

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Mixed Matrix Membranes of Silicone Rubber and Activated Carbon

The permeabilities of carbon dioxide,  $P_{CO_2/d}$ ; nitrogen,  $P_{N_2/d}$ ; hydrogen,  $P_{H_2/d}$ ; propane,  $P_{C_3H_8/d}$ ; propylene,  $P_{C_3H_6/d}$  and the selectivity of carbon dioxide to nitrogen,  $P_{CO_2/P_{N_2}}$ ; carbon dioxide to hydrogen,  $P_{CO_2/P_{H_2}}$ ; and propylene to propane,  $P_{C_3H_6/P_{C_3H_8}}$  were determined from steady state permeation rates of each gas through the membrane at room temperature and pressures between 5 and 100 psia to investigate the selectivities and plasticization phenomenon.

##### 4.1.1 Selectivities of Gases through Silicone Rubber Membrane and Activated Carbon/Silicone Rubber MMM

**Table 4.1** Selectivities of gases through membrane prepared from silicone rubber/polysulfone and various loading activated carbon/silicone rubber/polysulfone MMM (measured the fluxes at 50 psia)

Membrane	Selectivity		
	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>
SIL/PS <sup>1</sup>	12.069	4.574	0.876
10 wt% Act.C./SIL/PS MMM <sup>2</sup>	12.627	4.854	1.013
20 wt% Act.C./SIL/PS MMM <sup>2</sup>	15.101	4.545	1.022
30 wt% Act.C./SIL/PS MMM <sup>2</sup>	19.167	5.982	1.057

#### Notes

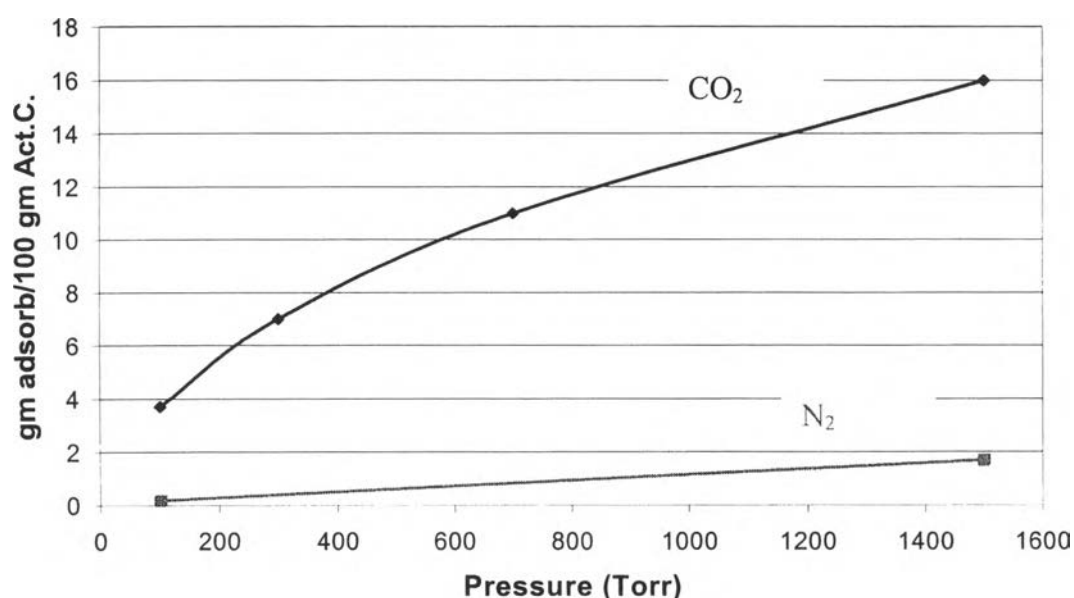
<sup>1</sup>SIL/PS = Silicone rubber coated on porous polysulfone

<sup>2</sup>X wt% Act.C./SIL/PS MMM = X wt% Activated carbon/silicone rubber coated on porous polysulfone

where X = 10, 20, or 30

Silicone rubber/polysulfone membrane and activated carbon/silicone rubber/polysulfone MMM varied amount of activated carbon in 10, 20, and 30 wt% were used to study the selectivity of  $\text{CO}_2/\text{N}_2$ ,  $\text{CO}_2/\text{H}_2$ , and  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ . Testing conditions were room temperature,  $P = 50$  psia and pure gas measurement.

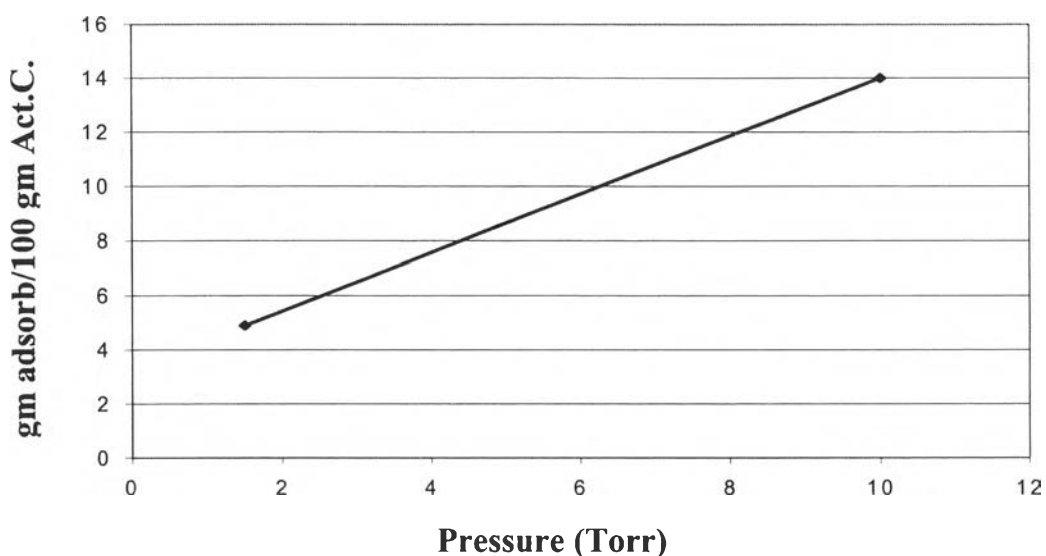
For  $\text{CO}_2/\text{N}_2$  separation, the result showed that  $\text{CO}_2/\text{N}_2$  selectivity increased with increasing amount of activated carbon. From adsorption isotherms of  $\text{CO}_2$  and  $\text{N}_2$  on activated carbon at 300 K as shown in Figure 4.1,  $\text{CO}_2$  can adsorb on activated carbon more than  $\text{N}_2$  over 100-1500 Torr. Therefore, increasing amount of activated carbon in silicone rubber/polysulfone membrane will allow  $\text{CO}_2$  to be adsorbed and pass through the membrane faster than  $\text{N}_2$ .



