# Polyurethane/Poly(vinyl alcohol) Blend Membranes for Gas Separation

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**Abstract:** This Study involves preparation and characterization of polyurethane (PU) and polyurethane/poly(vinyl alcohol) (PU/PVA) blend membranes for gas separation. PU was synthesized by two step polymerization based on isophorone diisocyanate (IPDI), 1,4-butanediamine (BDA), polytetramethylene glycol (PTMG) in the mole ratio of 3:2:1. The prepared blend membranes were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray Diffraction (XRD), and scanning electron microscopy (SEM). The effects of molecular weight of PVA, and blend composition on the gas transport properties of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> were investigated. Obtained results show that the permeability of gases decreased in blend membranes by poly(vinyl alcohol) (PVA) molecular weights while their gas selectivity enhanced. Comparison of the gas separation performance of the prepared membranes to Robeson upper bound, reveal the enhancement of membrane performance by introducing PVA in PU matrix.

Keywords: Gas separation, Membrane, Polyurethane, Poly(vinyl alcohol), Blend

## Introduction

Global warming, as a result of increasing emission of greenhouse gases, is one of the major concerns these days. Therefore, reduction of emission of these gases into the atmosphere is a vital challenge to various industries, and hence highly effective methods containing absorption, adsorption and cryogenic separations have been developed for  $CO_2$  capture and storage [1-6].

These days, separations of gases by membranes have obtained more attention because they are greatly reliable, energy-efficient, and have good durability, high mechanical strength and low capital costs. Therefore, many studies have been done to improve polymeric membranes in novel applications [5-19].

These studies result in better understanding of the relationship between structure and gas separation properties [6,7,20,21]. Polymer blends, modified polymers, new design of block copolymers and nanocomposite membranes are consequences of such research projects [6,22-26]. The valuable properties of two or more polymers can be altered to obtain the desired novel materials with improved properties [6,22,27-29]. Membranes made from blending a variety of polymers show outstanding gas separation properties. In blended membranes, the basic chemical, physical, mechanical, and morphological characteristics of each polymer is combined, so it is likely to improve membrane properties by blending. Therefore, blending a variety of polymers to obtain a membrane material with higher properties in comparison with those of initial discrete components has been considered as a remarkable way to achieve superior separation characteristics in membrane materials [12,22,30-33].

Polyurethanes (PUs) are a group of block copolymers, which are based on two different blocks: soft segments (polyol) and hard segments (urea and urethane groups). Hard segments are result of the reaction between diisocyanates and diols or diamines [6,12,22,33-36]. PUs, due to their high gas permeability, have been recognized as interesting candidates for gas separation, especially for the removal of polar, quadrupolar or acid gases (e.g.,  $CO_2$ ,  $H_2S$ ) from nonpolar gases (e.g.,  $H_2$ ,  $N_2$ , and  $CH_4$ ) [6,7,37].

Previous investigation showed that the gas permeation properties of PU membranes were affected by the length, type and amount of soft and hard segments, embedding different materials [6,18,19,30,38-43]. The types of chain extenders used in the synthesis of PUs also affect the permeation properties of the membranes, and therefore change the phase separated domain morphology, crystallinity, density and glass transition temperature of the membranes [6,44-46]. In our previous works, the effects of the polyol, diisocyanate and chain extender on the gas permeability of PUs were investigated [6,43,47,48]. For example, gas diffusivity and permeability increased in the studied PU membranes by increasing the urea linkage and chain mobility, as a result of using diamine chain extenders while selectivity of the membrane decreased. Changing the diisocyanate group from aromatic to aliphatic and from cyclic aliphatic to linear aliphatic resulted in an increase in phase separation of hard and soft segments, which caused higher permeabilities [6,47]. Other researchers [6,30] presented similar results.

Windmöller *et al.* also studied the performance of PU and PU-poly(methyl methacrylate) (PMMA) blends membranes. The effects of operating conditions (i.e. temperature and pressure) and blend composition were investigated on the permeability, diffusivity and solubility of  $CO_2$ ,  $H_2$ ,  $O_2$ ,  $CH_4$ , and  $N_2$  gases. They showed that the permeability of all gases

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decreases by approximately 55 % with the addition of 30 wt.% of PMMA [49]. On the other hand, Lin *et al.* desulphurized gasoline using polyethyleneglycol (PEG)/PU blend membranes. They revealed that PEG modifies PU membrane and improve its performance for the separation process [50].

