

CHAPTER IV RESULTS AND DISCUSSION

4.1 Plasticization Phenomenon in Membranes

In membrane separations, it is well known that the gas streams often contain high levels of plasticizing or condensable vapors, which degrade membrane performance thereof, making the separation process less economic. Plasticization is the major problem faced by CO₂-selective polymeric membrane. The increase in gas permeability of a membrane with increasing feed gas pressure is attributed to CO₂-induced plasticization of the polymer matrix. This plasticizing action of CO₂ decreases the ability of the membrane to separate molecules on the basis of size, thereby causing the reduction in selectivity. Therefore, it is very important to understand the plasticization phenomenon and search for methods to suppress it.

In order to investigate the plasticization phenomenon, the gas permeances of carbon dioxide (CO₂), methane (CH₄) and nitrogen (N₂) were determined from the steady state permeation rates of individual gases through the membrane at room temperature and a constant pressure between 25 and 250 psia. The relations between pressure and gas permeation rate for the studied membranes are shown in Figures 4.1 – 4.3.

4.1.1 Membranes from Cellulose Acetate Supporting Membrane

From Figures 4.1-4.2, CH₄ and N₂ permeation rates remained almost constant when the feed pressure was increased. However, CO₂ permeation rate increased with increasing feed pressure results from an increase in free volume and segmental mobility of the polymer matrix. This visualizes the significant plasticizing effect of CO₂ on the CA membrane. In comparison, CO₂ permeation rate for the porous supporting membrane was higher than CO₂ permeation rate for the dense supporting membrane due to the loosening of the polymer chains of the porous supporting membrane.

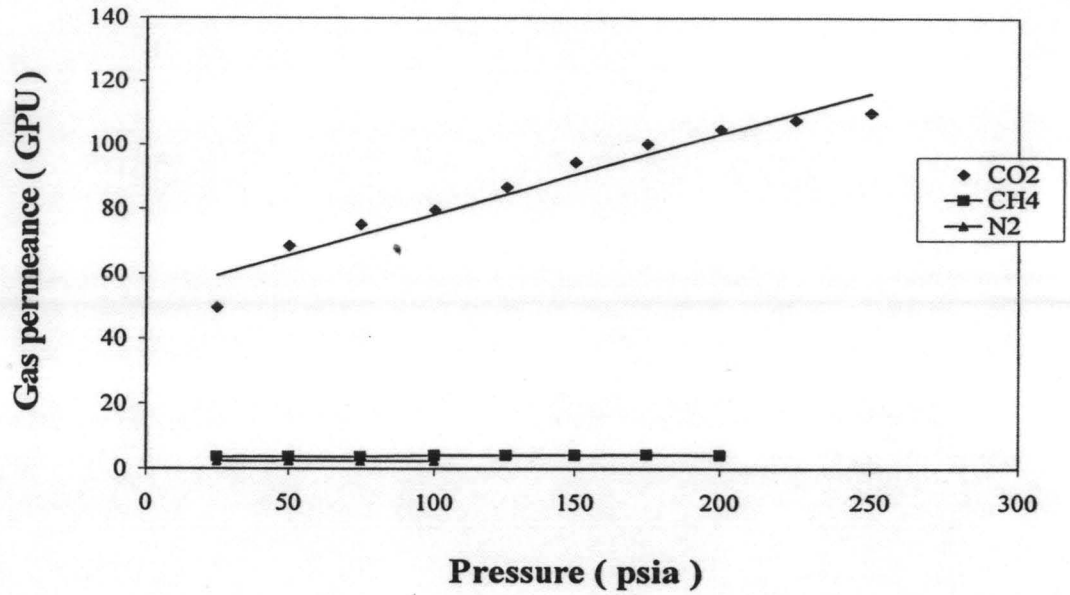


Figure 4.1 Relations between pressure and gas permeation rate for SR/porous supporting CA.

