Gas Permeation Properties of Polyvinylchloride/Polyethyleneglycol Blend Membranes

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ABSTRACT: In this study, the effect of the molecular weight of polyethyleneglycol (PEG) on the gas permeability and selectivity of a series of polyvinylchloride/polyethyleneglycol (PVC/PEG) blend membranes was investigated. The molecular weight of polyethylene glycol ranged from 400 to 4000. PVC/PEG blend membranes were prepared via thermal phase inversion of PVC/PEG/dimethylformamide solution at $60°C$. The permeabilities of pure CO_2, CH_4, O_2, and N_2 gases through prepared membranes were determined at room temperature ($25°C$) and 20 bar feed pressure. The blend membranes having PEG with 4000 molecular weight showed higher values of CO_2 permeability, and CO_2/CH_4 and CO_2/N_2 ideal selectivities (the ratio of pair gas permeabilities) compared with other blend membranes containing PEGs of lower molecular weights. It was also found that the gas permeabilities of PVC/PEG4000 blend membrane rapidly increased with an increase in PEG concentration (weight fraction). The PVC/PEG blends containing 10, 20, and 30 wt % of PEG4000 showed CO_2 permeabilities equal to 0.84, 2.38, and 5.82 Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg), respectively. The CO_2/N_2 ideal selectivities of 10, 20, and 30 wt % of PEG4000/PVC blend membranes were 49, 70, and 109, respectively. This is a great improvement compared with the pure PVC membrane, which showed CO_2 permeability and CO_2/N_2 ideal selectivity of 0.13 Barrer and 14.5, respectively. These results and comparison of CH_4 and N_2 permeabilities of PVC membrane and PVC/PEG blend membranes indicated that the gas solubility is dominant in the permeation of gases through abovementioned blend membranes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1093–1098, 2008

Key words: polyvinylchloride; polyethyleneglycol; blend membranes; molecular weight; gas permeation

INTRODUCTION

The enhancement of separation properties of polymeric membranes is one of the major concern of the researchers who are engaged in the development of new membranes, especially for CO_2 separation applications.[1,2] The CO_2 separation is one of the most important membrane gas separation processes since it has many potential industrial applications such as natural gas, landfill, or tail gas de-acidification.[3,4] As stated by other researchers, the membrane separation of CO_2 becomes economically feasible if CO_2 permeability and permeability ratios of CO_2 over N_2 exceed 100 Barrer and 70, respectively.[5] However, the commercial membrane materials such as polyimide (PI) and cellulose acetate (CA) have not necessarily satisfied these requirements. For example, the CA membranes show CO_2/N_2 ideal selectivity of 20–30 with a low CO_2 permeability of 5–6 Barrer at $30°C$,[6] and the polyimides having CO_2 permeability of 2–30 Barrer show CO_2/CH_4 ideal selectivity in the range of 30–60 at $35°C$.[7]

Fabrication of new membranes based on blend polymers is one of the most important research areas. Because in this method of membrane preparation, separation properties those can not be obtained by individual polymers, can be achieved by blending polymers. It should be noted that, in this method of membrane fabrication, the better mechanical and chemical stability of one polymer with hard segments like PVC may be combined with another polymer like polyethyleneoxide for better separation properties. In this blend, the soft segments of polyethyleneoxide provide a high selectivity because of its good affinity to CO_2 and high permeation rate related to its chain flexibility.[8]

Polyethyleneglycols or polyethyleneoxides (PEOs) with a molecular structure indicated as HO—$(CH_2—O—CH_2)_n$—OH, are liquids or low melting wax like solids. Polyethyleneoxides have some specific interactions with CO_2. It has been reported that, PEG segments can dissolve large amount of acidic gases.[9] The gas permeation flux through PEG segments is also high, because of its chain flexibility. However, it is difficult to obtain a thin film of PEG

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alone because of its weak mechanical and thermal strength. For that reason, a large number of PEG (PEO) based copolymers and polymer blend membranes have been prepared, where PEO segments provide high selectivity and high permeation rates. This is in addition the other component provides us with the film-forming ability with chemical and thermal stability. Polyethyleneoxides have been used as copolymer with cellulose acetate[10] or cellulose nitrate,[11] polyurethane (PU),[12] poly(ether imide) segmented copolymers,[13] poly(amide-6-b-ethylene oxide) block copolymers,[14] poly(amide-6-b-ethylene oxide)-silica hybrid membranes[15] and poly(ethylene glycol) methyl ester methacrylates[5] and in almost all of these cases gas permeation properties have been studied.

