Polyvinyl acetate/poly(amide-12-b-ethylene oxide) blend membranes for carbon dioxide separation

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Abstract
In this paper, blend membranes from polyvinyl acetate (PVAc) and block copolymer poly(amide-12-b-ethylene oxide) (Pebax1074) are prepared by solution casting and solvent evaporation method. Although they are homogeneous on a macro-scale, the observations from DSC and SEM indicate micro-phase separation for PVAc/Pebax1074 blend membranes. With the increase of Pebax1074 content, gas permeabilities of CO\(_2\), H\(_2\), N\(_2\) and CH\(_4\) all increase greatly. PVAc/Pebax1074 blend membranes with high PVAc content are appropriate for CO\(_2\)/CH\(_4\) separation. The temperature dependence of gas permeability is divided into rubbery region and glassy region. The activation energies of permeation in rubbery region are smaller than those in glassy region, and they all decrease with increasing Pebax1074 content. For N\(_2\), H\(_2\) and CH\(_4\), their gas permeation properties are mainly influenced by the dual-mode sorption and hydrostatic pressure effect. But for CO\(_2\), its permeability increases with the increase of pressure due to CO\(_2\)-induced plasticization effect, which is more obvious for PVAc/Pebax1074 blend membranes with high PVAc content.

Key words
polyvinyl acetate; poly(amide-12-b-ethylene oxide); blend membrane; carbon dioxide separation

1. Introduction

Recently, global atmospheric concentration of CO\(_2\) has increased markedly. It is estimated that CO\(_2\) concentration will double around 2050 if no special actions are taken [1]. The continued increase of CO\(_2\) concentration in the atmosphere is predicted to lead to significant changes in climate, and some potential implications including rising sea levels, changes in ecosystems, loss of biodiversity and reduction in crop yields [2–4]. So the reduction of CO\(_2\) emission into the atmosphere or recycle CO\(_2\) [5] is especially significant. One way to reduce CO\(_2\) emissions is carbon capture and storage (CCS), in which capturing CO\(_2\) is the first and critical step [6]. Currently, technologies used for capturing CO\(_2\) mainly include absorption, adsorption, cryogenic and membrane technology [7]. When product purity requirements are not extremely stringent, membrane technology may be advantageous in small and medium scale separations due to its high energy efficiency, enhanced space efficiency, absence of moving parts and so on [8,9].

For a membrane to be suitable for capturing CO\(_2\), it should possess a number of properties, such as high CO\(_2\) permeability, high CO\(_2\)/light gas selectivity, good thermal and chemical properties and so on [3]. But polymeric membranes usually undergo the tradeoff relationship between permeability and selectivity: as permeability increases, selectivity decreases, and vice versa [10]. For this reason, many efforts have been focused on the optimization of membrane materials to achieve better CO\(_2\) separation performance [11–14]. Polymer blending as a way to optimize membrane materials can combine the advantages of different polymers, and then improve mechanical properties and gas performance [15,16]. Compared with the synthesis of new polymers and interfacial polymerization [17] or cross-linking, polymer blending is characteristic of simplicity, reproducibility and commercial feasibility [15], which is becoming essential for membrane technology.

CO\(_2\) is considerably more polarizable than light gas (N\(_2\), H\(_2\) and CH\(_4\)) [3], which is classified as a hard acid by Pearson’s hard and soft acid-base principles [18,19]. Therefore, it is appropriate to select polymers containing carbonyl, ether, acetate groups as CO\(_2\) separation membrane materials, since...
these functional groups are hard bases [18] and can interact with CO₂. Polyvinyl acetate (PVAc), whose structure is shown in Scheme 1, is an attractive cost-efficient, high tonnage bulk commodity polymer [20]. Due to the existence of polar acetate groups in its structure, PVAc is considered as the most CO₂-phlic oxygenated hydrocarbon-based polymer to date [21]. Chen et al. [22] and Yuan et al. [23] reported that some specific interactions between polar acetate groups in PVAc and CO₂ existed, which resulted in high CO₂ solubility in PVAc [24]. In this regard, PVAc is considered as a suitable membrane material for CO₂ separation. But in membranes fabrication, PVAc cannot be used as an individual membrane material because of its low mechanical strength and low gas permeability [20,25]. Therefore, in the case of using PVAc in membrane applications, it is more suitable to form its blend membrane with a rubbery polymer. This will combine the high selectivity of PVAc with the high permeability of rubbery polymer and achieve a better separation performance [26]. Because of high thermal and mechanical stabilities, good chemical resistance and favorable membrane-forming properties [27,28], poly(ether-block-amide) (Pebax) is an appropriate choice that not only meets the need for the mechanical strength, but also has suitable gas separation properties. The chemical structure of Pebax is shown in Scheme 1, where PA is an aliphatic polyamide “hard” block (i.e., nylon 6 [PA6], or nylon 12 [PA12]), and PE is a polyether “soft” block, either poly(ethylene oxide) (PEO) or poly(tetramethylene oxide) (PTMEO) [29,30]. The hard crystalline amide block as an impermeable phase forms the structural frame and provides mechanical strength, and the soft polyether block usually forms continuous micro-domains and acts as the permeable phase due to its high chain mobility [30–32]. Because of the strong affinity between EO units and CO₂, CO₂ permeability for Pebax1074 and Pebax1657 can be up to 120 Barrer [31] and 73 Barrer [33], respectively.