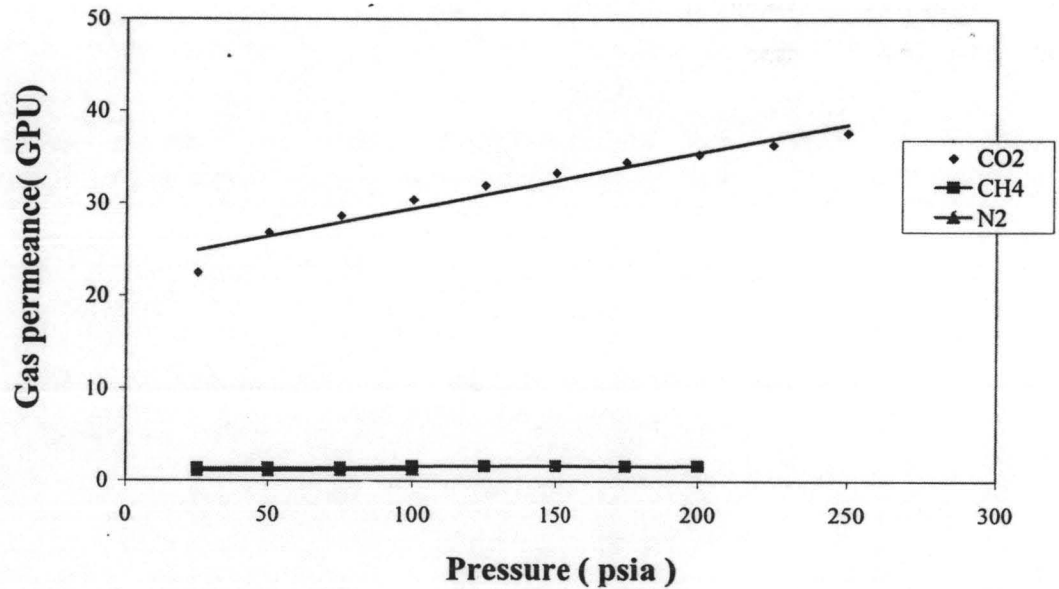


Figure 4.2 Relations between pressure and gas permeation rate for SR/dense supporting CA.

4.1.2 Membranes from Cellulose Acetate Powder

Like the result from CA supporting membrane, CH₄ and N₂ permeation rates were independent on feed pressure. However, CO₂ permeation rate shows an increase with increasing feed pressure as shown in Figure 4.3. The reason for this behavior is the same as discussing in section 4.1.1.

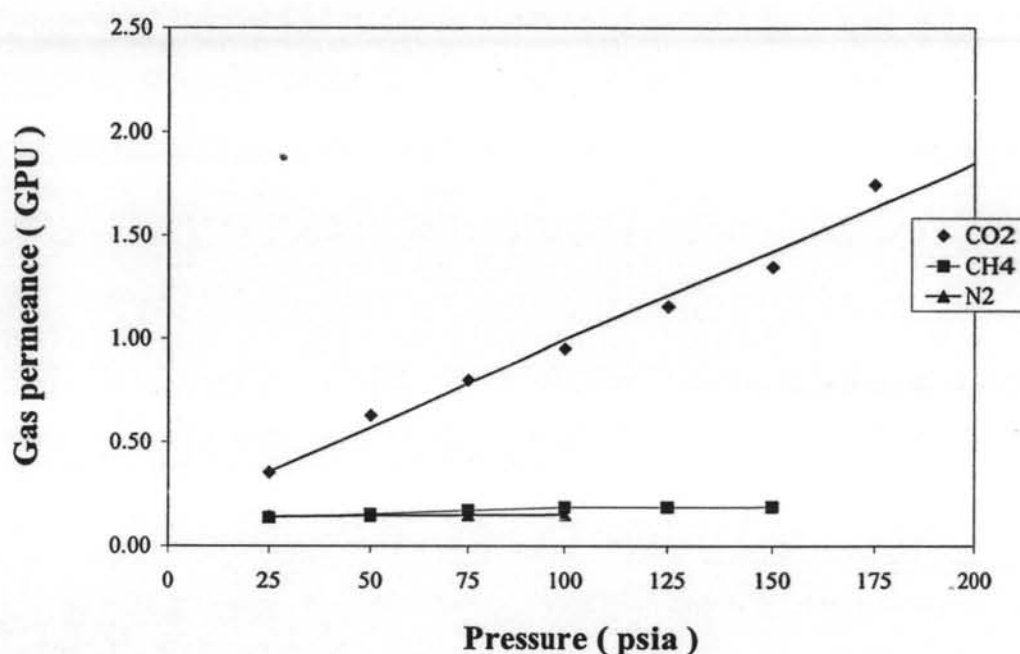


Figure 4.3 Relations between pressure and gas permeation rate for CA powder membrane.