Poly(vinyl alcohol) (PVA) is an aliphatic, semicrystalline material often used for the preparation of different types of membranes. It is intrinsically hydrophilic due to many hydroxyl groups in the polymer chain. Moreover, it is appropriate for membrane preparation due to its superb chemical strength and film-forming capability. However, in aqueous feed mixtures, PVA membranes undergo extreme swelling; therefore, PVA is always altered by ways such as chemical crosslinking, polymer grafting, blending with different polymers, creation of PVA copolymers, and thermal treatment. [19,51-57].

Ariyaskul *et al.* prepared PVA membranes blended with chitosan for the PV and separation of IPA mixtures, and they have reported that a membrane having 75 % chitosan (CS) shows the greatest outcomes [58].

Chaudhari *et al.* investigated the pervaporation performances of the PVA and poly(vinyl amine) (PVAm) blend membranes. It was seen that as the amount of added PVAm increased from PVAm 0 to PVAm1.5, the flux increased from 0.023 to 0.10 kg/m<sup>2</sup> h at a water/IPA feed ratio of 85/15 at 30 °C. Their results revealed that by controlling the thickness of the blend membrane, an enormous development in the permeation flux with only a negligible reduction in the separation factor was achieved [51]. Pourjafar *et al.* [59,60] prepared a PVA /PES composite membrane, which was modified by TiO<sub>2</sub> nanoparticles on the surfaces by the coating method. The surface hydrophilicity and roughness of modified membranes were increased by coating of TiO<sub>2</sub> nanoparticles.

PVA has been used considering its anticipated characteristics such as hydrophilicity, good film forming ability, resistance to oxidation and excellent mechanical and adhesive properties [61,62]. The blending strategy has been adopted to promote hydrophilicity, easy handling, mechanical characteristics and adhesive properties.

The above outcomes were based on research done before it became evident that PVA can be a good candidate for blending with PU to improve the selectivity properties of PU membranes; so far, no data has been reported for the gas separation properties of PU/PVA blend. Therefore, in the present study, PU/PVA blend membranes were prepared in order to improve the selectivity of gases in PU. In particular, the influence of molecular weight of PVA blend composition on the gas permeation properties of PU/PVA membranes is reported. Also, the morphology of PU/PVA blend membranes has been investigated.

#### Experimental

## Materials

Polytetramethylene-glycol (PTMG, Mw=2000 gmol<sup>-1</sup>), was obtained from Arak Petrochemical Complex (Arak, Iran). 1,4-butanediamine (BDA) and isophoren diisocyanate (IPDI) were purchased from Merck. *N,N*-Dimethylacetamid (DMAc) was purchased from Merck and used as a solvent. The chain extender (BDA) was dried over 4Å molecular sieves before use. CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> gases (purity 99.99) used for gas permeation tests were purchased from Ardestan Gas Co. (Iran) and CH<sub>4</sub> (purity 99.9) was purchased from Technical Gas Service Co. (Iran). PVA with 99+% hydrolysis degree with different molecular weights (15000, 30000, 60000, 145000, and 200000) was purchased from Merck.

#### **Polymer Synthesis**

The polymer was synthesized in a mole ratio of 1:3:2 of polyol: diisocyanate: chain extender by bulk two-step polymerization method (Figure 1) [63]. Polytetramethylene-glycol reacted with isophoren diisocyanate (IPDI) for 2 h at



Figure 1. Molecular structure of synthesized PU.

Table 1. Name and characteristic of prepared membranes			
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Pland	Blend composition						
Dicilu	Part	[	Part 2				
Membranes	Name	wt.%	Name	Molecular weight (g/mole)	wt.%		
PU/PVA15				15000			
PU/PVA30				30000			
PU/PVA60	Polyurethane	90	Poly(vinyl- alcohol)	60000	10		
PU/PVA145				145000			
PU/PVA200				200000			

85-90 °C under nitrogen atmosphere to obtain macrodiisocyanate pre-polymer. The chain extension of polymer happened by adding of BDA after a pre-polymerization step at room temperature.

#### **Preparation of PU Membranes**

PU membranes were prepared by thermal phase inversion method. The synthesized PUs were dissolved in DMAc at 100 °C (10 wt.% solution) and cast in petri dishes at room temperature. To prepare the homogenous dense membrane the membranes were formed by evaporating the solvent in an oven for 24 h at 60 °C.

