymer chains decreases the free volumes of the PVA polymer. The net effect of fumaric acid cross-linking on the free volume depends on the trade off between these two factors. Usually, PVA membranes shrink after fumaric acid cross-linking indicating that free volumes of the membrane are decreased.[34] Despite
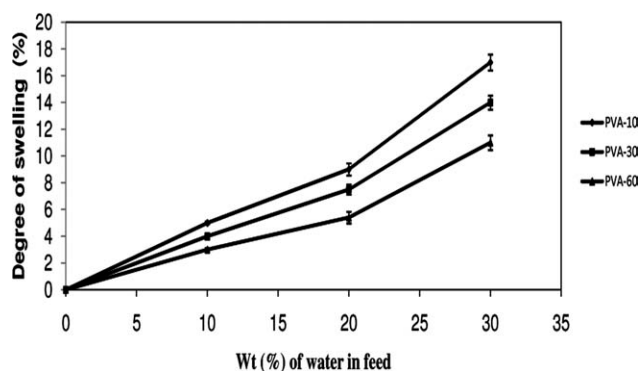
Figure 8. Variation of degree of swelling with feed water content.

quantitative determination of free volumes needs using specific techniques and instruments such as positron annihilation lifetime spectroscopy (PALS)[35] and Doppler Broadening Energy Spectroscopy (DBES),[36] but generally speaking, the interstitial spaces between chains in the molecular conformation are modified with cross-linking and fractional free volume (FFV) decreases. Therefore, by decreasing the free volumes the mass transfer and penetration of the species (such as water) through the membrane is limited or even reduced in comparison with the membranes with shorter cross-linking times.

To study the effect of feed composition on the membrane swelling, swelling tests were conducted at 30°C by using water/IPA mixtures at several different water content values. The results for variation of DS with feed composition for different crosslinked membranes are shown in Figure 8. It is seen that DS increased with increases in the water content of the mixture for all of the membrane types. This was due to the strong interaction between water molecules and —OH groups in the PVA membrane matrix. In addition, PVA-60 had smaller DS values for all feed compositions in comparison with other membranes, namely PVA-10 and PVA-30. This is due to higher degree of cross-linking obtained in PVA-60 with higher duration of crosslinking. These results revealed that by increasing the cross-linking time, more stable membranes can be achieved. On the other hand, it could be expected that the membrane performance would be affected from selectivity and permeability points of view, which will be discussed in the following sections.

Pervaporation Experiments

Effect of Feed Concentration. Figure 9 shows the effect of feed concentration on the total permeation flux for PV dehydration of water/isopropanol mixtures at 60°C. The results presented in this figure revealed that with increasing water content of the feed mixtures, the total flux increased for all of the membranes. This effect might be attributed to the plasticization effect in the hydrophilic membranes at high water contents which would agree with the results obtained for the swelling tests. Free volumes inside PVA membranes could be influenced by molecular motions in the polymer network. Presence of water molecules in the polymer matrix increased the chain mobility of the polymer and as a result the number of free volumes increased. This effect eased the molecular passage across the membrane. Conse-

quently, as shown in Table II, the permeation of both water and isopropanol molecules improved with increasing of water concentration in feed mixtures for all the membranes synthesized with different cross-linking time. Also water molecules could enter into the free volumes of the polymer structure and diminish polymer crystallinity by attaching to the hydroxyl groups on the macromolecules.[37] In fact destruction of hydrogen bindings by water molecules increased chain mobility and permeation flux.

The results reported in Table II show that contrary to selectivity, the partial fluxes of both species increased with increases to the water content of the feed solution. This effect can be explained by considering the effect of water molecules on the free volumes discussed earlier. By increasing the number of free volumes, isopropanol molecules find better chances to pass through the membrane matrix and therefore membrane selectivity for water is reduced.

Seen in Table II, the highest selectivity was attributed to PVA-60 when used for dehydration of 10 wt % water-containing feed mixture. This could be due to increase in cross-linking density which affects the membrane morphology. As mentioned before decreasing the number of free volumes due to increased crosslinking density restricts the passage of species through the membrane matrix. This negative effect on the permeation flux is stronger for large molecules of isopropanol in comparison with the small molecules of water.