4.2 Effect of Thermal Treatment on CO₂ Permeation Rate

Due to the results from section 4.1, the membranes shows the increase in permeation rate of CO₂ gas with increasing feed gas pressure which attributed to CO₂ induced plasticization of membranes. The CO₂-induced plasticization generally leads to a loss in selectivity of a membrane. Therefore, the plasticization should be suppressed.

In this section, membranes were thermally treated using various temperatures (170°C and 190°C) in order to suppress CO₂ induced plasticization. The CO₂ permeation rate of the treated membranes at 170°C and 190°C were compared

with those of untreated membranes. The obtained results are shown in Figures 4.4-4.6. The slope of graph represents how easy the membrane was plasticized by CO₂. The higher the value of slope, the higher the tendency to be plasticized of membranes.

4.2.1 Membranes from Cellulose Acetate Supporting Membrane

As seen in Figure 4.4 that the CO₂ permeation rate of the untreated membrane increased with increasing feed pressure. Apparently, the slopes of graphs were decreased from 0.256 to 0.0712 and 0.0221 when increased the heat treating temperatures to 170°C and 190°C, respectively. However, the CO₂ permeation rate of the treated membrane at 170°C slightly increased with increasing feed pressure. This indicated a reduction in CO₂ induced plasticization of membranes but it was considered not sufficient to completely suppress the plasticization. The possible reason is CA has the glass transition temperature at 187°C (Bos, 1998). Therefore, thermal treatment at 170°C was not enough to suppress the plasticization. Interestingly, the CO₂ induced plasticization can be substantially suppressed when further increase the heat treating temperature to 190°C.

From Figures 4.5, the same results as the porous supporting CA were observed. The slopes of graphs were declined from 0.0605 to 0.0405 and 0.0182 when increase heat treating temperature of 170°C and 190°C respectively. According to the obtain results from Figure 4.4 and 4.5, it was revealed that the thermal treatment was a successful method to suppress the plasticizing effect of membranes. The heat treatment has caused a densification of the polymer matrix and results in a reduction of chain mobility and simultaneously minimizes the membrane plasticization. Consequently, the treated membranes gave the lower CO₂ permeation rate than the untreated membranes

In comparison, the CO₂ permeation rates for an untreated and heat-treated SR/ dense supporting CA were lower than those for an untreated and heat-treated SR/ porous supporting CA due to the densely packed chains in polymer of dense supporting CA.

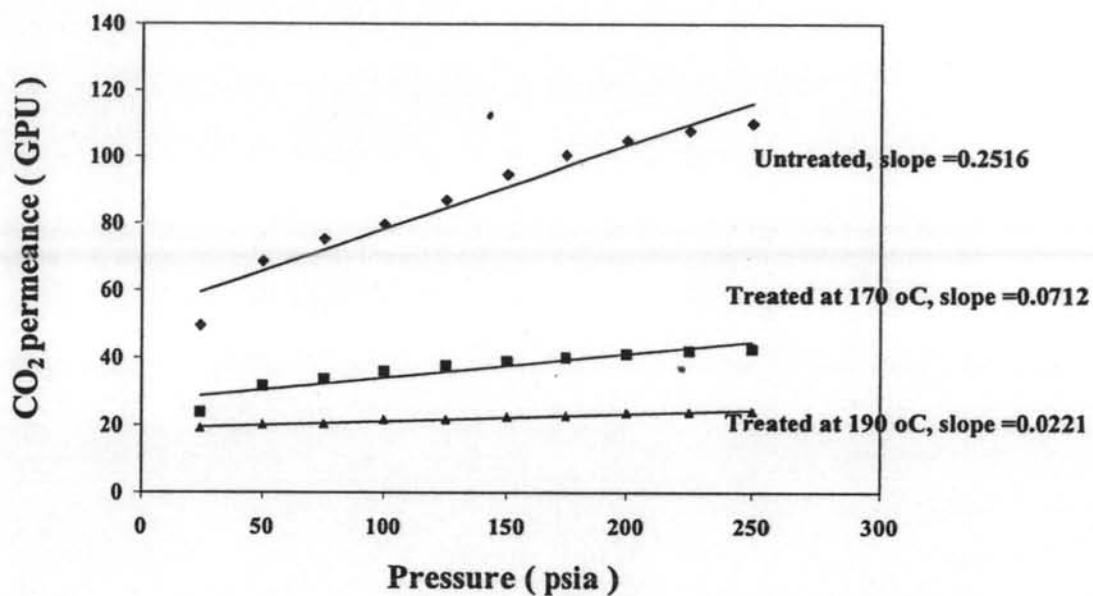


Figure 4.4 Relations between pressure and CO₂ permeation rate for an untreated and heat-treated SR/ porous supporting CA.