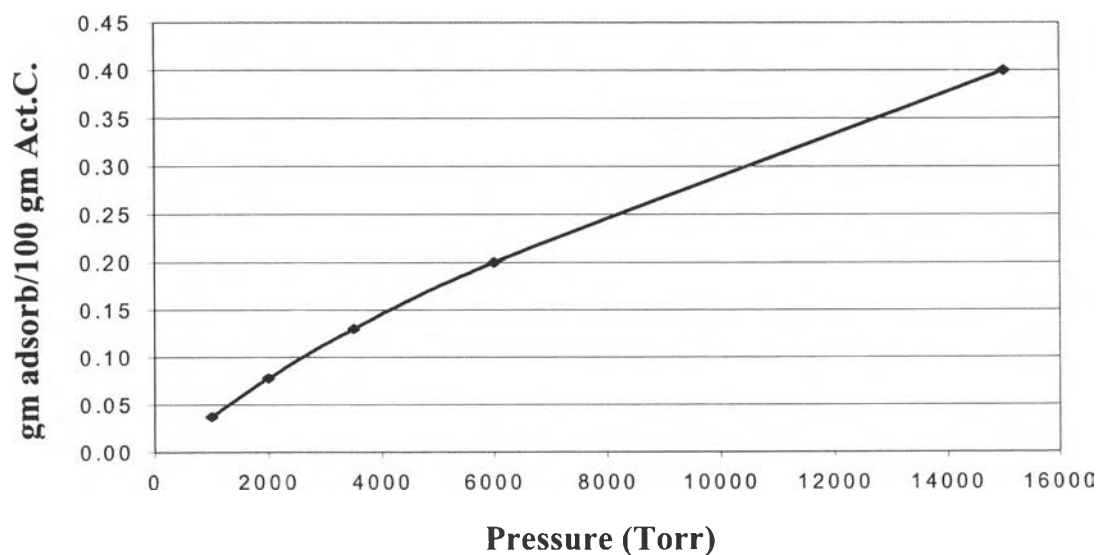
**Figure 4.1** Adsorption isotherms of  $\text{CO}_2$  and  $\text{N}_2$  on activated carbon at 300 K (Low Temperature Measurements Group, 1962 (TM D-11)).

For  $\text{CO}_2/\text{H}_2$  separation,  $\text{CO}_2/\text{H}_2$  selectivity increased slightly with increasing amount of activated carbon. From adsorption isotherms of  $\text{CO}_2$  and  $\text{H}_2$  on activated carbon at 195 K as shown in Figure 4.2(a),(b) at low pressure around 10 Torr activated carbon can adsorb  $\text{CO}_2$  around 14g/100g activated carbon which was higher than  $\text{H}_2$  that used high pressure around 15000 Torr to adsorb. Therefore, activated carbon

can adsorb  $\text{CO}_2$  more than  $\text{H}_2$  at the same pressure. When increasing amount of activated carbon in silicone rubber membrane, it will increase  $\text{CO}_2$  to adsorb and pass through membrane to permeate side faster than  $\text{H}_2$ . However the  $\text{CO}_2/\text{H}_2$  selectivity did not increase significantly, hydrogen molecule was very small. The effect of small hydrogen molecules can help them to pass through the membrane.

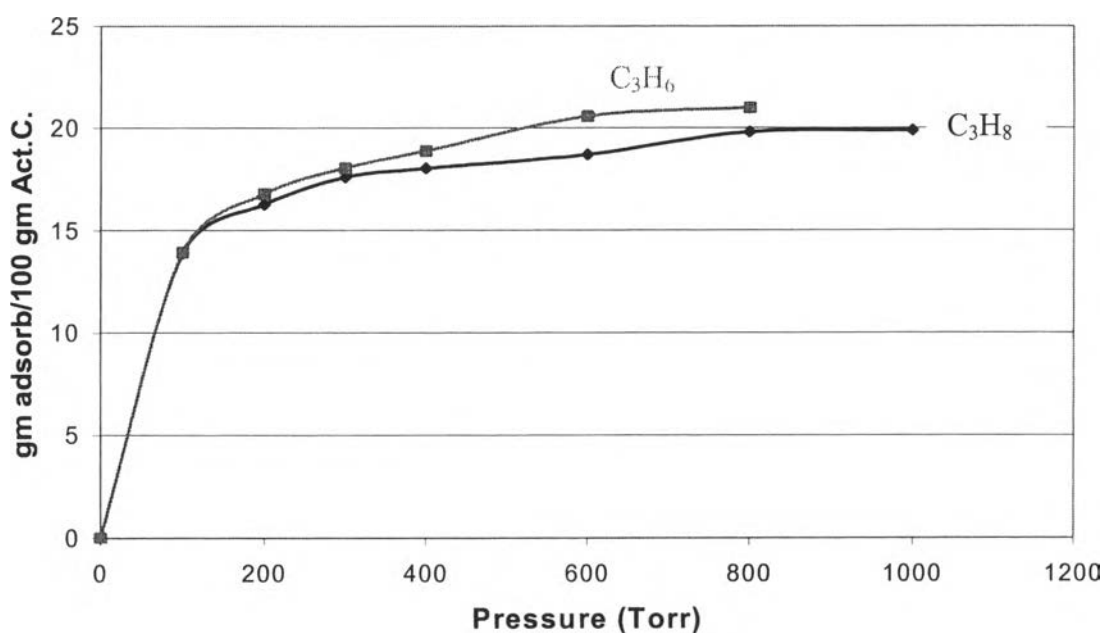


**Figure 4.2 (a)** Adsorption isotherm of  $\text{CO}_2$  on activated carbon at 195 K (Temperature Measurements Group, 1962 (TM D-11)).



**Figure 4.2 (b)** Adsorption isotherm of  $\text{H}_2$  on activated carbon at 195 K (Low Temperature Measurements Group, 1962 (TM D-11)).