![Scheme 1. Chemical structure of polyvinyl acetate (PVAc) and poly(amide-b-ethylene oxide) (Pebax)](image)

In this paper, polyvinyl acetate (PVAc) and block copolymer poly(amide-12-b-ethylene oxide) (Pebax1074) are used to prepare PVAc/Pebax1074 blend membranes. The physical properties of prepared membranes are observed by DSC and SEM in order to investigate their miscibility. The temperature dependence of gas permeability is discussed in two regions according to the transition of PVAc from glassy to amorphous state. And then the gas permeation characteristics are investigated for PVAc/Pebax1074 blend membranes with different blend ratios. Maxwell model is used to predict gas permeability for blend membranes. Finally, gas transport properties at different pressures are also investigated.

2. Theory

The gas transport properties of dense membranes are described by the solution-diffusion transport model. In this model, the permeability $P$, is described with Equation (1)

$$P = D \times S$$

where, $D$ is the diffusivity and $S$ is the solubility.

Maxwell model [34] is usually used to predict the permeability of polymer blends with one component dispersed in a matrix of another component, which is expressed as follows:

$$P_b = P_m \left\{ \frac{P_d + 2P_m - 2\varphi_d(P_m - P_d)}{P_d + 2P_m + \varphi_d(P_m - P_d)} \right\}$$

where, $b$, $m$, and $d$ represent the blends, the matrix phase, and the dispersed phase, respectively, and $\varphi_d$ is the volume fractions of the dispersed phase.

The volume fraction of the dispersed phase, $\varphi_d$, is calculated using Equation (3),

$$\varphi_d = \frac{X_d/\rho_d}{X_d/\rho_d + (1 - X_d)/\rho_m}$$

where, $X_d$ is the mass fraction of dispersed phase, and $\rho_d$ and $\rho_m$ are the densities of dispersed phase and matrix phase, respectively.

3. Experimental

3.1. Materials

Pebax® MV 1074 (Pebax1074) ($\rho = 1.07$ g cm$^{-3}$), comprising 55 wt% of PEO and 45 wt% PA12, in the form of elliptic pellets, was supplied by Arkema. Polyvinyl acetate (PVAc) ($M_W = 170000$, $\rho = 1.18$ g cm$^{-3}$) was obtained from Acros, and is used without further purification. Dimethylacetamide (DMAc) and 1-butanol were bought from Tianjin Bodi Chemical Engineering Co. Ltd. All gases used for gas permeation test were of research grade (>99.9% pure), and they were supplied by Dalian Gases Company. All gases and solvents were used as received.

3.2. Preparation of PVAc/Pebax1074 blend membranes

PVAc/Pebax1074 blend membranes were prepared by solution casting and solvent evaporation method. Casting solutions were prepared from the co-dissolution of PVAc and Pebax1074 in DMAc at a total polymer concentration of 5 wt% with continuous stirring under reflux at 85 °C.
The two polymers were mixed in the following proportions: PVAc/Pebax1074: 100/0, 80/20, 50/50, 30/70, 20/80, 10/90 (wt% / wt%). Only in the case of pure Pebax1074, 1-butanol was used as the solvent. After the homogenous solution is obtained, it was still kept at 80 °C for 24 h to remove gas bubbles. And then the bubble-free solution was cast on a Teflon ring mold. The cast membranes were dried at about 50 °C for 15 h to evaporate the solvent. Subsequently, the prepared dense membranes were removed from the Teflon ring mold and further dried in a vacuum oven at room temperature for at least 3 days to remove the residual solvent, and then they were kept in a desiccator for use.