## Preparation of PU/PVA Blend Membranes

For PU/PVA blend membranes, initially, the polymer solution of PU (10 wt.%) and PVA (1 wt.%) was prepared using DMAc as solvent (Table 1). Then, a certain amount of the above solutions was mixed together at ambient temperature, which was stirred continuously for 45 min. at 140 °C to prepare the polymer blend, then the mixture was stirred and the blend membranes were cast on clean Teflon petri dishes and incubated at 60 °C for 24 hours to allow the solvent to evaporate.

#### **Membrane Characterization**

## Membrane Analyses

A BIO-RAD FTS-7 Fourier Transform Infrared Spectrometer was used to characterize the synthesized PU and PU/PVA blend membranes at room temperature. The scanning frequency range was 4000-400 cm<sup>-1</sup>.

The morphology of the membranes was examined using scanning electron microscopy (SEM). All the samples were coated with gold/palladium and observed with a Philips XL30 (Philips, The Netherlands) scanning electron microscope.

Due to the presence of semi crystalline PVA in blend membranes and polar groups in PU polymer, changes in the structure of PU and PU/PVA blends evaluated by X-ray diffraction patterns (XRD, Philips Co. Poland).

#### **Gas Permeation Tests**

Prepared membranes were exposed to four different pure gases,  $N_2$ ,  $O_2$ ,  $CH_4$ , and  $CO_2$ , and permeation properties were assessed using the constant pressure method (P=10 bar). The flux of the permeated gases was measured by a U-



**Figure 2.** Schematic design of gas permeation apparatus; (1) gas cylinder, (2) regulator, (3) barrometer, (4) membrance cell, and (5) flow meter.

shape flow meter. Figure 2 shows the schematic representation of the gas permeation equipment. By plotting the flux of the permeated gas versus time, the permeability coefficient was calculated via the slope of the linear section of flux-time curve. The gas permeability of membranes was determined using the following equation [10,12,13]:

$$P = \frac{ql}{A(p1-p2)}$$

where *P* is permeability expressed in Barrer (1 Barrer= $10^{-10}$  cm<sup>3</sup> (STP) cm/(cm<sup>2</sup> s cmHg), *q* is the flow rate of the permeate gas passing through the membrane (cm<sup>3</sup>(STP)/s), *l* is the membrane thickness (cm), *p*1 and *p*2 are the absolute pressures of feed side and permeate side, respectively (cmHg), and *A* is the effective membrane area (cm<sup>2</sup>). The ideal selectivity (or permselectivity),  $\alpha_{A/B}$ , of membranes was calculated from pure gas permeation experiments [10, 12,13]:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Gas permeation test was repeated three times on two of each of the membrane samples. The reported permeation data was averaged on three repeated experiments. The reported gas permeation data has less than 10 % error.

## **Results and Discussion**

The most significant aspect of polymer blends related to transport processes contains the phase behavior. The phase behavior (miscibility and phase separation) explained the gas transport properties of polymer blend membranes. On the other hand, the functional groups existing on the molecular structures of polymers and interaction between them determine the phase behavior, and hence the gas transport properties of polymer blend membranes. Therefore, the characterization methods were used to determine the morphology and phase behavior of the prepared PU/PVA blend membranes.

#### FTIR Analysis

Structural characteristics of synthesized PU, PVA, and PU/ PVA blend membranes were carried out by using FTIR analysis. Figure 3 represents the FT-IR spectra of PVA,



Figure 3. ATR-FTIR spectra of PU, PVA and PU-PVA blend membranes.