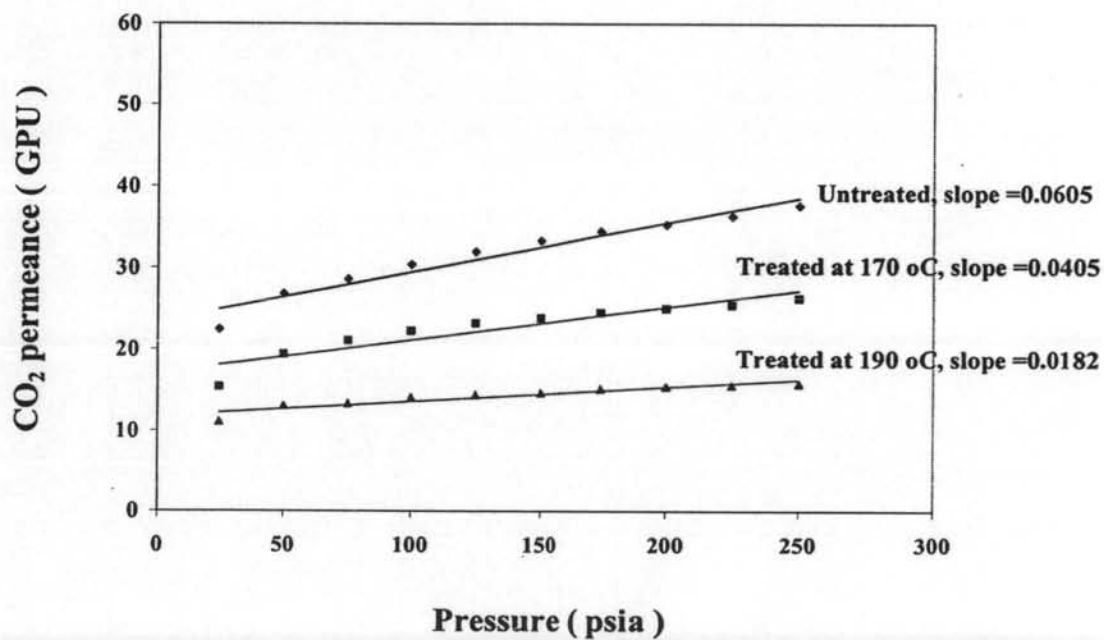


Figure 4.5 Relations between pressure and CO₂ permeation rate for an untreated and heat-treated SR/ dense supporting CA.

4.2.2 Membranes from Cellulose Acetate Powder

Membranes from CA powder were also thermally treated in order to study the possibilities of suppress the plasticization. The given results were shown in Figure 4.6. Like the results from section 4.2.2, thermal treatment can suppress the plasticization of membranes due to the reduction in slope of graphs. From Figure 4.6, slope of graphs decline when further increase the heat treating temperature. The obtained result was confirmed that thermal treatment near the glass transition temperature of polymer was the successful method to suppress plasticization.