Diffusion Coefficient Study. Pervaporation transfer of species from a liquid mixture through a membrane is usually explained by the solution-diffusion model.[38] One important parameter in this model is diffusion coefficient of the species. Diffusion coefficient, D_i, for permeating molecule type i can be calculated by using Fick's law which is expressed as

$$J_i = -D_i \left(\frac{dC_i}{dX} \right) \qquad (7)$$

where J_i is permeation flux per unit area in kg m^{-2} s^{-1} and D_i (m^2 s^{-1}) and C_i (kg m^{-3}) represent the diffusion coefficient and concentration of the permeating species, respectively. Also x (m) is diffusional distance perpendicular to the membrane surface. For simplicity, it is assumed that the concentration profile
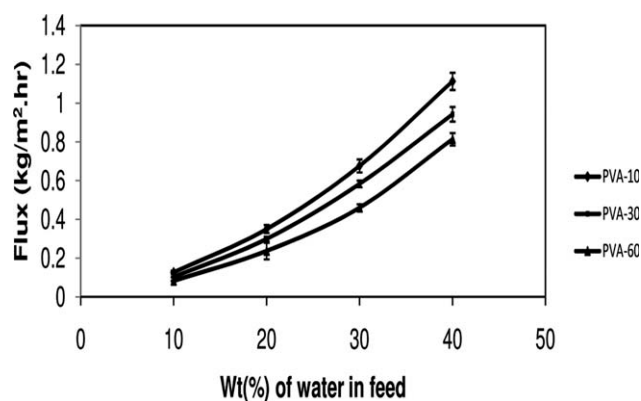

Figure 9. Variation of total flux with feed water content.

Table III. Diffusion Coefficients of Water and Isopropanol for Different Feed Compositions and Membrane Types at 60°C

Feed water content (wt %)	$D_w \times 10^{11}$ (m^2 s^{-1})			$D_{IPA} \times 10^{13}$ (m^2 s^{-1})		
	PVA-10	PVA-30	PVA-60	PVA-10	PVA-30	PVA-60
10	2.17 ± 0. 15	1.75 ± 0.02	1.41 ± 0.03	0.17 ± 0.012	0.13 ± 0.001	0.098 ± 0.002
20	2.92 ± 0.18	2.52 ± 0.10	1.99 ± 0.06	0.74 ± 0.05	0.57 ± 0.02	0.40 ± 0.012
30	3.66 ± 0.18	3.16 ± 0.09	2.50 ± 0.10	2.71 ± 0.14	2.17 ± 0.07	1.52 ± 0.07
40	4.39 ± 0.17	3.73 ± 0.15	3.22 ± 0.13	6.74 ± 0.26	5.31 ± 0.2	4.12 ± 0.17

along the diffusion length is linear. Also, the concentration of the species in the downstream can be neglected due to very low partial pressure of the permeating species in the permeate side. Thus, the diffusion coefficient of component i can be simply calculated using the following equation:

$$D_i = \frac{J_i \cdot \delta}{C_{i,f}} \qquad (8)$$

where δ (m) is the membrane thickness (50 μm in this study) and $C_{i,f}$ is the feed concentration for species i.

The calculated values for diffusion coefficients of water (D_w) and isopropanol (D_{IPA}) at 60°C are reported in Table III.