3.3. Thermal characterization

Thermal properties of samples were characterized in the temperature range of −100–200 °C using Q2000 DSC (TA, USA). Measurements were performed at the scan rate of 10 K·min⁻¹.

3.4. Scanning electron microscopy

The dried membrane samples were sputtered with a thin layer of gold using Quorum Q150T sputtering device. And the cross-sectional morphologies of the prepared membranes were studied by FEI scanning electron microscopy (SEM) using a NOVA Nanosem 450 microscope.

3.5. Permeation measurements

The pure gas permeation properties for PVAc/Pebax1074 blend membranes were determined using constant volume/variable pressure method. The permeation cell was a stainless steel holder with an area of 7.07 cm². Before testing, both upstream and downstream volumes were exposed to vacuum overnight for degassing.

Gas permeability was calculated from the steady-state rate of pressure increase at a fixed downstream volume, the equation was as follows:

\[ P = \frac{1}{760} \cdot \frac{V \cdot 273.15 \cdot l \cdot \frac{dp}{dt}}{A \cdot T \cdot p} \]  

(4)

where,  \( P \) was the gas permeability (1 Barrer = \( 10^{-10} \) cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹),  \( V \) was the downstream volume (cm³),  \( A \) was the area of the membrane (cm²),  \( T \) was the operating temperature (K),  \( p \) was the transmembrane pressure difference (cmHg),  \( l \) was the membrane thickness (cm) and  \( \frac{dp}{dt} \) was the steady-state rate of pressure increase (mmHg/s) in the downstream volume at a fixed upstream pressure.

The ideal selectivity (\( \alpha \)) for gas (A) and gas (B) was defined as a ratio of the permeabilities of two gases:

\[ \alpha_{A/B} = \frac{P_A}{P_B} \]  

(5)

4. Results and discussion

4.1. Physical properties

Figure 1 shows DSC thermograms of Pebax1074, PVAc and PVAc/Pebax1074 blend membranes. In Figure 1(1)–1(4), the peaks around 10 °C and 160 °C refer to the melting of PEO and PA crystalline phase in Pebax1074, respectively [33], both of which become weaker with the increase of PVAc content. For PVAc membrane, only one glass transition around 40 °C can be observed in Figure 1(5). For PVAc/Pebax1074 blend membranes, except PVAc/Pebax1074 (10/90), two glass transition temperatures can be observed. The low glass transition temperature (\( T_{g1} \), about −55 °C) is corresponding to PE phase in Pebax1074, and the high glass transition (\( T_{g2} \), about 40–50 °C) referred to PVAc. \( T_{g2} \) becomes weaker and slightly shifts to low temperature with the increase of Pebax1074 content. Even for PVAc/Pebax1074 (10/90), it becomes too weak to be detected by DSC method. The existence of two \( T_{g} \) implies the occurrence of phase separation in PVAc/Pebax1074 blend membranes, which will influence gas permeation properties greatly.

![Figure 1](image)

Figure 1. DSC thermograms for prepared membranes Pebax1074 membrane (1), PVAc/Pebax1074 (10/90) blend membrane (2), PVAc/Pebax1074 (30/70) blend membrane (3), PVAc/Pebax1074 (50/50) blend membrane (4) and PVAc membrane (5).

The cross-sectional morphologies of Pebax1074, PVAc and PVAc/Pebax1074 blend membranes are investigated by SEM and shown in Figure 2. With the magnification of 10000 (Figure 2a1–2d1), membrane morphologies are all homogeneous and no crack or defect is observed, which suggests miscibility exists between Pebax1074 and PVAc on a macro-scale. With the magnification of 150000 (Figure 2a2–2d2), it can be observed that PVAc phase is dispersed uniformly in Pebax1074 continuous phase for PVAc/Pebax1074 blend membranes.