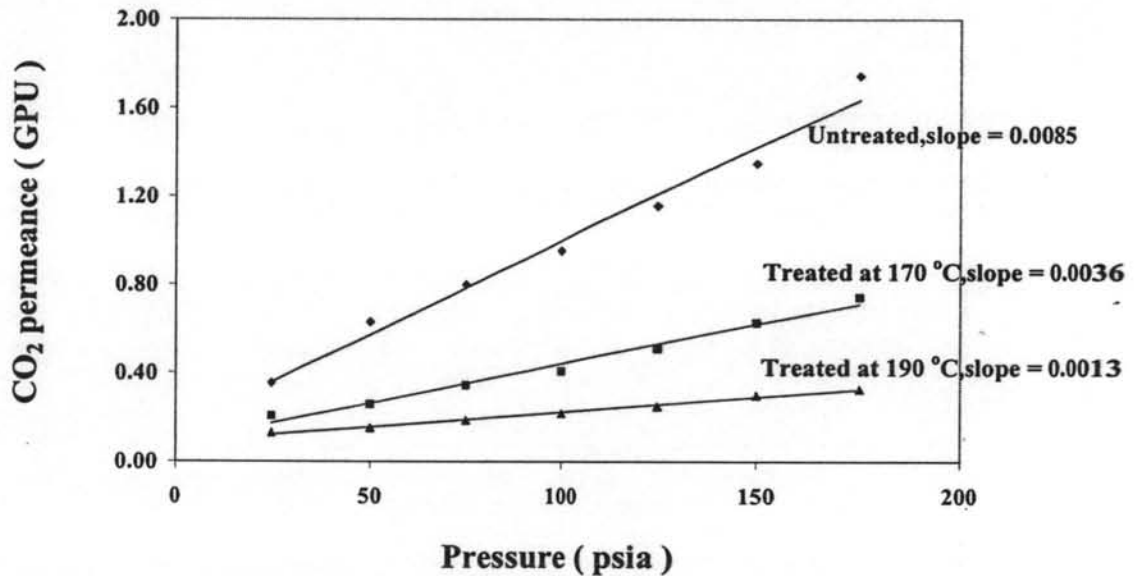


Figure 4.6 Relations between pressure and CO₂ permeation rate for an untreated and heat-treated CA powder.

4.3 Effect of NaX-zeolite on CO₂ Permeation Rate

The incorporation of NaX-zeolite into the polymeric membrane provided the good separation performance of MMMs (Soontararatpong, 2005) but its effect on the plasticization suppression was not clearly understood. Therefore, in an attempt to understand and remedy the plasticization, NaX-zeolite was incorporated into membranes to study the CO₂ permeation behavior. The obtained results are shown in Figures 4.7 – 4.9.

4.3.1 Mixed Mmatrix Membranes from Cellulose Acetate Supporting Membrane

It was found in Figure 4.7 that the slopes of graphs were decreased when incorporating NaX-zeolite into membranes. This is because CO₂ induced plasticization was reduced. The results also showed that the slopes were further declined as an increase in amount of NaX-zeolite into membranes. This indicates a further reduction in CO₂ induced plasticization when increasing amount of NaX-zeolite in membranes. Therefore, it can be stated that NaX-zeolite was improved the stability of membranes in terms of plasticization suppression. A possible reason is that NaX-zeolite hindered the diffusion path of gas molecules resulting in densification of MMMs. From Figure 4.7, NaX-zeolite membranes not only reduced the plasticizing effect but also reduced the gas permeation through membranes. It was also found that CO₂ permeance was further decreased with increasing amount of NaX-zeolite.

From Figure 4.8, the slopes were also decreased with increasing amount of NaX-zeolite. Therefore, the incorporation of NaX-zeolite into SR/ dense supporting CA can reduce the plasticization.

Similarly to the results from the previous sections, the CO₂ permeation rate for an untreated NaX-zeolite and heat-treated NaX-zeolite SR/ dense supporting CA were lower than those for an untreated NaX-zeolite and heat-treated NaX-zeolite SR/ porous supporting CA due to the densification of polymer in dense supporting CA.

In comparison of the thermal treatment method and the incorporation of NaX-zeolite, the former method can give a significant decrease in slope of graphs to a lower value than the latter method. This denotes that thermal treatment cause the better efficient chain-packing in polymer than the incorporation of NaX-zeolite. In other word, thermal treatment made membranes more ordered structures than the incorporation of NaX-zeolite. Therefore, the thermal treatment method was more effective in plasticization suppression than the incorporation of NaX-zeolite.