According to the data reported for diffusion coefficients in Table III, the diffusion coefficients of water are higher than those of isopropanol by two orders of magnitude. This different in the diffusion coefficients shows hydrophilic nature and highly water selectivity of the membranes cross-linked with fumaric acid, which is in favor of dehydration process. It is clear from Table III that with increasing the cross-linking time the diffusion coefficients for both species have significantly decreased, which is due to significant restriction of chain mobility at higher degrees of cross-linking. On the other hand, the diffusion coefficients enhanced with increasing water content of the feed mixture. The enhancement is due to water selective nature of PVA membranes and interaction between polar water molecules with —OH groups of PVA which resulted in increasing in chain mobility and increasing the diffusion rate. It is worth mentioning that the increasing effect of feed composition on the diffusion coefficient of isopropanol is stronger than that of water which

resulted in reduction of membrane water selectivity (see Table II). This was due to enhancement of membrane swelling and formation of more free volumes at higher water contents. To have a better view about this effect, the ratio of the diffusion coefficients (D_w/D_{IPA}) versus water content of the feed mixture is plotted in Figure 10.

Effect of Pervaporation Operating Temperature. The performance of membranes during pervaporation process is strongly influenced by the feed temperature. To evaluate this effect some experiments were conducted at different temperatures of the feed solutions containing 20 wt % water. Similar to the findings by other researchers,[39,40] the total flux increased almost linearly with feed temperature increases. As temperature increases, chain mobility in the polymeric membrane enhances and consequently more free volumes will be available. Therefore penetrants can diffuse more easily through the membrane and as a result total flux increases. In addition, increasing the operating temperature enlarges the partial pressure of the species in the feed solution which in turn has positive effect on the mass transfer driving force through the membrane. The temperature dependence of flux can be evaluated by using the Arrhenius relationship:

$$j = j_O \exp\left(\frac{-E_d}{RT}\right) \qquad (9)$$

where J represents the total permeation flux and J_o is the pre-exponential factor. In this equation, E_d represents activation energy for permeation, R is gas constant, and T is the absolute
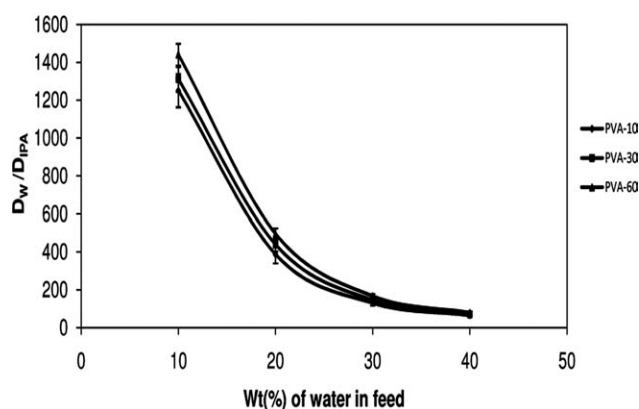
Figure 10. Variation of D_w/D_{IPA} with feed water content
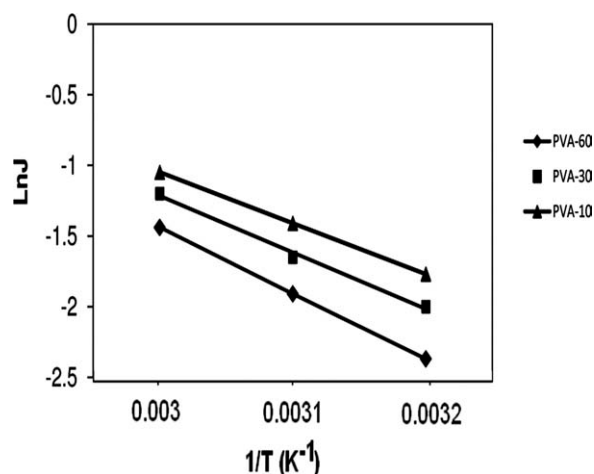
**Figure 11.** Variation of ln J with $1/T$ for 20 wt % feed solution.

Table IV. Arrhenius Activation Parameters (Feed Composition: 20 wt % Water)

Parameter (kJ mol^{-1})	PVA-10	PVA-30	PVA-60
E_p	29.97	33.25	38.70
E_{pw}	29.52	32.55	38.33
E_{pIPA}	41.15	43.64	45.72
E_{pw}/E_{pIpa}	0.72	0.75	0.84

temperature in Kelvin. If activation energy is positive then flux increases with increasing temperature.