synthesized PU as well as the spectrum of blend PU/PVA membranes. The disappearance of NCO peak at 2270 cm<sup>-1</sup> indicates that the isocyanate reaction was completed. N-H Stretching of urethanes appears at 3319 cm<sup>-1</sup> and C=O stretching at 1714-1720 cm<sup>-1</sup> and 1683 cm<sup>-1</sup>. The signals of the urethane ether and the C-O-C of ether appear at 1112 and 1105 cm<sup>-1</sup>, respectively. We can clearly see the presence of a large peak at 3400 cm<sup>-1</sup>. This peak is linked to the stretching of O-H from the intramolecular and intermolecular hydrogen bonds. The peaks observed at 2840 cm<sup>-1</sup> and 2940 cm<sup>-1</sup> are respectively related to the symmetric and anti-symmetric stretching vibrational of C-H from alkyl groups. Furthermore, the signals at around 1443 cm<sup>-1</sup> may be related to the -CH<sub>2</sub> bending [38]. Moreover, the peaks between 1715-1750 cm<sup>-1</sup> are due to the stretching C=O and C-O from acetate group remaining from PVA, respectively. The presence of crystalline region in PVA was obtained from Infrared Spectroscopy through the peak at 1143 cm<sup>-1</sup>. The intensity of this peak is influenced by the crystalline portion of the polymeric chains. According to the literature [63] this peak is related to the symmetric C-C stretching mode or stretching of the C-O of a portion of the chain where an intramolecular hydrogen bond is formed between two neighboring OH groups that are on the same side of the plane of the carbon chain [63]. By adding PVA to PU (Figure 4) the absorption peak of O-H reduced greatly; also, by adding PVA to PU the N-H stretching vibration in PU shifted to a lower frequency region. This effect can be attributed to the interaction of the NH groups in PU to OH groups in PVA, which verify the suitable chain interaction between two polymers. The peaks related to carbonyl groups appeared in Figure 4(b) in the range of 1600-1800 cm<sup>-1</sup>. As shown, the intensity of the peak related to bonded carbonyl (the carbonyl groups of PU hard segments interacted to NH groups of hard segments via hydrogen bonding) at 1640 cm<sup>-1</sup> in comparison to free carbonyl (the carbonyl groups of PU hard segment which connect to soft domains) at 1730 cm<sup>-1</sup> reduced by incorporation of PVA. It shows more phases mixing in PU after introducing



Figure 4. ATR-FTIR spectra in three different ranges for prepared membranes.



Figure 5. XRD pattern of the PU, PVA, and blend membranes.

PVA membranes, which may be due to hydrogen bonding of PVA to NH groups of PU. The disappearance of the peak at 1143 cm<sup>-1</sup> is the representation of lack of crystalline regions due to the formation of intramolecular hydrogen bonding between adjacent OH groups in the structure of PVA, and this is because of the influence of PU chain in the PVA chain and disruption of structural order in the structure of PVA.

## WAXD Analysis

Wide angle X-ray diffraction (WAXD) is performed on the pure polymer and hybrid membranes in an effort to observe any morphological changes. Figure 5 illustrate the XRD pattern of the PVA, PU, and blend membranes. As shown, the sharp peak appears at a  $2\theta$  value of  $20^{\circ}$  in PVA while PU shows a hollow one at  $2\theta$ =20. This observation verifies the crystalline structure of PVA while in PU it represents the amorphous region or small crystalline regions dispersed in polymer media. The observed descending trend in the intensity of the peak at  $2\theta$ =20 by molecular weight of PVA implies the reduction in the crystallinity of blend membranes by increasing the molecular weight of PVA. It may relate to the increased chain connection of PVA-200 to PU chains which prevents the PVA chain to order in crystalline cells.

## Scanning Electron Microscopy (SEM)

SEM micrographs of PU/PVA blend membranes with different molecular weight of PVA are presented in Figure 6. From this figure, it is easily recognized that blend membranes are fully dense. From Figure 6(b) (which is related to the blend membrane of PU/PVA containing PVA with molecular weight of 15000 g/mole (PU/PVA15)), some new regions are observed which may be related to PVA domains in blend membrane. While in blends containing higher molecular weight PVAs, these regions vanished. This effect can be attributed to increasing the more interaction between PU chain and PVA with increasing molecular weight of PVA. As reported in XRD, by increasing the molecular weight of PVA in blend membranes the crystallinity decreased. So, the disappearance of separated regions in blend membranes in SEM pictures can relate to more interaction of PVA chains to PU ones which leads to more dispersion of PVA in PU and



Figure 6. SEM micrographs of (a) PU, (b) PU/PVA15, (c) PU/PVA60, and (d) PU/PVA200.

Mambrana	Permeability (Barrer)			Selectivity			
Wieliforane	$N_2$	$O_2$	$CH_4$	$CO_2$	$O_2/N_2$	$CO_2/N_2$	CO <sub>2</sub> /CH <sub>4</sub>
PU	5.51	15.28	20.14	142	2.78	25.77	7.05
PU/PVA15	5.3	13.24	18.8	137	2.38	25.84	7.28
PU/PVA30	5.28	12.43	17.9	136.8	2.39	25.9	7.64
PU/PVA60	4.65	12.08	15.9	122.5	2.67	26.34	8.7
PU/PVA145	4.16	10.94	14.6	117	2.58	28.1	8.01
PU/PVA200	2.86	8.3	9.82	93.24	2.53	32.6	9.49

Table 2. Permeability of Pure Gases through Pure PU and PU/PVA blend membranes with different molecular weight at T=35 °C, P=10 bar

eventually prohibit the ordering of the PVA chains in crystalline cells.