Sanchez et al. investigated the gas permeation properties of poly(ethylene oxide-co-epichlorohydrin) (P(EO/EP)) membranes. Their results revealed that a wide range of gas transport properties is obtainable according to the ethylene oxide/epichlorohydrin ratio in the copolymer. The copolymers showed very high CO_2 permeabilities (up to 105 Barrer) and CO_2/N_2 and CO_2/CH_4 ideal selectivities (P_{CO2}/P_{N2}: 63 and P_{CO2}/P_{CH4}: 17.2).[16]

Sanchez et al. also determined the gas permeation properties of crosslinked membranes prepared from a series of (P(EO/EP)) copolymers with different contents of ethylene oxide. Their gas permeation results showed that the permeabilities are nearly constant up to an EO content of about 75–80 mol %, then increase rapidly up to a maximum at around 90 mol % of EO in the copolymers. Sanchez et al. also showed that copolymers present very high CO_2 permeability and selectivity compared to other permanent gases.[17]

Kim et al. applied pore-filling concept to prepare selective composite membranes for CO_2 separation. Their composite membranes were composed of two polymeric materials: a porous substrate and filling polymer that filled the pore of the substrate. In their study, asymmetric polyacrylonitrile (PAN) membrane was used as substrate and methoxy poly(ethylene glycol) acrylate (MePEGA, Mw D 454) was used for the preparation of photoinitiated graft copolymer. Kim et al. also obtained high CO_2/N_2 selectivity by this pore-filling membrane: carbon dioxide permeation flux, J_{CO2} = 65 GPU (1 GPU = 10^{-6} cm^3 (STP)/cm^2 s cmHg) and CO_2/N_2 ideal selectivity, P_{CO2}/P_{N2} = 32.4 at 30°C.[18]

Polyvinylchloride (PVC) with molecular structure of $(CH_2—CHCl)_n$, which was used in this study, is a thermoplastic polymer with glass transition temperature of 87°C. It is a glassy polymer with high chain compactness and low polymeric chain segmental motion. Therefore, its gas permeability is low.[19] PVC is a chemically and mechanically stable polymer that can be easily processed. By blending the PEG to PVC the high gas selectivity properties of PEG and high mechanical and chemical stability of PVC are combined and the membrane with high performance ability can be prepared.

In this study, we aimed to prepare some PVC/PEG blend membranes and investigate the effects of PEG content (its molecular weight and weight fraction in the range where two polymers are easily miscible) on CO_2, N_2, CH_4, and O_2 gas permeation properties.

EXPERIMENTAL SETUP AND MATERIALS

Materials

Merck Company (Tehran, Iran) supplied polyethyleneglycol with different molecular weights (400, 1000, 1500, and 4000) and dimethylformamide (DMF) as solvent, and polyvinylchloride with K-value of 67, was obtained from Abadan Petrochemical (Abadan, Iran).

Membrane preparation

PVC and PVC/PEG blend membranes were prepared using thermal phase inversion technique. Initially, PVC was dissolved in DMF at 60°C to prepare 10 wt % of PVC/DMF solution. A reflux condenser was used. The PVC/DMF solution was cast on a glass plate using a doctor blade.

The solution of PVC/PEG blend was also prepared by adding a desired amount of PEG into the prepared solution of PVC/DMF and mixing it to obtain a homogeneous and clear solution. Then, the prepared solution was cast on a horizontal glass plate with a doctor blade. The cast membranes were placed in an oven and the temperature was kept at 55°C for 12 h. To ensure complete solvent removal, the prepared membranes were heated at 70°C for another 5 h under vacuum. The membrane samples were, then, loaded to the permeation cells and kept under pure nitrogen pressure for 2 h before pure gas permeation experiments were conducted.