Arrhenius plot of ln J versus $1/T$ is shown in Figure 11. The linear plot indicates that the total permeation flux follows the Arrhenius behavior. Similarly, the plots for water and isopropanol fluxes showed linear behavior but the plots are not given to avoid the crowdness. Using slopes of the plots, the activation energy for total permeation flux (E_p) as well as those of partial fluxes of water and IPA, namely E_{pw} and E_{pIPA}, were estimated and summarized in Table IV.

Data reported in Table IV reveal that the lowest activation energy values belonged to the membrane cross-linked for 10 min (PVA-10). Also, it is clear that the permeation flux of isopropanol was more dependent on operating temperature than that of water, which in turn led to smaller water selectivity at higher temperatures—as shown in Figure 12. It should be noted that the magnitude of activation energy for a specific membrane shows the degree of temperature dependency of permeation flux through the membrane. Data reported in Table IV revealed this dependency is stronger for PVA-60. This is due to the fact that this membrane had higher cross-linking density and therefore less free volumes. The ratios of E_{pw}/E_{pIPA}, reported in Table IV, show that this ratio increased with increasing cross-linking time. In the first glance, it might be concluded that by increasing this ratio the selectivity of the membrane for water permeation should be reduced. But the results of permeation tests and selectivities reported in Table II show that higher selectivity val-
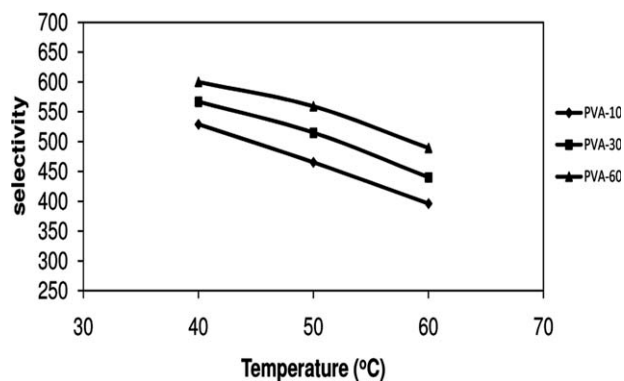
Figure 12. Variation of selectivity with temperature for 20 wt % feed solution.

ues were obtained for PVA-60. This opposition between observations for selectivity values and prediction from E_{pw}/E_{pIPA} ratios can be explained by considering the effect of increased cross-linking time on the morphology of the membranes. By increasing cross-linking time, more hydroxyl groups are used for ester groups formation which leads to lowered hydrophilicity of membrane[1] and higher activation energy for water permeation. But on the other hand, increasing the cross-linking time and consequently higher cross-linking density reduces the free volumes between polymer chains. This secondary effect strongly restricts the permeation of isopropanol molecules with larger molecular size in comparison with small molecules of water. The net effect of these two opposite effects on the permeation of water and isopropanol molecules will be enhancement in the selectivity of membrane for water permeation.

Comparison of PV Performance. Table V summarizes the comparison between the flux and selectivity data for pervaporation separation of water/isopropanol mixtures at high temperatures by using different modified PVA membranes. It is clearly observed that the PVA membranes cross-linked with fumaric

Table V. Comparison of Pervaporation Performance of PVA-60 with Those of Other Cross-Linked Membranes for Dehydration of Isopropanol

Membranes	Temp. (°C)	Feed water content (wt %)	Total permeation flux (kg (m^2 h)$^{-1}$)	Selectivity	Reference
PVA-3TMC	60	10	0.11	550	22
PVA-3TMC	60	20	0.32	396	22
PVA-GA	60	10	0.15	191	29
CSPVA7525	60	10	0.644	∞	30
PVA-SSA	70	10	0.206	1969	38
PVA-PAAH/GA	70	15	3.14	2930	39
PVA-PDDA/CMCNa/PS	70	10	1.35	1002	40
PVA-ceramic	60	5	0.3	127	41
CMPVA-ClHAC	80	15	0.831	362	42
PVA-60	60	10	0.082	1492	This work
PVA-60	60	20	0.24	489	This work