#### **Gas Permeation Results**

In this study, the permeation of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> gases through pure PU and PU/PVA blend membranes were investigated at 35 °C and pressure of 10 bar. In this evaluation, the effect of molecular weight of PVA on the properties of prepared PU/PVA blend membranes was investigated. In order to evaluate the effect of molecular weight of PVA on the permeability properties of PU/PVA blend membrane, blend membranes with the following composition from each of the available molecular weight of PVA was prepared: PU:PVA was 90:10 (Table 1).

Pure gas permeation test result is shown in Table 2. As shown in this table, the permeability coefficient of gases decreases in the subsequent order:

 $P(CO_2) >> P(CH_4) > P(O_2) > P(N_2)$ 

The higher permeability of  $CO_2$  in comparison with other gases is related to its low kinetic diameter and high condensability (Table 3), which facilitate the penetration of this gas through the membranes [64]. Furthermore,  $CO_2$  is a polar gas that can interact with the polar ethereal groups in the soft segments of the synthesized PUs. As shown in Table 2,  $CH_4$  is more permeable than the smaller molecules of  $N_2$ and  $O_2$ . This behavior indicates the predominance of a solution mechanism for the gas permeation process in the pure PU and PU/PVA membranes. The fact that the solution mechanism prevailed reveals that the PU and PU/PVA blend membranes exhibit rubbery properties. The above stated results were observed in our previous works [22,64]. As shown in Table 2, the permeability of all gases decreased by

Table 3. Condensability and Kinetic diameter of studied gases

Gas	Kinetic diameter (Å)	Condensability (K)
$CO_2$	3.3	195
$O_2$	3.46	107
$N_2$	3.64	71
$CH_4$	3.8	149

adding the PVA to the PU based blend membranes, and also by increasing the molecular weight of PVA from 15000 to 200000 (g/mole). The trend of decreasing permeability for each of the gases is as follows:

## CO<sub>2</sub>:

PU/PVA200 (34.33 %)>> PU/PVA145 (17.6 %)> PU/PVA60 (13.73 %)>> PU/PVA30 (3.66 %)> PU/PVA15 (3.52 %).

#### $CH_4$ :

PU/PVA200 (51.24 %)>> PU/PVA145 (27.5 %)> PU/PVA60 (19.21 %)>> PU/PVA30 (8.34 %)> PU/PVA15 (6.2 %)

#### $O_2$ :

PU/PVA200 (45.68 %)>>PU/PVA145 (27.29 %)> PU/PVA60 (18.84 %)>PU/PVA30 (8.4 %)> PU/PVA15 (6.41 %).

#### N<sub>2</sub>:

PU/PVA200 (48.09 %)>>PU/PVA145 (27.58 %)> PU/PVA60 (19.23 %)>>PU/PVA30 (8.53 %)> PU/PVA15 (6.53 %).

The above comparison indicates that by increasing the molecular weight of PVA in the blend membranes, permeation of non-condensable gases, such as  $O_2$ ,  $N_2$ , and also gas with a larger molecular size, such as  $CH_4$  decreased more in comparison with the polar, condensable, and smaller molecular size gas (CO<sub>2</sub>). However, the amount of reduction for permeation of gases that passes through the membrane in a certain molecular weight of PVA of prepared blend membrane is totally different and is as follows:

 $\begin{array}{l} PU/PVA15 \ Blend \ Membrane: \\ N_2 \ (6.53 \ \%) < O_2 \ (6.41 \ \%) < CH_4 \ (6.2 \ \%) < CO_2 \ (3.52 \ \%) \end{array}$ 

PU/PVA30 Blend Membrane:

 $N_2$  (8.53 %)  $< O_2$  (8.40 %)  $< CH_4$  (8.34 %)  $< CO_2$  (3.66 %)

PU/PVA60 Blend Membrane:

N<sub>2</sub> (19.23 %) < CH<sub>4</sub> (19.21 %) < O<sub>2</sub> (18.84 %) < CO<sub>2</sub> (13.73 %)

PU/PVA145 Blend Membrane:

N<sub>2</sub>(27.58%) < CH<sub>4</sub>(27.50%) < O<sub>2</sub>(27.29) < CO<sub>2</sub>(17.60%)

PU/PVA200 Blend Membrane: CH<sub>4</sub>(51.24 %) < N<sub>2</sub>(48.09 %) < CO<sub>2</sub>(34.33 %) < O<sub>2</sub>(45.68 %)