For  $C_3H_6/C_3H_8$  separation, silicone rubber/polysulfone membrane was selective for propane, but adding activated carbon in silicone rubber/polysulfone membrane can change the selectivity from propane to propylene. Silicone rubber/polysulfone membrane was selective for propylene after adding 10, 20 and 30 wt% activated carbon.. From adsorption isotherms of  $C_3H_6$  and  $C_3H_8$  on activated carbon at 298 K as shown in Figure 4.3, propylene can adsorb on activated carbon more than propane over 100-800 Torr. Therefore, increasing amount of activated carbon in silicone rubber membrane will increase propylene to adsorb and pass through the membrane faster than propane.

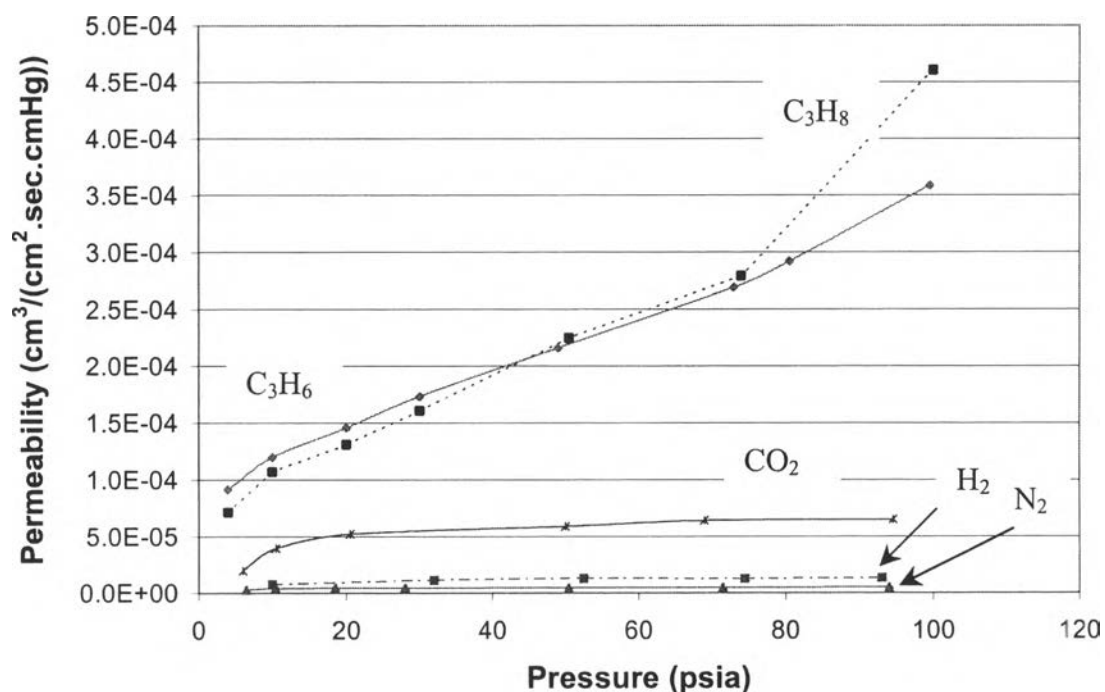


**Figure 4.3** Adsorption isotherms of  $C_3H_6$  and  $C_3H_8$  on activated carbon at 298 K (Low Temperature Measurements Group, 1962 (TM D-11)).

#### 4.1.2 Effects of pressure to membrane permeabilities

It was found from the literature that polymeric membrane can occur plasticization (Bos *et al.*, 1999). Plasticization was the one of stability problems in membrane. When plasticization occurred, permeability increased and then membrane lose selectivity. Therefore, in this part silicone rubber/polysulfone membrane and activated carbon/silicone rubber/polysulfone MMM were used to study the effect of pressure to membrane permeabilities by using CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> as the feed and varying pressures from 5-100 psia.

##### 1) Silicone rubber/polysulfone membrane (SIL/PS)



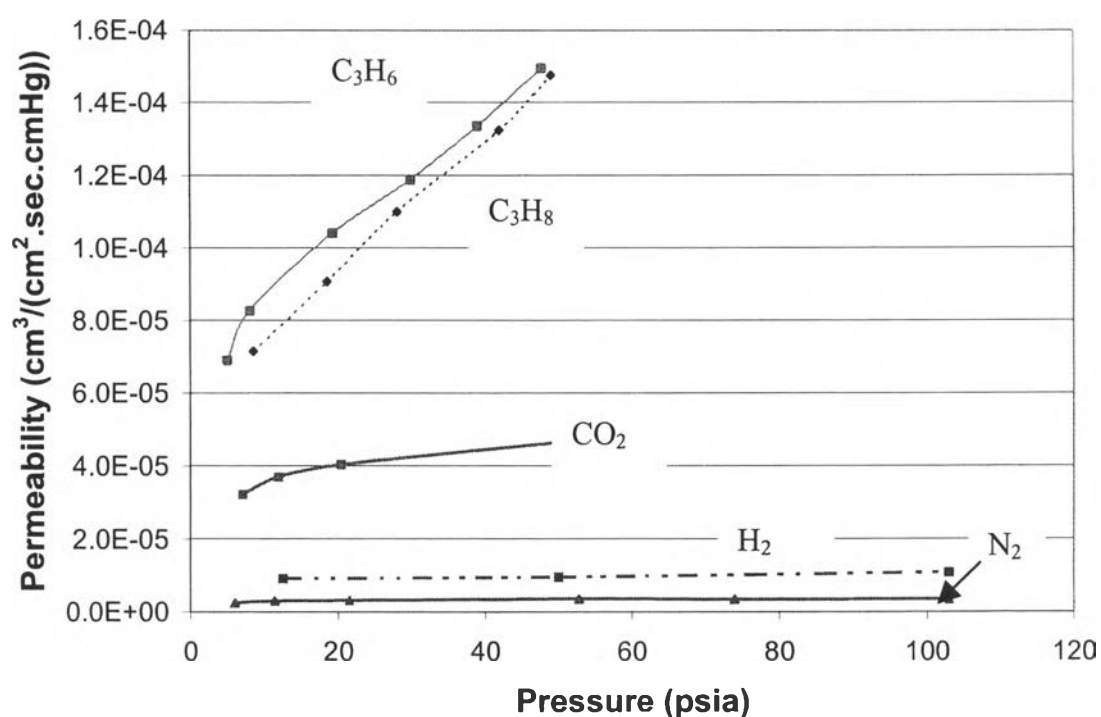
**Figure 4.4** Relation between pressure and permeability of silicone rubber/polysulfone membrane.