acid, synthesized in this work, had the lowest flux in comparison to other membranes due to their denser structure. But the selectivity values obtained by these membranes were significantly higher than most of others' reported membranes. However, the selectivities for three types of the membranes—namely PVA-SSA,[41] PVA-PAAH/GA,[42] and CSPVA7525[30]—are higher than those of membranes made in this work. This might be due to the presence of larger number of hydrophilic groups in the membrane structure. In the case of PVA-SSA membrane, the hydrophilicity of the membrane has been strongly enhanced by incorporating —SO$_3$H groups due to cross-linking of PVA by sulfur–succinic acid (SSA). For PVA-PAAH/GA membrane, incorporation of poly(allylamine hydrochloride) in the membrane matrix increased the selectivity toward water due to the presence of aminehydrochloride functional groups which show high selectivity to water.[42] Finally, by incorporation of chitosan in the polymer matrix and consequent large number of hydroxyl groups in the polymer backbone of CSPVA7525 membrane, the hydrophilicity and water selectivity of this membrane have significantly increased.[30] Comparison between the performance of PVA-60 membranes (synthesized in this work) and PVA-3TMC membranes[22] revealed that when the water content of the feed mixture decreased from 20 to 10 wt %, the ratio of permeation fluxes remained almost constant (about 0.75). However, by decreasing the water content the ratio of selectivity values increased significantly from 1.24 to 2.71. It means that the effect of feed composition on the selectivity of PVA-60 was much stronger than its effect on the selectivity of PVA-3TMC membrane. Further comparison between the data reported in Table V and the performance characterizations for other membranes synthesized in this works, shown in Table II, reveals that the overall performances of the latter are clearly better than those of some other membranes made by others.

CONCLUSION

In the present study, PVA membranes were cross-linked by fumaric acid at 150°C and the effects of cross-linking time on the thermal and mechanical properties and also pervaporation performance of the membranes were investigated. The membranes were cross-linked for three different times of 10, 30, and 60 min. According to the results, by increasing the cross-linking duration, the thermal stability of the membranes was improved. It was also observed that tensile strength at break increased when the membrane was cross-linked for 10 min. But, further increase in the cross-linking time resulted in a decrease in the aforementioned parameters. This could be explained by considering the competition between the two opposite effects. By increasing the cross-linking time, the amorphous regions are grown and become more compact. As a result, the rigidity of the polymer increases. On the other hand, when the polymer is cross-linked for a longer time, the crystalline regions are reduced, resulting in lower rigidity of the polymer. As regards this work, the net effect of these two opposite responses to cross-linking is reduction in the rigidity for the membranes cross-linked for more than 10 min. The results of the sorption tests showed that by increasing the cross-linking time, the membranes became more compact and therefore the degree of swelling was reduced.

The synthesized membranes were used for dehydration of water/isopropanol mixtures with different water contents. The water content of the feed mixture had significant influence on the membrane selectivity and permeation flux for all of the membranes synthesized in this work. All the membranes showed high separation factors for water removal, ranging from 65 to 1492. The obtained values of selectivity were higher than those obtained by using some other cross-linking agents such as glutaraldehyde and TMC. However, the water flux through the membrane was fairly low, especially at low water contents of the feed mixture. The temperature dependency of the permeation flux followed the Arrhenius trend. Calculated activation energy for permeation flux showed that the activation energy of water was lower than that of IPA, leading to high selectivity for water permeation. However, by increasing the cross-linking time the difference between activation energy of the two components became smaller which was due to larger increase in water activation energy. But interestingly, despite large increase in the activation energy of water with prolonging cross-linking time, the selectivity was improved. This could be explained by considering the fact that at prolonged cross-linking times the rigidity of the polymer chains increased which in turn avoided from passing the large molecules of IPA in comparison with water. Finally, the results obtained in this work indicated that the cross-linked membranes made in this work can be considered as promising candidates for dehydration of aqueous IPA mixtures by pervaporation processes.

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