Membrane characterization

The morphological behavior of the prepared membranes was studied with scanning electron microscopy (Philips, Netherlands). The membrane samples were fractured in liquid nitrogen and then coated with gold to observe the cross section structures by SEM.

Gas permeation measurements

Permeability measurements of pure CO_2, CH_4, N_2, and O_2 gases were conducted at room temperature
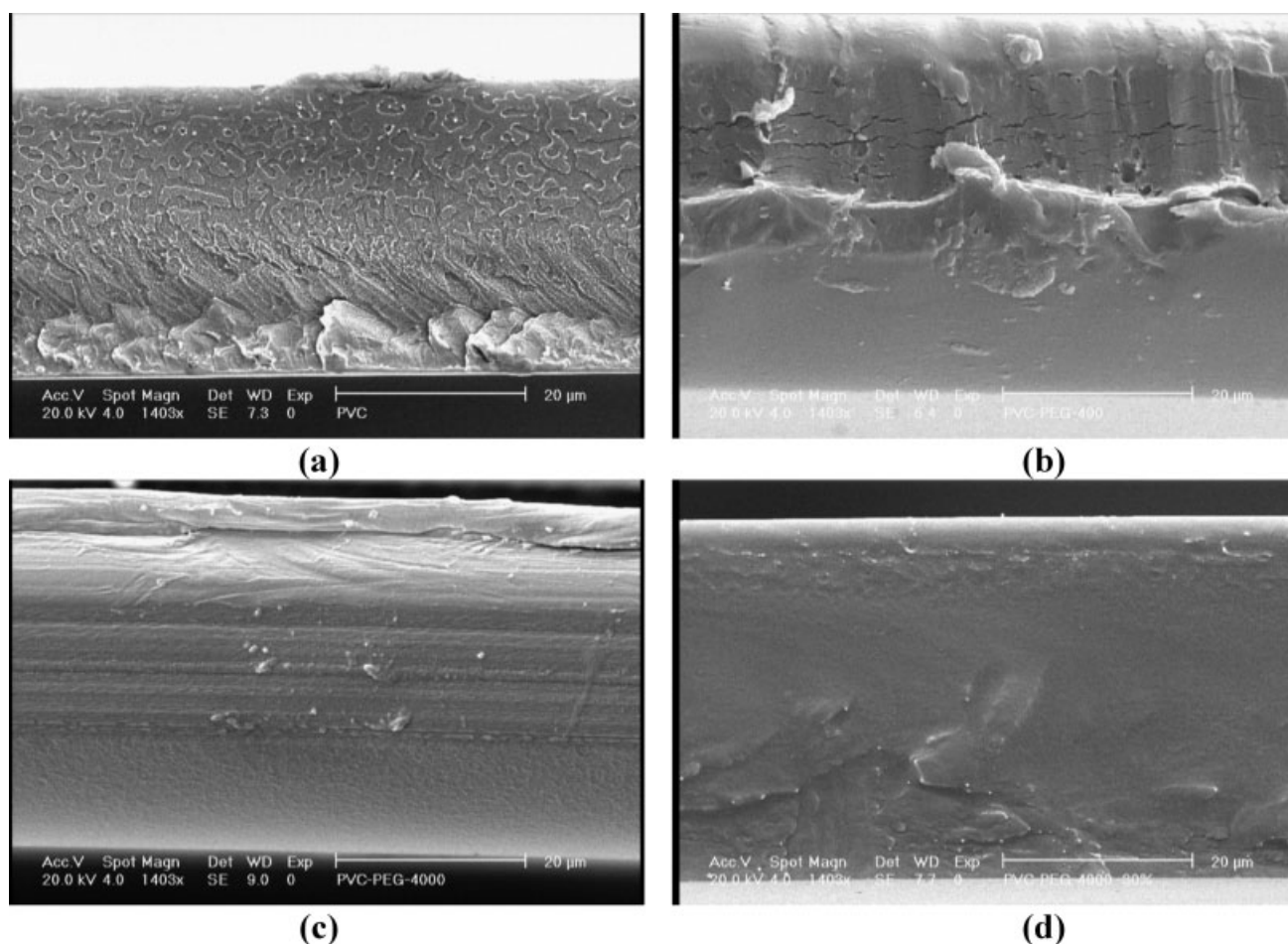
Figure 1 Cross-sectional SEM micrographs of (a) pure PVC, (b) 10 wt % of PEG400/PVC, (c) 10 wt % of PEG4000/PVC, and (d) 30 wt % of PEG4000/PVC blend membranes.