Figure 4.4 shows effect of pressure on silicone rubber/polysulfone membrane permeability. Permeabilities of propylene, propane and carbon dioxide increased with increasing pressure; however, permeabilities of H<sub>2</sub> and N<sub>2</sub> were

relatively constant. The membrane changed  $C_3H_6/C_3H_8$  selectivity from propylene at low pressures to propane at high pressures. Because propylene has smaller effective diameter than propane. The C=C bond which is made up of a strong  $\sigma$  bond and a weak  $\pi$  bond has greater total bond energy (e.g., 146 kcal for ethylene) than the C-C bond (e.g., 88 kcal for ethane). The atoms would be held tighter together where the double bond length is 1.34 Å as compared to the single bond length, 1.53 Å. Therefore, olefins have higher diffusivity than paraffins of the same C number likely due to the smaller effective diameters for diffusion (Chan *et al.*, 2002). So, at low pressures propylene would be able to diffuse through a membrane faster than propane. However at high pressures the phenomenon is in contrast, in which the membrane is selective to propane. Because the effect of solubility dominated the size effect. The critical temperature of propane is higher than propylene. It meant that propane was more soluble than propylene (Chan *et al.*, 2002). Therefore, propane will pass through membrane faster than propylene at high pressures.

2) 10 wt% Activated carbon/silicone rubber/polysulfone MMM  
(10 wt%Act.C./SIL/PS MMM)

Figure 4.5 shows effect of pressure on 10 wt%Act.C./SIL/PS MMM permeability. The permeability of propane, propylene and carbon dioxide increased with increasing pressure; however, permeabilities of H<sub>2</sub> and N<sub>2</sub> were relatively constant.



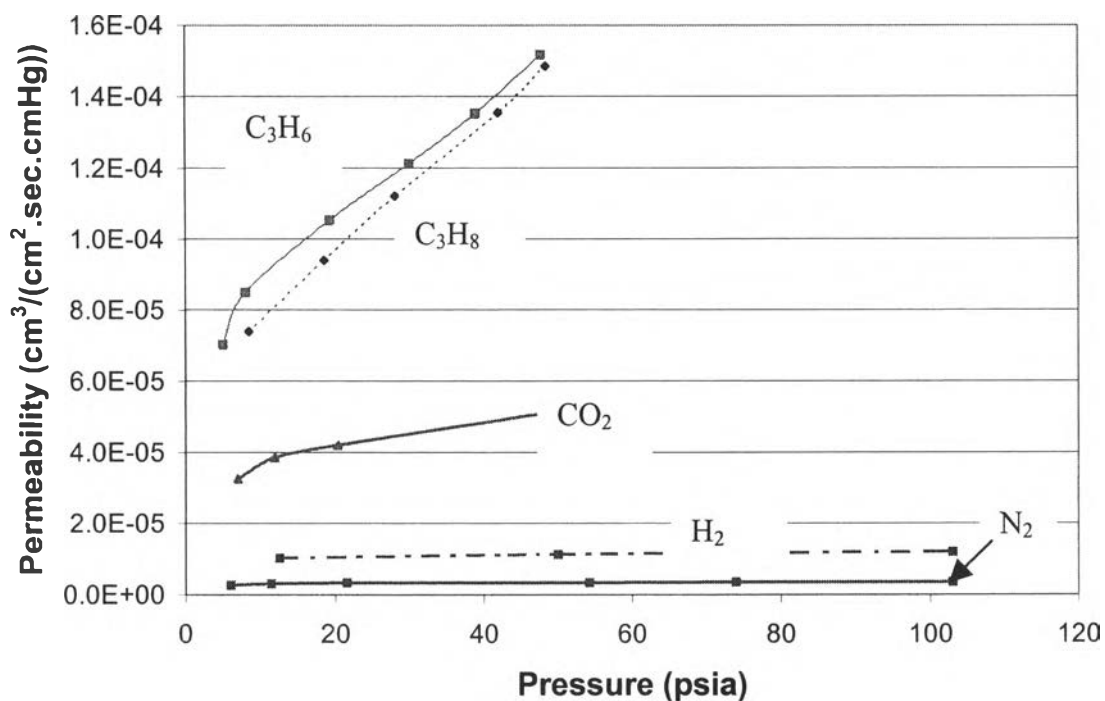
**Figure 4.5** Relation between pressure and permeability of 10 wt%Activated carbon/silicone rubber/polysulfone MMM.

In comparison of SIL/PS membrane and 10 wt%Act.C./SIL/PS MMM, the later did not occur the reversibility of C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity. Because activated carbon was selective for propylene more than propane.

Propylene, propane and carbon dioxide were more soluble gases than hydrogen and nitrogen (Chan *et al.*, 2002). Therefore, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> will be able to plasticize in membrane.

3) 20 wt% Activated carbon/silicone rubber/polysulfone MMM  
(20 wt% Act.C./SIL/PS MMM)

The result of 20 wt% activated carbon/silicone rubber/polysulfone MMM showed the same trend as 10 wt% activated carbon/silicone rubber/polysulfone MMM.