![Figure 2](image)
4.2. Effect of operating temperature on gas permeation properties

The effect of operating temperature on gas permeability for Pebax1074 and PVAc/Pebax1074 blend membranes with 50/50, 30/70, 10/90 compositions is shown in Figure 3. For Pebax1074 membrane (Figure 3a), the gas permeabilities of \( \text{N}_2 \), \( \text{H}_2 \), \( \text{CH}_4 \) and \( \text{CO}_2 \) increase with the increasing operating temperature, which can be described by Arrhenius equation:

\[
P = P_0 \exp \left( \frac{-E_p}{RT} \right)
\]  

(6)

where, \( P_0 \) is the pre-exponential factor, \( E_p \) is the apparent activation energy for permeation, \( R \) is the gas constant, and \( T \) is the absolute temperature. The activation energies for different gases calculated by Equation (6) are listed in Table 1. But for PVAc/Pebax1074 (50/50) membrane (Figure 3b), a break-point in gas permeability as a function of \( T \) has been observed around 50 °C, resulting in the linear relationship unavailable throughout the whole operating temperature range. This result suggests that PVAc/Pebax1074 (50/50) membrane has experienced a significant thermal transition. From DSC experiments, there is a glass transition of PVAc around 40 ∼ 50 °C, so it can be concluded that it is the glass transition of PVAc that induces the break-point in gas permeability. The temperature corresponding to the break-point in gas permeability is defined as the transition temperature \( T_t \), which is about 50 °C for PVAc/Pebax1074 (50/50) membrane. According to \( T_t \), the relationship between gas permeability and operating temperature can be described with glassy region and rubbery region, although there is some deviation between \( T_t \) (obtained by gas permeation) and \( T_g \) (obtained by DSC). For \( T<T_t \), PVAc is mainly in glassy state, which results in a great influence on gas permeability by operating temperature due to the rigid chains. But for \( T>T_t \), PVAc chains change into flexible, and induce less influence on gas permeability by operating temperature than that in glassy region. For PVAc/Pebax1074 (30/70) and PVAc/Pebax1074 (10/90) blend membranes (shown in Figure 3c and 3d), similar experimental phenomenon can be observed, and the transition temperature \( T_t \) is about 40 °C.

Table 1. Activation energies of permeation for \( \text{CO}_2 \), \( \text{H}_2 \), \( \text{N}_2 \) and \( \text{CH}_4 \) through Pebax1074 membrane

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_p ) (kJ·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>13.41</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>24.15</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>30.28</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>26.06</td>
</tr>
</tbody>
</table>

Due to no thermal transition in glassy and rubbery regions, the gas permeability also can be described by two different Arrhenius equations and \( E_p \) for different gases in the two regions can also be obtained, which is listed in Table 2. The \( E_p \) values in these membranes all follow the order of \( \text{N}_2>\text{CH}_4>\text{H}_2>\text{CO}_2 \), which reflects the order of gas condensability except \( \text{H}_2 \). That is, gases with lower critical temperature are usually difficult to condense, resulting in higher \( E_p \). But for \( \text{H}_2 \), it has the smallest kinetic diameter (Table 3), which results in the smallest activation energy of diffusion and induces lower \( E_p \) than \( \text{N}_2 \) and \( \text{CH}_4 \). From Table 2, the \( E_p \) values of \( \text{CO}_2 \), \( \text{H}_2 \), \( \text{N}_2 \) and \( \text{CH}_4 \) at \( T<T_t \) (PVAc in glassy region) are higher than those at \( T>T_t \) (PVAc in rubbery region), because PVAc chains in rubbery region become more flexible, which enhances FFV, making activation energies of diffusion lower than that in glass region. With the increase of Pebax1074 content in PVAc/Pebax1074 membranes, the \( E_p \) values of \( \text{CO}_2 \), \( \text{H}_2 \), \( \text{N}_2 \) and \( \text{CH}_4 \) in glassy and rubbery regions are all decreased due to the increased permeable phase resulting from the additive amorphous PEO phase in Pebax1074 [30–32].
Table 2. Activation energies of permeation for CO$_2$, H$_2$, N$_2$ and CH$_4$ through PVAc/Pebax1074 blend membranes

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T &gt; T_g$ (kJ·mol$^{-1}$)</th>
<th>$T &lt; T_g$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc/Pebax1074 (50/50)</td>
<td>17.54</td>
<td>31.10</td>
</tr>
<tr>
<td>PVAc/Pebax1074 (30/70)</td>
<td>15.48</td>
<td>29.65</td>
</tr>
<tr>
<td>PVAc/Pebax1074 (10/90)</td>
<td>8.03</td>
<td>22.85</td>
</tr>
</tbody>
</table>