using an experimental setup like that one described elsewhere.[20] The gas permeability of the cast films (*P*) in Barrer was calculated as follows:

$$P = \frac{Ql}{A\Delta p} 10^{10} \qquad (1)$$

where Q is the steady-state permeation rate [cm^3(STP)/s], l is the membrane thickness (cm), A is the permeation area of the film (cm^2), and Δp is the pressure difference across the film (cmHg).

Reproducibility and repeatability of data were checked randomly in some occasions and variabilities in the range of 3–5% were obtained.

RESULTS AND DISCUSSION

Morphological behavior

Figure 1 shows the SEM micrographs of pure PVC and PVC/PEG blend membranes. The figure shows that the blending of PEG in PVC led to a homogeneous structure.

The uniform dense structure of PVC/PEG blends without any defects makes these membranes acceptable for our gas permeation studies.

Gas permeation results

In this study, the effects of PEG molecular weight and its weight fraction on the gas permeabilities of PVC/PEG membranes were studied. All permeabilities were determined at room temperature (25°C) and 20 bar feed pressure. Based on the obtained gas permeabilities, CO_2/CH_4 and CO_2/N_2 ideal selectivities (*the ratio of pair gas permeabilities*) were also calculated. Figures 2–5 show the results.

As can be seen in Figure 2, blending higher molecular weights of PEG with PVC enhances the gas permeabilities of PVC/PEG membranes to greater degrees, especially for CO_2 gas. It should be mentioned that the presented data in this figure at zero molecular weight of the PEG belongs to the pure PVC membrane.

PVC is a glassy polymer with high chain compactness and low polymeric chain segmental motion.
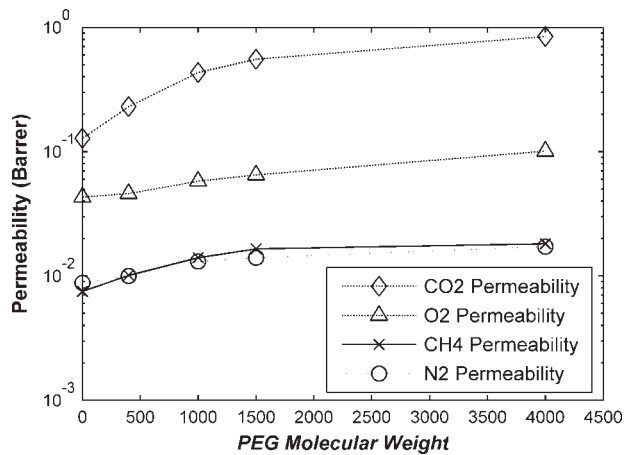
Figure 2 Pure CO_2, O_2, N_2, and CH_4 permeabilities through PVC and PVC/10 wt % PEG blend membranes versus PEG molecular weight. Feed pressure: 20 bar and temperature: 25°C.