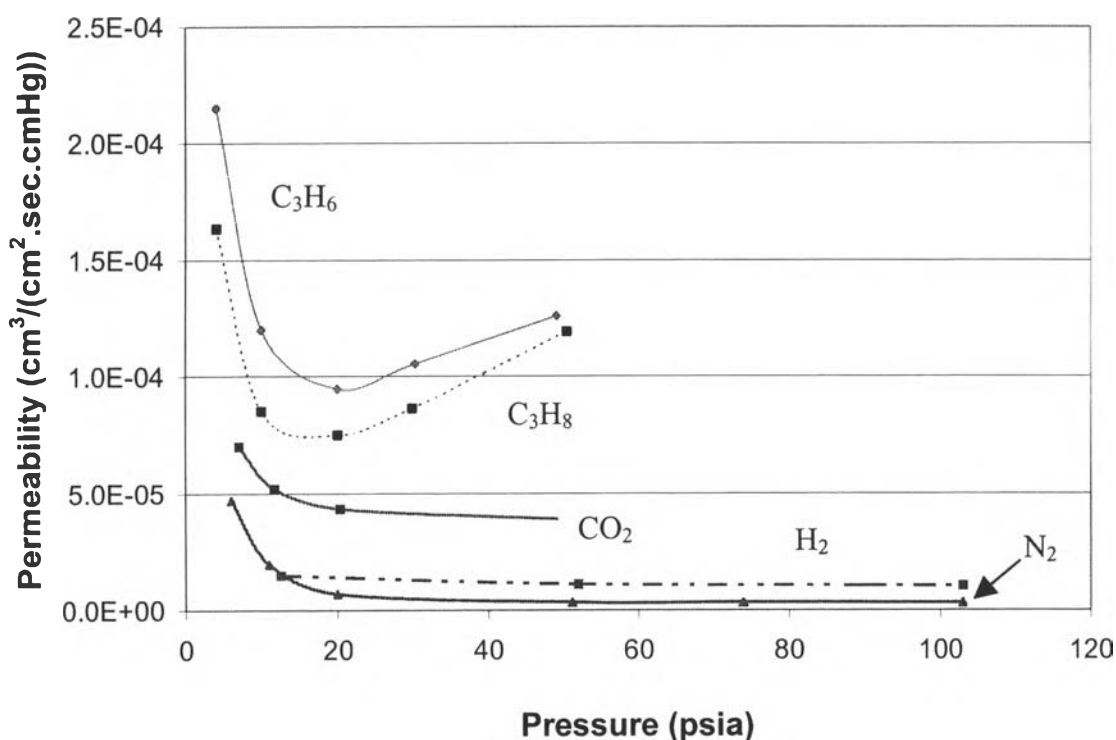
**Figure 4.6** Relation between pressure and permeability of 20 wt% Activated carbon/silicone rubber/polysulfone MMM.

However, adding activated carbon to 30 wt% showed the strong different behavior.



4) 30 wt% Activated carbon/silicone rubber/polysulfone MMM  
(30 wt% Act.C./SIL/PS MMM)

Figure 4.7 shows the effect of pressure to 30 wt% activated carbon/silicone rubber/polysulfone MMM permeability. At low pressure, permeability of  $C_3H_6$ ,  $C_3H_8$ ,  $CO_2$  and  $N_2$  sharply decreased with increasing pressure because of hydrostatic compression effect. 30 wt% activated carbon was enough to increase the glassy state in membrane. Therefore, increasing pressure will reduce free volume in membrane and then decrease permeability.



**Figure 4.7** Relation between pressure and permeability of 30 wt% Activated carbon/silicone rubber/polysulfone MMM.

However, at high pressure permeability of  $C_3H_6$  and  $C_3H_8$  increased with increasing pressure.  $CO_2$  permeability slowly decreased and  $H_2$ ,  $N_2$  permeability remained constant. Because propylene and propane were more soluble in membrane than  $CO_2$ . So the enough pressure can overcome the compression effect.

About H<sub>2</sub>, N<sub>2</sub> they were the less soluble gases, so pressure did not have the effect to their permeabilities.

#### 4.2 Mixed Matrix Membranes of Silicone Rubber, Activated Carbon and Polyethylene glycol (PEG)

According to the previous work (Charoenphol, 2002), the CO<sub>2</sub>/N<sub>2</sub> selectivity increased as the concentration of PEG in the membranes increased and form the first part of my work CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivities increased with increasing amount of Act.C. Therefore, in order to enhance these selectivities the combined membrane will be created. 20 wt%Act.C./SIL/PS MMM added with PEG from 5, 10 to 15 wt% was investigated for CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub>, and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separations and have also studied plasticization phenomenon.

##### 4.2.1 Selectivities of Gases through Silicone Rubber/Polysulfone, Activated Carbon/Silicone Rubber/Polysulfone MMM and PEG+Activated Carbon/Silicone Rubber/Polysulfone MMM

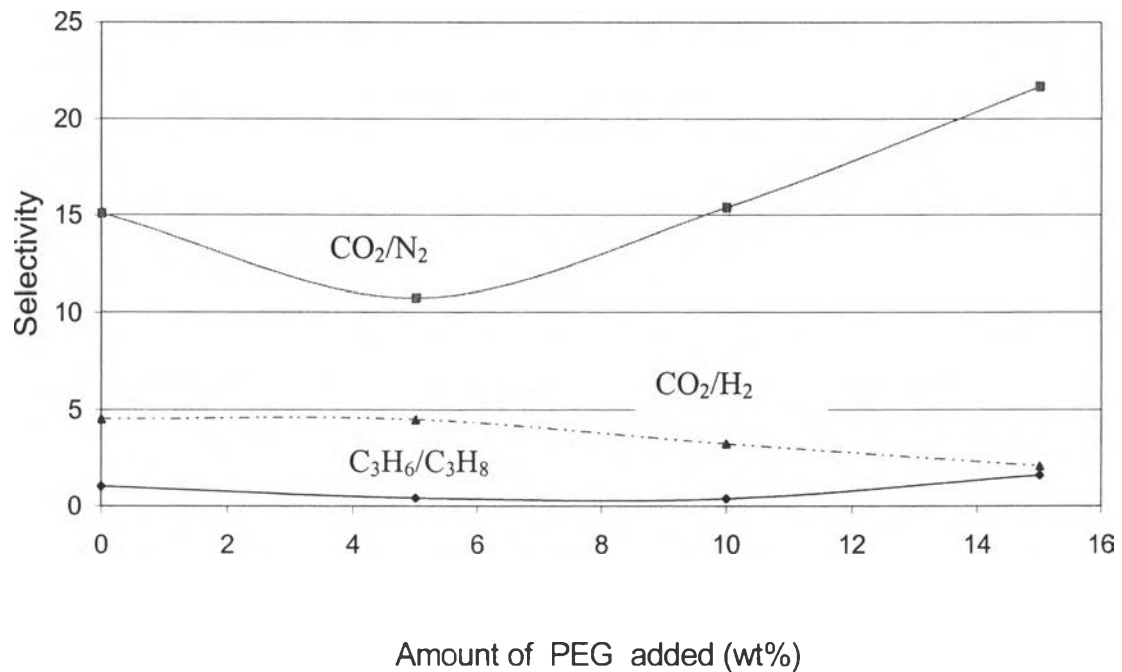
**Table 4.2** Selectivities of gases through membrane prepared from silicone rubber/polysulfone and various loading of PEG + 20wt%activated carbon/silicone rubber/polysulfone MMM (measured the fluxes at 50psia)

Membrane	Selectivity		
	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>
SIL/PS	12.069	4.574	0.876
20wt%Act.C./SIL/PS MMM	15.101	4.545	1.022
5wt%PEG+20wt%Act.C./SIL/PS MMM	10.747	4.511	0.414
10wt%PEG+20wt%Act.C./SIL/PS MMM	15.420	3.250	0.382
15wt%PEG+20wt%Act.C./SIL/PS MMM	21.679	2.087	1.598