4.3. Effect of PVAc/Pebax1074 blend composition on gas permeation properties

Figure 4 shows the influence of Pebax1074 content on CO$_2$ permeability for PVAc/Pebax1074 blend membranes at 35 °C and 55 °C, which represent the glassy region and rubbery region of blend membranes, respectively. CO$_2$ permeability increases greatly with the increase of Pebax1074 content in the two regions. This increase mainly attributes to the increase of solubility and diffusivity. First, the additive Pebax1074 can introduce EO units which can interact with CO$_2$. Furthermore, additive Pebax1074 can improve the chain mobility due to the decreased $T_g$ in DSC, resulting in higher free volume and subsequently increasing gas diffusivity. Simultaneously, the rubbery Pebax1074 also can create a diffusion pathway for the penetrant gases in its amorphous soft phase. CO$_2$ permeability predicted by Maxwell model is also shown in Figure 4. At 35 °C, CO$_2$ permeation through PVAc/Pebax1074 blend membranes can be described well by Maxwell model with Pebax1074 as continuous phase. This result suggests that PVAc disperses uniformly in Pebax1074 matrix phase, as show in SEM. But for CO$_2$ permeability at 55 °C, the experimental values are all above the predicted values of Maxwell Model, which implies that the rubbery PVAc in PVAc/Pebax1074 blend membranes can enhance gas transport properties greatly.
the blend membranes [35].

By increasing Pebax1074 content, the gas permeabilities of N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} all increase strongly. For H\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4}, due to their absence of specific polymer-penetrant interactions, additive Pebax1074 has few influences on their gas solubility. And the relative increase of gas permeabilities of N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} is in the order of CH\textsubscript{4} > N\textsubscript{2} > H\textsubscript{2}, which is positively correlated with the gas kinetic diameter (Table 3). Therefore, it seems that the main contribution to the increase in gas permeabilities of H\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} is the increase in diffusivity through the blend membranes [35].

![Figure 4. Influence of Pebax1074 content on CO\textsubscript{2} permeability for PVAc/Pebax1074 blend membranes at 5 atm (●: experimental values at 35 °C; □: estimated values at 35 °C; ●: experimental values at 55 °C; △: estimated values at 55 °C)](image)

Figure 5 shows the influence of Pebax1074 content on gas permeabilities of H\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} for PVAc/Pebax1074 blend membranes at 35 °C and 5 atm. From Figure 5, with increasing Pebax1074 content, the gas permeabilities of N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} all increase strongly. For H\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4}, due to their absence of specific polymer-penetrant interactions, additive Pebax1074 has few influences on their gas solubility. And the relative increase of gas permeabilities of N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} is in the order of CH\textsubscript{4} > N\textsubscript{2} > H\textsubscript{2}, which is positively correlated with the gas kinetic diameter (Table 3). Therefore, it seems that the main contribution to the increase in gas permeabilities of H\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} is the increase in diffusivity through the blend membranes [35].

![Figure 5. Influence of Pebax1074 content on gas permeabilities of H\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} for PVAc/Pebax1074 blend membranes at 35 °C and 5 atm (■: experimental values of H\textsubscript{2} permeability; □: estimated values of H\textsubscript{2} permeability; ●: experimental values of CH\textsubscript{4} permeability; △: estimated values of CH\textsubscript{4} permeability; ●: experimental values of N\textsubscript{2} permeability; ○: estimated values of N\textsubscript{2} permeability)](image)

The estimated gas permeabilities of N\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2} for PVAc/Pebax1074 blend membranes using Maxwell model with Pebax1074 as continuous phase are also shown in Figure 5. As observed, the experimental values of N\textsubscript{2} permeability show an agreement with the predicted line. But for CH\textsubscript{4} and H\textsubscript{2}, the predicted lines can not be fit well with the experimental values in the whole composition range of PVAc/Pebax1074 blend membranes. Therefore, it seems that the gas transport through blend membranes is strongly influenced by gas molecular properties.