Therefore, its gas permeability is low. On the other hand, PEG has soft and flexible segments. Therefore, blending PEG with PVC reduces the chain compactness of PVC, and introduces flexible sites that enhance the diffusion of gases through blend membrane. The presence of long polyether chains in the blend membranes increases the length of the segmental jump too. As it was mentioned before, the observed increase in CO_2 permeability (from 0.23 to 0.85 Barrer as PEG molecular weight increased from 400 to 4000) was greater than any other gases. This can be attributed to the high affinity of polar CO_2 molecules to the polyether segments. It should be noted that CO_2 is the smaller gas used in this study and the presences of longer polyether chains should also result in an enhancement diffusion. The gas permeabilities in PVC membrane decreased in the
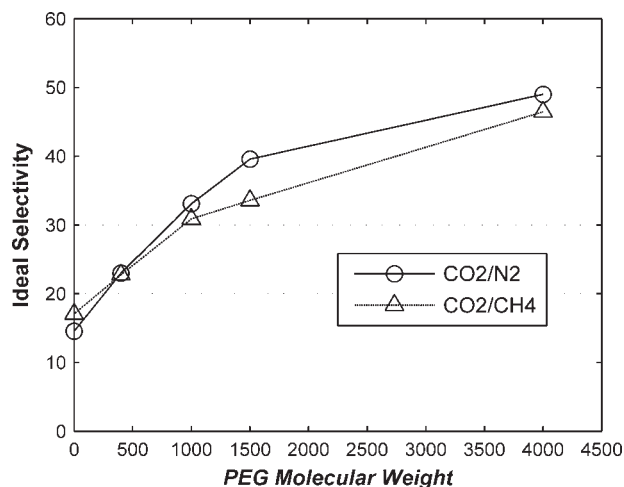
Figure 3 CO_2/CH_4 and CO_2/N_2 ideal selectivities of PVC and PVC/10 wt % PEG blend membranes versus PEG molecular weight. Feed pressure: 20 bar and temperature: 25°C.
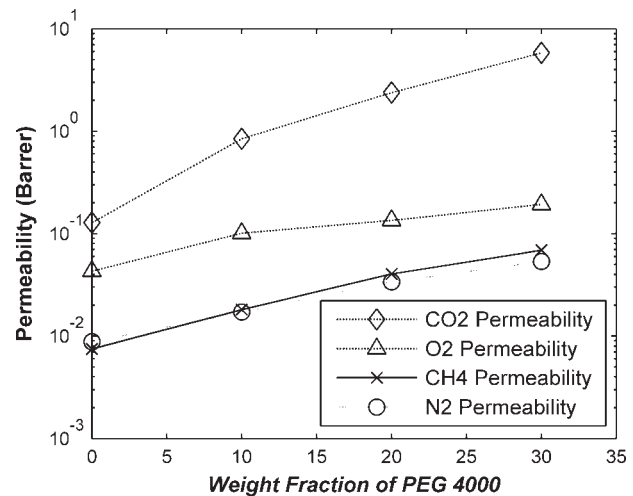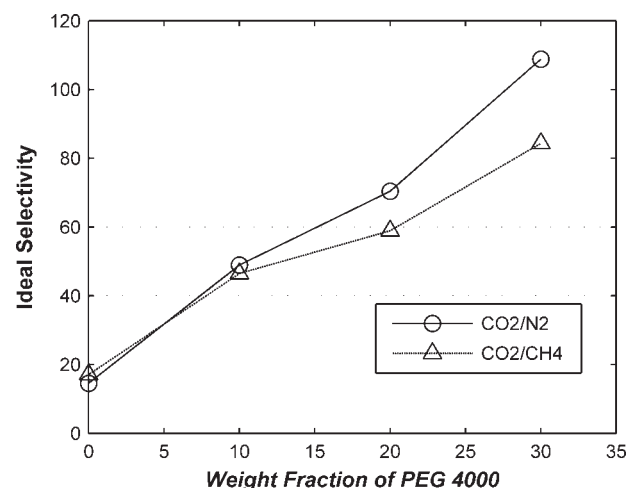

Figure 4 Pure CO_2, O_2, N_2, and CH_4 permeabilities through PVC and PVC/PEG4000 blend membranes versus PEG concentration. Feed pressure: 20 bar and temperature: 25°C.

order, $P(CO_2) > P(O_2) > P(N_2) > P(CH_4)$, but the order of gas permeabilities changed in PVC/PEG blend membranes to $P(CO_2) \gg P(O_2) > P(CH_4) > P(N_2)$. This means the permeability of CH_4 in PVC membrane is lower than that of N_2, while the opposite is the case for PVC/PEG blend membranes. The generally accepted solution-diffusion model of gas transport in polymers can explain this discrepancy. In terms of the solution-diffusion mechanism, the permeability coefficient (P) is expressed as a product of the average diffusion coefficient (D) and the solubility coefficient (S)[21]:

$$P = DS \qquad (2)$$

The solubility coefficient, S, is a thermodynamic property and determined by (i) the inherent