Notes

X wt% PEG+20wt%Act.C./SIL/PS MMM = Xwt% PEG + 20wt%Activated carbon/silicone rubber coated on porous polysulfone

where x = 0,5,10 or 15



**Figure 4.8** Relation between wt% PEG in 20 wt%Activated carbon/silicone rubber/polysulfone MMM and selectivities.

From Table 4.1 the CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivities increased with increasing amount of activated carbon in activated carbon/silicone rubber/polysulfone MMM. In this study, 20wt%activated carbon/silicone rubber/polysulfone MMM was chosen and then adding PEG at 5, 10, 15 wt%. Because this amount of Act.C. can mix with PEG and did not precipitate. So it was suitable for casting the membrane. Besides, to study these three selectivities plasticization phenomenon has been considered. The selectivities are shown in Table 4.2 and Figure 4.8. This experiment was done at room temperature, different pressure = 50 psia and pure gas measurement.

The  $\text{CO}_2/\text{N}_2$  selectivity decreased when adding 5 wt% PEG and then increased when adding 10, 15 wt% PEG in 20wt%activated carbon/silicone rubber/polysulfone MMM. Because little amount of PEG at 5 wt% will adsorb in pore of activated carbon. So PEG will not show the effect to enhance selectivity. From the previous work (Charoenphol, 2002) PEG suspended in silicone rubber/polysulfone membrane improved the  $\text{CO}_2/\text{N}_2$  selectivity when compared to pure silicone rubber/polysulfone membrane. It can be concluded that the  $\text{CO}_2/\text{N}_2$  selectivity can be enhanced when PEG suspended in the polymer phase. The other possible reason is change of activated carbon property after adsorbed PEG. The property of activated carbon maybe change after PEG adsorb in activated carbon. So PEG reduced the impact of activated carbon for  $\text{CO}_2/\text{N}_2$  selectivity.

After adding 10, 15wt% PEG in 20wt%activated carbon/silicone rubber/polysulfone MMM,  $\text{CO}_2/\text{N}_2$  selectivity increased. Because 10, 15 wt%PEG is enough to adsorb in pore of activated carbon and the rest can suspend in polymer phase to enhance this selectivity.

$\text{CO}_2/\text{H}_2$  selectivity decreased with increasing amount of PEG. Adding PEG in activated carbon/silicone rubber/polysulfone reduced the permeability of gas. Due to the dominance of PEG crystallinity in membrane, it reduced the segmental motion in membrane (Li et al.,). Gas molecule moves harder than without PEG. When compared the reducing in permeability of  $\text{CO}_2$  and  $\text{H}_2$ , the  $\text{CO}_2$  permeability decreased more than the  $\text{H}_2$  permeability. Because of smaller molecule of  $\text{H}_2$ , it will be able to pass through PEG crystallinity more easily than larger molecule like  $\text{CO}_2$ . Therefore  $\text{CO}_2/\text{H}_2$  selectivity decreased when increasing amount of PEG in PEG /Act.C./SIL/PS MMM, selectivity is the product of permeability shown in Eq. (2.5).

$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  selectivity was lower than one at 5, 10 wt%PEG in PEG /20wt%Act.C./SIL/PS MMM and then increased higher than one and higher than pure 20wt%Act.C./SIL/PS MMM when adding 15 wt%PEG in 20wt%Act.C./SIL/PS MMM. From the last result 20wt%Act.C./SIL/PS MMM was selective for olefin. From the previous work (Sukapintha, 2000) PEG/silicone rubber/polysulfone MMM was selective for olefin.  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  selectivity was around 1.70. So mixing PEG and activated carbon in silicone rubber/polysulfone membrane will be possible to enhance olefin/paraffin selectivity. However, the result showed inverse selectivity at

5, 10 wt%PEG and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity enhanced at 15 wt%PEG. Because little amount of PEG will be able to adsorb in pore of activated carbon. It may change property of activated carbon after PEG adsorb in activated carbon. PEG can enhance C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity when amount of PEG is much enough to have the rest in polymer phase like 15wt%PEG.

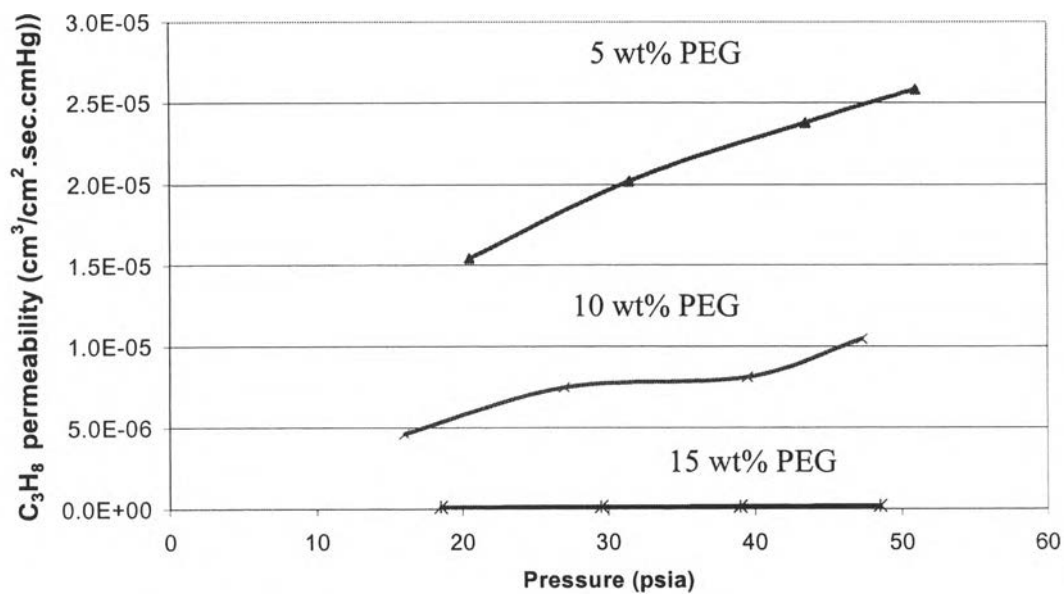
**Table 4.3** Permeabilities of gases through membrane prepared from silicone rubber/polysulfone membrane and various loading of PEG + 20wt%activated carbon/silicone rubber/polysulfone MMM at 50 psia