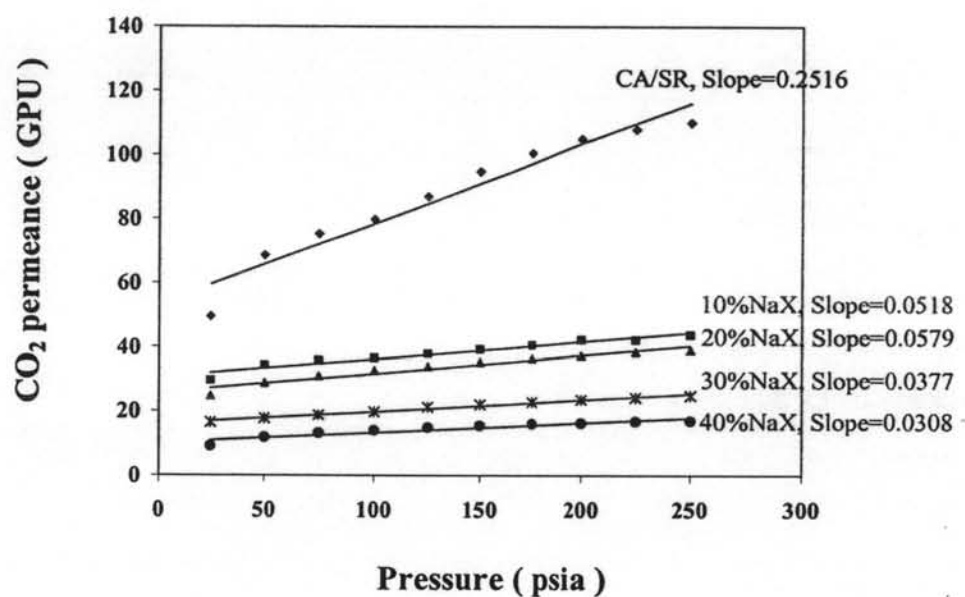


Figure 4.7 Relations between pressure and CO₂ permeation rate in 10, 20, 30, 40%NaX/ SR/ porous supporting CA.

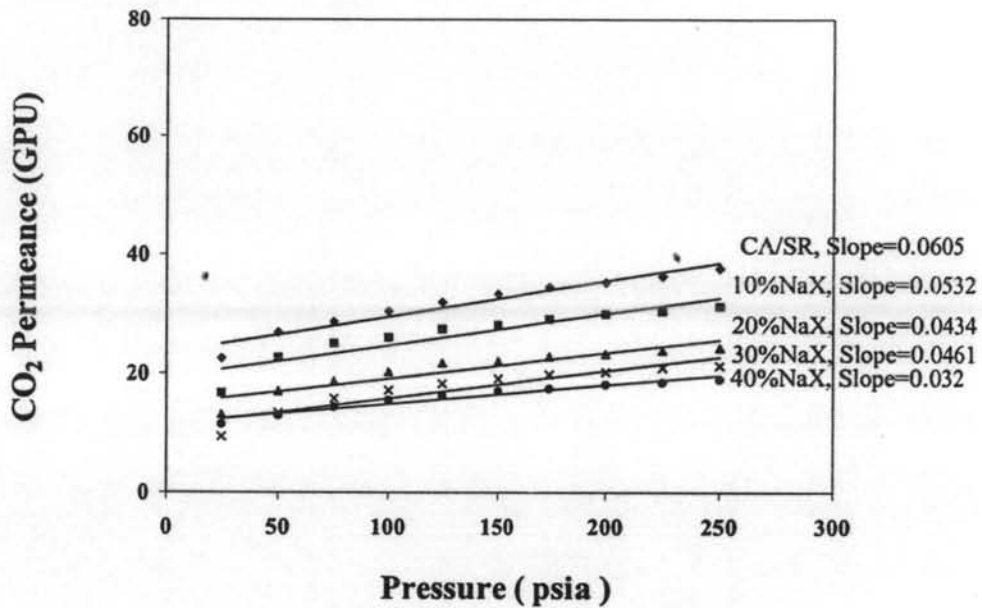


Figure 4.8 Relations between pressure and CO₂ permeation rate in 10, 20, 30, 40%NaX/ SR/ dense supporting CA.

4.3.2 Mixed Matrix Membranes from Cellulose Acetate Powder

This type of MMMs was different from the CA supporting MMMs because NaX-zeolite was directly incorporated into the CA instead of coated on the CA. From Figure 4.9, the incorporation of NaX-zeolite into MMMs reduced the slope of the CO₂ permeance graphs. These indicated that the incorporation of NaX-zeolite into MMMs had the positive effect in plasticization suppression. The possible reason was due to the inhibition of polymer chain mobility near the polymer-zeolite interface which means NaX-zeolite rigidify polymeric chains in MMMs. However, the further increase amount of NaX-zeolite seems to slightly increase the slopes but it still lower than the pure CA powder MMMs. The results showed the lowest slope at 10% NaX-zeolite and slopes start to increase when further increase amount of NaX-zeolite. The possible may be due to at higher NaX-zeolite contents MMMs appeared small channels or microvoids around zeolite-polymer interface as a result of the loosening of MMMs (Rattanawong, 2001).