Figure 5 CO_2/CH_4 and CO_2/N_2 ideal selectivities of PVC and PVC/PEG4000 blend membranes versus PEG concentration. Feed pressure: 20 bar and temperature: 25°C.
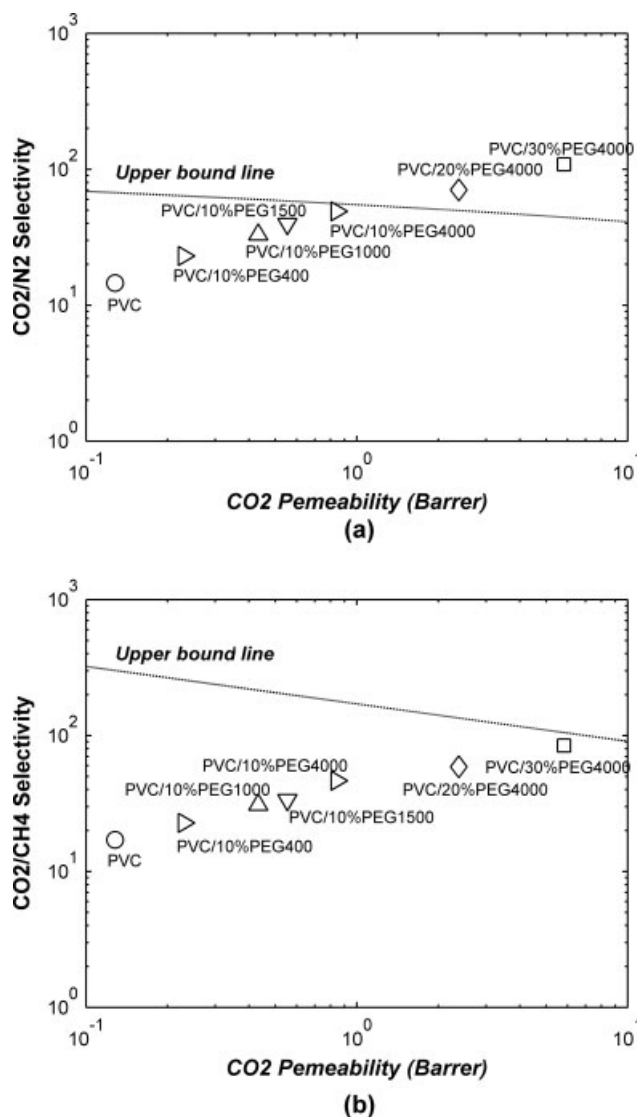
condensability of the penetrant (critical temperature, T_c, is a measure of condensability), (ii) polymer–penetrant interactions, and (iii) the amount of free volumes existing in glassy polymer that contribute to enhance the gas solubility in the polymer. The average diffusion coefficient, D, is a kinetic term that is a measure of the mobility of the penetrant in the polymer matrix and depends on the upstream and downstream conditions in the membrane. Therefore, the packing and motion of the polymer segments and the size of the penetrant molecule determine it.

Table I presents the kinetic diameter and the condensability of gases. As shown in this table, the kinetic diameter and condensability of CH_4 are greater than those of N_2. It should be noted that these molecular properties have opposing effects on the permeability of gases. Greater kinetic diameter of CH_4 leads to small diffusion coefficient, while its greater condensability directs to large solubility coefficient. Looking into the permeability data of the PVC membrane, $P(N_2) > P(CH_4)$, which means the kinetic diameter has a dominant effect on the gas permeability. This is because of the high density and glassy behavior of PVC.[22] On the other hand, with respect to the blend PVC/PEG membranes, $P(CH_4) > P(N_2)$. It indicates that the gas condensability is dominant. In the case of blend PVC/PEG membranes, the presence of soft and mobile polyether segments of PEG enhances the sorption of the gases. The higher condensability of CH_4 and the stronger interaction between CH_4 and PEG also help CH_4 to have a greater solubility coefficient and consequently a greater permeability. A similar argument can be applied for the CO_2/CH_4 and CO_2/N_2 selectivity. As shown in Figure 3, the selectivity of CO_2/N_2 increased from 14.55 of the PVC membrane to 49.01 of the PVC/PEG blend membrane (PEG 4000). As well, the selectivity of CO_2/CH_4 increased from 16 of PVC membrane to 46.47 for PVC/PEG blend membrane (PEG 4000). This is because of the high condensability of CO_2 and the high affinity of polar CO_2 molecule to polar PEG segments.