Membrane	Permeability (cm <sup>3</sup> /(cm <sup>2</sup> .sec.cmHg))				
	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
20wt%Act.C./SIL/PS MMM	5.158E-5	3.416E-6	1.135E-5	1.518E-4	1.486E-4
5wt%PEG + 20wt%Act.C./SSIL/PS MMM	1.819E-5	1.692E-6	0.403E-5	0.107E-4	0.258E-4
10wt%PEG + 20wt%Act.C./SSIL/PS MMM	1.388E-5	0.900E-6	0.392E-5	0.040E-4	0.105E-4
15wt%PEG + 20wt%Act.C./SSIL/PS MMM	0.695E-5	0.320E-6	0.333E-5	0.003E-4	0.002E-4

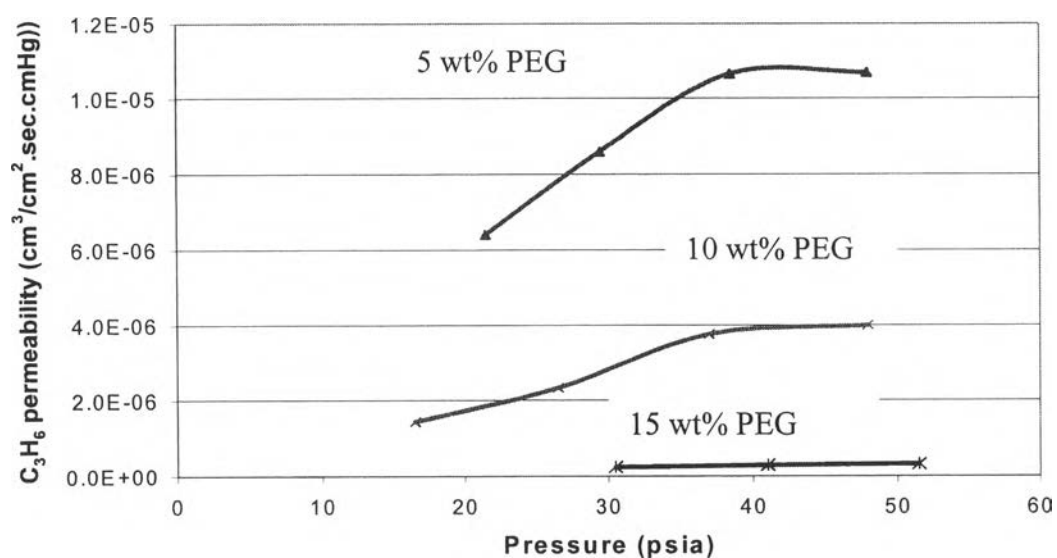
From Table 4.3 the permeabilities of the gases reduced with adding of PEG in 20wt%activated carbon/silicone rubber/polysulfone MMM. One may infer that higher amount of PEG caused denser intersegmental chain packing in MMM. So it is difficult for gas molecule to diffuse in membrane. From the results amount of PEG affected to the decreasing in permeability of C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> more than other gases. Because molecule of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> are bigger than N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>. So the larger molecules are, the harder they diffuse.

#### 4.2.2 Effects of Pressure to Membrane Permeabilities

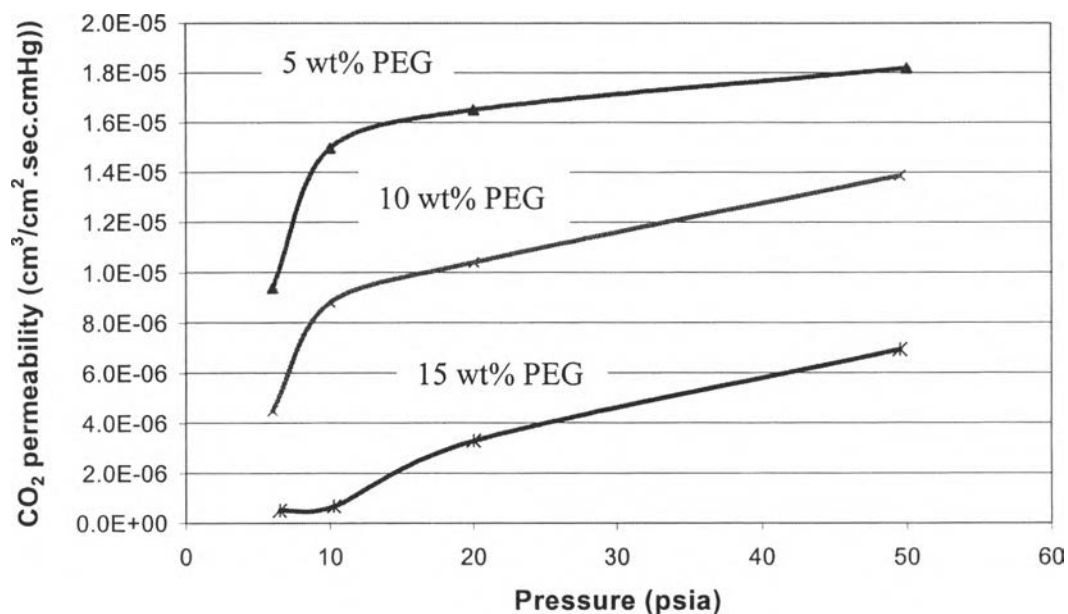
In this part PEG / 20wt%Act.C./SIL/PS MMM was used to investigate the effect of amount of PEG on plasticization by using CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> as the feed and varying pressures from 5 – 100 psia.

1) C<sub>3</sub>H<sub>8</sub> permeability

**Figure 4.9** Relation between pressure and C<sub>3</sub>H<sub>8</sub> permeability in 5, 10, 15 wt%PEG/20 wt%Act.C./SIL/PS MMM.

2) C<sub>3</sub>H<sub>6</sub> permeability

**Figure 4.10** Relation between pressure and C<sub>3</sub>H<sub>6</sub> permeability in 5, 10, 15 wt%PEG/20 wt%Act.C./SIL/PS MMM.