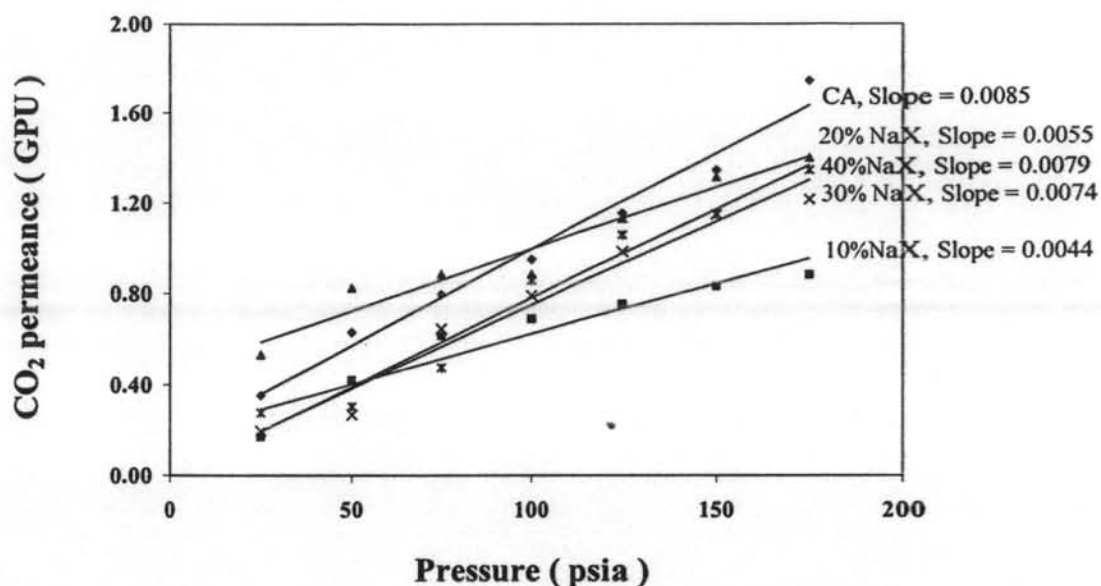


Figure 4.9 Relations between pressure and CO₂ permeation rate in 10, 20, 30, 40%NaX/CA powder.

4.4 Combined Effect of Thermal Treatment and NaX-zeolite on CO₂ Permeation Rate

According to Sections 4.2 and 4.3, either heat treating temperature or NaX-zeolite had the positive effect on the plasticization suppression. Therefore, NaX-zeolite MMMs were treated at 170°C and 190°C in order to study the combined effect of both factors on the plasticization suppression.

4.3.1 Mixed Matrix Membranes from Cellulose Acetate Supporting Membrane

Figure 4.10 shows the CO₂ permeation behavior of the treated NaX/SR/porous supporting CA at 170°C. As can be seen from this figure, the thermal treatment at 170°C showed the further decrease in slope of graphs. The slope of the treated NaX MMMs was lower than that of the untreated membrane. Moreover, the slopes of graphs further decreased with increasing amounts of NaX-

zeolite. This indicates that the combination of thermal treatment and NaX-zeolite can synergistically reduce the CO₂ induced plasticization of MMMs.

In addition, Figure 4.11 shows the CO₂ permeation behavior of the treated NaX/SR/ porous supporting CA at 190°C. The results showed that the slopes of graphs were decreased with increasing amounts of NaX-zeolite indicating that the CO₂ induced plasticization was suppressed. In comparison of the treated NaX/SR/ porous supporting CA at 170°C and the treated NaX/SR/porous supporting CA at 190°C, the latter gave more effective in the plasticization suppression than the former due to the lower in slope of graph.

For the treated NaX/SR/dense supporting CA, the treated NaX/SR/dense supporting CA at 170°C also show the lower in slope of graph than that of untreated NaX/SR/dense supporting CA as shown in Figure 4.12. Furthermore, the further decrease in slope of graphs was observed with increasing amount of NaX-zeolite into MMMs. From Figure 4.13, the slope of the graph was substantially decline when treated NaX/SR/dense supporting CA at 190°C. Apparently, the combination of thermal treatment at 190°C and the incorporation of NaX-zeolite was the most effective way to suppress the plasticization due to the lowest slope of graph. It was also found that the treated NaX-zeolite membranes not only reduce the plasticizing effect but also reduce the gas permeation through membranes.

The combination of thermal treatment and NaX-zeolite was a successful way to suppress the plasticization. It can more effective in densify the polymer chain than apply only thermal treatment or incorporate NaX-zeolite into MMMs.