The effect of the content of PEG4000 (its weight fraction) in the PVC/PEG blend membranes was studied and the results are given in Figures 4 and 5. As shown in Figure 4, by increasing the PEG content, the permeability of all gases increased. This can

Figure 6 Selectivity versus CO_2 permeability for PVC/PEG blend membranes. (a) CO_2/N_2 ideal selectivity versus CO_2 permeability and (b) CO_2/CH_4 ideal selectivity versus CO_2 permeability. Feed pressure: 20 bar and temperature: 25°C.

be attributed to the easy diffusion of gas molecules through blend membranes when the content of flexible and mobile PEG segments increased which contributes to the dynamic chain mobility of the structure. In the case of CO_2 permeation, the gas permeation is further enhanced by the strong affinity between the CO_2 molecule and the polyether chain of the PEG. As a result, the CO_2 gas permeability of PVC/10% PEG4000 is 0.84 Barrer, whereas the CO_2 gas permeability of the PVC/30% PEG4000 is 5.82 Barrer. This is about sevenfold higher. As it was shown in Figure 4, the rate of permeability increase of nonpolar gases is not as high as that of CO_2 gas. Therefore, the larger PEG content leads to an increase in CO_2/N_2 and CO_2/CH_4 ideal selectivities

TABLE I
Condensability and Kinetic Diameter of Studied Gases

Gas component	Kinetic diameter (°A)	Condensability, critical temperature (K)
CO_2	3.3	304.2
O_2	3.46	154.6
N_2	3.64	126.2
CH_4	3.8	190.6

(Fig. 5). For CO_2/N_2, the ideal selectivity increased from 49 (PEG content 10%) to 109 (PEG content 30%), which is a reasonable quantity (more than 70).[5] Similarly the CO_2/CH_4 ideal selectivity increased from 46.47 (PEG content 10%) to 84 (PEG content 30%). The obtained CO_2/CH_4 ideal selectivity for PVC/30% PEG4000 is 84. The lower CO_2/CH_4 selectivity compared to CO_2/N_2 selectivity could be due to the greater condensability of CH_4 than that of N_2 (Table I).

The obtained results from these prepared blend membranes were compared with Robeson's upper bound line.[23] This comparison can be seen in Figure 6. From the figure, PVC/PEG4000 blend membranes with PEG contents of 20 and 30 wt % lie above the Robeson's upper bound line for CO_2/N_2 separation. On the other hand, for the CO_2/CH_4 separation, the PVC/30 wt % PEG4000 blend membrane is close to the Robeson's upper bound. It can be concluded that PVC/PEG4000 blend membranes with PEG contents of 20 and 30 wt % would have the potential for becoming commercial.

CONCLUSIONS

In this article, the effects of PEG molecular weight and concentration in PVC/PEG blend membranes on pure gas permeation properties were investigated. It was shown that the blend membranes having PEG with high molecular weights showed higher values of CO_2 permeability, and CO_2/CH_4 and CO_2/N_2 ideal selectivities in comparison with other blend membranes containing PEGs of lower molecular weights.

It was also found that the gas permeabilities of PVC/PEG blend membranes rapidly increased with an increase in PEG concentration (weight fraction). Comparison of CH_4 and N_2 permeabilities of PVC membrane and PVC/PEG blend membranes revealed that the gas solubility could be dominant in the permeation of gases through the prepared blend membranes.

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