3) CO<sub>2</sub> permeability

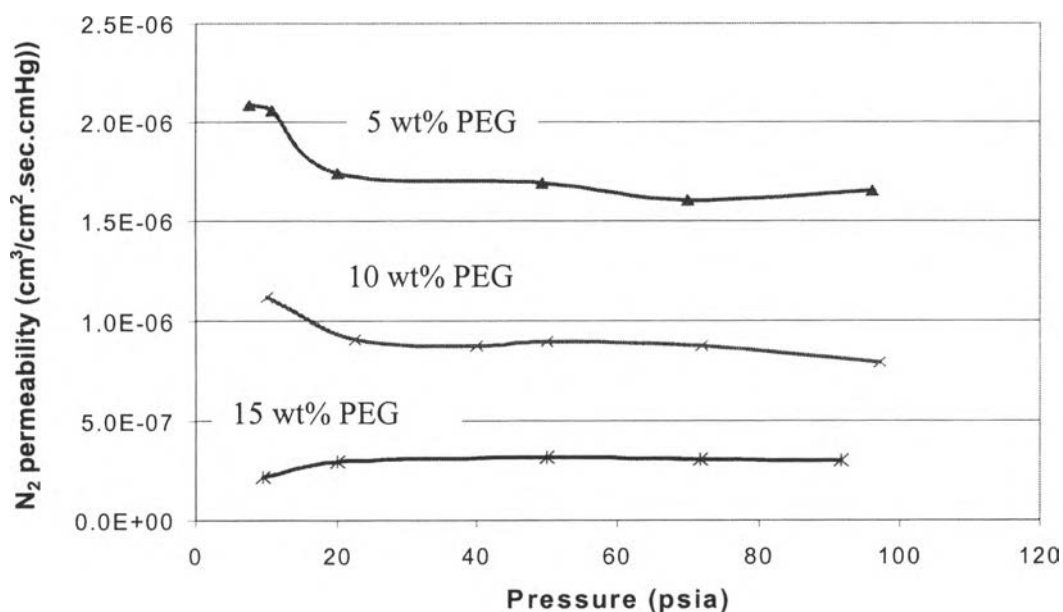
**Figure 4.11** Relation between pressure and CO<sub>2</sub> permeability in 5, 10, 15 wt%PEG/20 wt%Act.C./SIL/PS MMM.

Figures 4.9-4.11 shows effect of amount of PEG on C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub> and CO<sub>2</sub> plasticization, respectively. The plasticization of three gases shows the same trend because they are more soluble. The plasticization of them decreased with increasing the amount of PEG. This is because adding PEG will reduce free volume in the membrane resulting in difficulty for gas molecules to solute and plasticize in membrane.

4) N<sub>2</sub> permeability

Figure 4.12 shows effect of amount of PEG on N<sub>2</sub> plasticization. The plasticization of N<sub>2</sub> shows the different trade with C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub> and CO<sub>2</sub>. N<sub>2</sub> permeability decreased with increasing pressure when adding PEG at 5 and 10 wt% because of hydrostatic compression effect. For less soluble gas like N<sub>2</sub>, H<sub>2</sub> they are hard to plasticize in membrane and adding PEG will increase crystallinity in membrane. It means that PEG reduces the flexibility of polymer chains. Therefore, when increasing pressure, it reduces the free volume in membrane and then decreasing permeability.

However, adding PEG to 15 wt% shows the plasticization of N<sub>2</sub> in membrane. One may infer that the large amount of PEG will be able to increase the rubbery state in membrane. Because PEG itself may be more flexible than polymer chain.

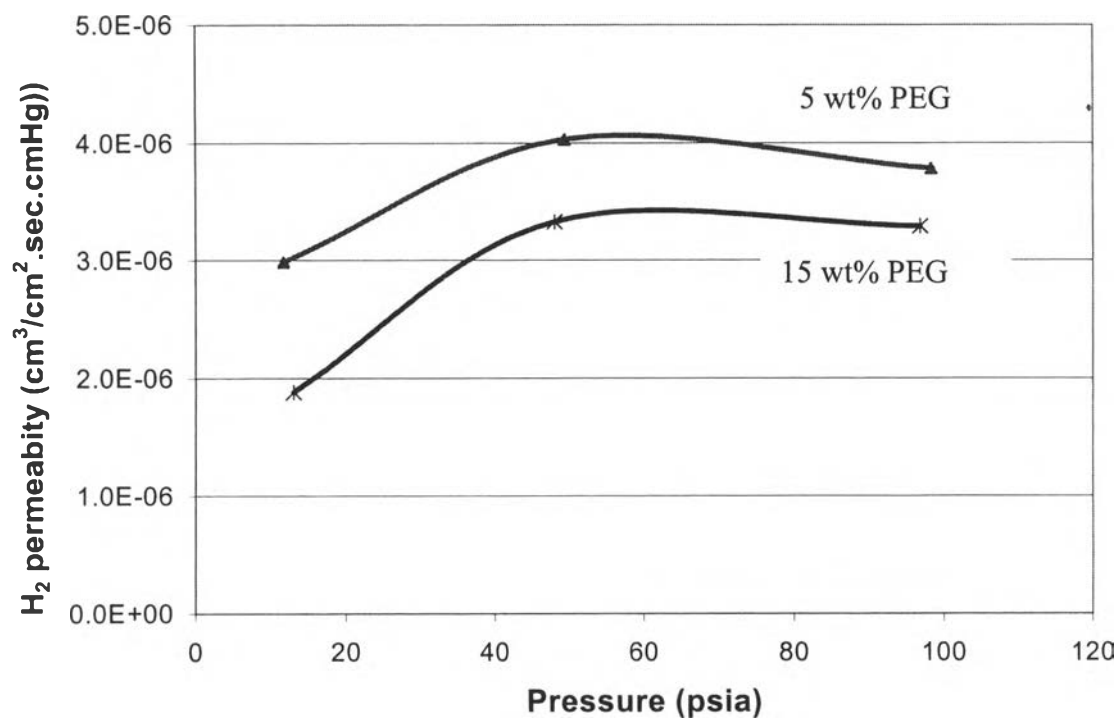


**Figure 4.12** Relation between pressure and N<sub>2</sub> permeability in 5, 10, 15 wt%PEG/20 wt%Act.C./SIL/PS MMM.



5) H<sub>2</sub> permeability

Figure 4.13 shows effect of amount of PEG on H<sub>2</sub> plasticization. Although H<sub>2</sub> is less soluble gas like N<sub>2</sub>, it can plasticize in membrane. Because H<sub>2</sub> molecule is smaller than N<sub>2</sub>. It can use this benefit to plasticize in membrane.



**Figure 4.13** Relation between pressure and H<sub>2</sub> permeability in 5, 10, 15 wt%PEG/20 wt%Act.C./SIL/PS MMM.