As we know, in the majority of PUs micro phase separation occurs and this phase separation leads to increase in the permeability of PU membranes. Increasing phase separation in the PU structure is occurred by decrease in the interference of soft segments and hard segments of polymer and this leads to increase in molecular mobility of soft segments and finally leads to increase in the permeability of gases. So, any factors that reduce the phase separation in the PU structure, or in other words, reduce the molecular mobility of the soft phase, will reduce the permeability of gases [45]. As mentioned in FT-IR study, by incorporation of PVA in PU matrix, the phase separation of hard and soft domain in PU decreases and higher phase mixing occur in blend membrane. Also, the molecular weight of the polymer significantly affects the transport process. So, by increasing the molecular weight of the polymer, the number of the end of the chains will be reduced. The end of the chains is representation of lack of continuity and most of them make the absorption places of molecules that pass from glassy polymers [65]. The reduction in the permeability of the PU/ PVA15 blend membrane can be attributed to the dispersing of droplets (small crystals) of PVA with low molecular weight to the soft segment of PU. These small crystals are due to the absence of flexible groups that act as physical cross links and reduce the molecular mobility of PU soft phase [66].

The above observations showed that by increasing molecular weight of PVA in blend membranes, trend of reduction in permeability of gases changes from noncondensable gases with larger molecular size to the gases with the larger molecular size and higher condensability. By increasing molecular weight of PVA in blend membranes, the structure of the membranes changed from rubbery to glassy and this leads to increase in the size selectivity mechanism, which is the characteristic of the glassy polymers. Therefore, the reduction in permeability increased by increasing the size of the gas molecules passed through the membrane. Moreover, it can be assumed that phase separation that happened at low molecular weight of PVA in the structure of blend membranes is due to the glassy phase of PVA that dispersed in the form of droplets in the matrix of PU. Therefore, the reduction in the permeability of condensable gases, such as CO<sub>2</sub> and CH<sub>4</sub>, is less than the permeability of gases with larger molecular size and smaller condensability  $(i.e. N_2, O_2).$ 

#### Selection of the Best Structure of the Blend Membranes

For commercial use of polymer membranes in gas separation processes, the polymers that have high permeability and selectivity for desired separation get more attention. Based



**Figure 7.** Comparison of  $CO_2/CH_4$  separation performance of blend membranes with Robeson's upper bound line.



**Figure 8.** Comparison of  $CO_2/N_2$  separation performance of blend membranes with Robeson's upper bound line.

on the obtained results from the permeability of membranes, it is observable that pure PU has the highest permeability of carbon dioxide but less selectivity in comparison with blend membranes.

From Table 2 it is obvious that the PU/PVA200 blend membrane has the highest selectivity of carbon dioxide in comparison with other gases, while it has the lowest permeability of carbon dioxide. In order to select the best membrane, the curves provided by Robson, are suitable criterion. Therefore, the obtained results from prepared PU/ PVA blend membranes were compared with Robeson's upper bound in Figures 7 and 8. As shown in Figure 7, by increasing the molecular weight of PVA, the gas separation properties of the blend membranes for CO<sub>2</sub>/CH<sub>4</sub> gas pair improved and were closer to Robeson's upper bound line. From Figure 8 it is observable that all points are above Robson's line in 1991 and below Robson's line in 2008 [67]. It showed that by increasing the molecular weight of PVA in the blend membranes, the distance from the Robson line in 2008 decreased. Therefore, the PU/PVA200 blend membrane that is closer to the Robson line in Figures 7 and 8 selected as the best structure and consider for our further investigation.

#### Conclusion

In the present work, improvement of the gas separation performance of PU membrane was investigated by blending it with compatible and polar polymer of PVA. For this purpose, PVA with different molecular weights with certain composition added to PU and their physical and gas separation properties were investigated.

PU/PVA blend membranes based on PU are classified as immiscible compatible blends that our results reveal immiscibility decreased by increasing the molecular weight of PVA in the blend membranes. By increasing the molecular weight of PVA in the blend membranes, the selectivity of membranes increased. The reduction in the permeability of gases passing through the membrane in a certain molecular weight was different than the prepared membranes. So that, by increasing the molecular weight of PVA in the blend membranes, the trend of reduction in the permeability of gases varies for non-condensable gases with larger molecules to condensable gases with smaller size. The results displayed that PU/PVA200 blend membranes are able to offer higher selectivity in comparison with pure membrane.

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