Figure 6 shows CO\textsubscript{2}/light gas selectivity for PVAc/Pebax1074 blend membranes. Additive Pebax1074 can not only increase the content of EO units resulting in higher CO\textsubscript{2} solubility, but also increase the gas diffusivity due to the additive amorphous PEO chains, especially for big molecular. Because the order of kinetic diameter is CH\textsubscript{4} > N\textsubscript{2} > CO\textsubscript{2} > H\textsubscript{2} as listed in Table 3, the competing effect of the two aspects leads to the selectivities to CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/H\textsubscript{2} change differently according to gas kinetic diameter. As shown in Figure 6, relative small change of CO\textsubscript{2}/N\textsubscript{2} selectivity is observed in the whole composition range, and PVAc/Pebax1074 blend membranes with high PVAc content are beneficial to enhance CO\textsubscript{2}/CH\textsubscript{4} gas selectivity, while those with high Pebax1074 content are beneficial to enhance CO\textsubscript{2}/H\textsubscript{2} gas selectivity.

![Figure 6. Influence of Pebax1074 content on CO\textsubscript{2}/light gas selectivity for PVAc/Pebax1074 blend membranes at 35 °C and 5 atm](image)

4.4. Effect of operating pressure on gas permeation properties

The effect of operating pressure on gas permeabilities of N\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4} and CO\textsubscript{2} for PVAc/Pebax1074 blends with 50/50, 30/70, 10/90 compositions is shown in Figure 7. As the operating pressure increases, the permeabilities of N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} decrease but CO\textsubscript{2} permeability increases. For N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4}, the decrease in permeability is due to the dual-mode sorption [36] in glassy polymer PVAc and hydrostatic pressure effect [35] in rubbery polymer Pebax1074. For the strongly sorbing penetrant CO\textsubscript{2}, its high concentration absorbed in polymer membrane can plasticize the polymer chains, increase fractional free volume, and then enhance gas diffusivity and permeability [37].

Seen from Figure 7, the pressure dependence of gas permeability can be expressed empirically by Equation (7) [37]:

\[ P_A = P_{A,0}(1 + mp_1) \] (7)
where, $P_{A,0}$ is the permeability when the upstream pressure $p_1$ approaches 0 (i.e., infinite dilution permeability); $m$ (atm$^{-1}$) is a constant, which characterizes the significance of the pressure dependence of permeability. The calculated $m$ values for PVAc/Pebax1074 blend membranes are presented in Table 4. For $N_2$, $H_2$ and $CH_4$, the values of $m$

for PVAc/Pebax1074 (30/70) are smallest due to the competition between dual-mode sorption and hydrostatic pressure effect. For $CO_2$, the value of $m$ decreases with the increasing Pebax1074 content, which suggests the permeability of $CO_2$ increases greatly with the increase of pressure at high PVAc content.

Figure 7. Influence of operating pressure on gas permeabilities of $CH_4$, $N_2$, $H_2$ and $CO_2$ for PVAc/Pebax1074 blend membranes at 25 °C ( ■ PVAc/Pebax1074(10/90); ● PVAc/Pebax1074(30/70); ▲ PVAc/Pebax1074(50/50))

Table 4. Parameters characterizing pressure dependence of the gas permeability

<table>
<thead>
<tr>
<th>Samples</th>
<th>$m \times 100$ (atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$CH_4$</td>
</tr>
<tr>
<td>PVAc/Pebax1074(50/50)</td>
<td>−2.38</td>
</tr>
<tr>
<td>PVAc/Pebax1074(30/70)</td>
<td>−2.04</td>
</tr>
<tr>
<td>PVAc/Pebax1074(10/90)</td>
<td>−2.29</td>
</tr>
</tbody>
</table>

5. Conclusions

PVAc/Pebax1074 blend membranes with different compositions are prepared by solution casting and solvent evaporation method. Their physical properties and gas transport characteristics are investigated, and some conclusions can be made as follows:

(1) According to SEM and DSC observations, micro-phase separation appears in PVAc/Pebax1074 blend membranes.

(2) The temperature dependence of gas permeability for PVAc/Pebax1074 blend membranes is divided into rubbery region and glassy region. The activation energies of permeation in rubbery region are smaller than those in glassy region. And they all decrease with the increasing Pebax1074 content.

(3) With the increase of Pebax1074 content, gas permeabilities of $CO_2$, $H_2$, $N_2$ and $CH_4$ all increase greatly both in rubbery or glassy state. PVAc/Pebax1074 blend membranes with high PVAc content enhance $CO_2$/$CH_4$ selectivity, while those with high Pebax1074 content improve $CO_2$/$H_2$ selectivity.

(4) An increase in feed pressure induces low gas permeabilities of $N_2$, $H_2$ and $CH_4$. But $CO_2$ permeability increases with the increase of pressure due to its plasticization effect.

References