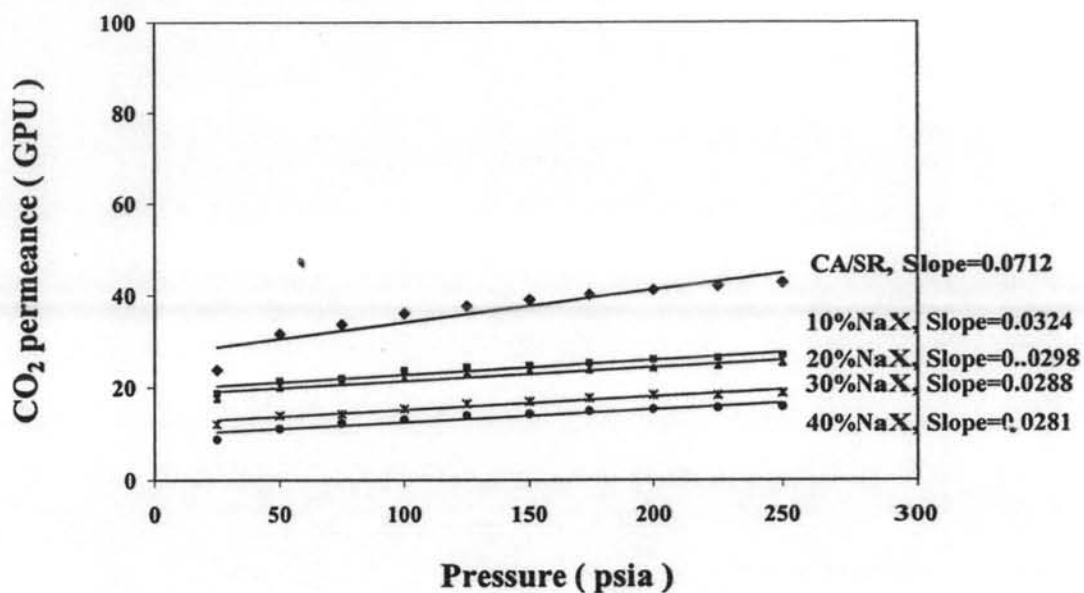


Figure 4.10 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/ SR/ porous supporting CA at 170 °C.

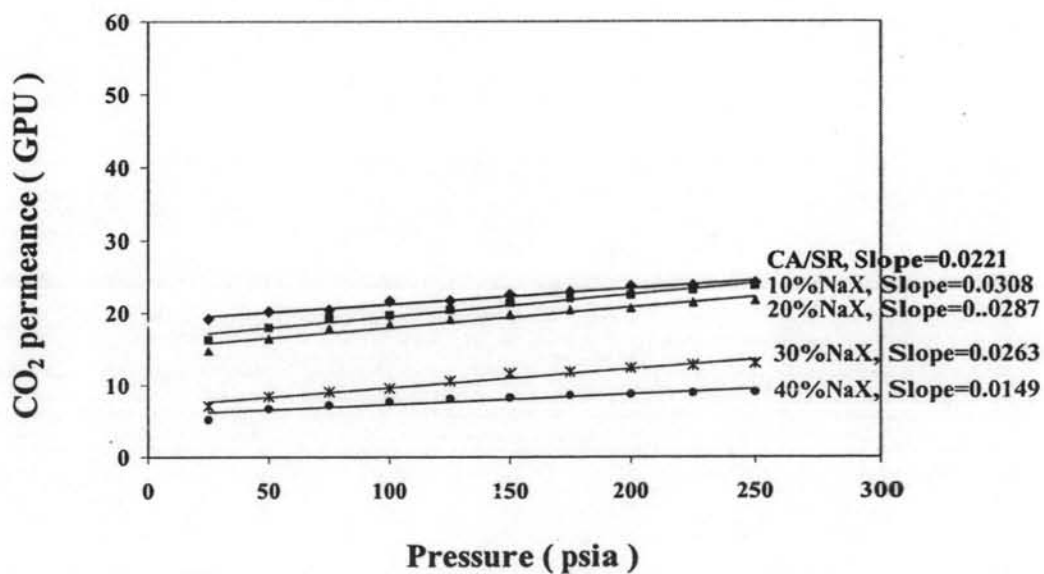


Figure 4.11 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/ SR/ porous supporting CA at 190 °C.

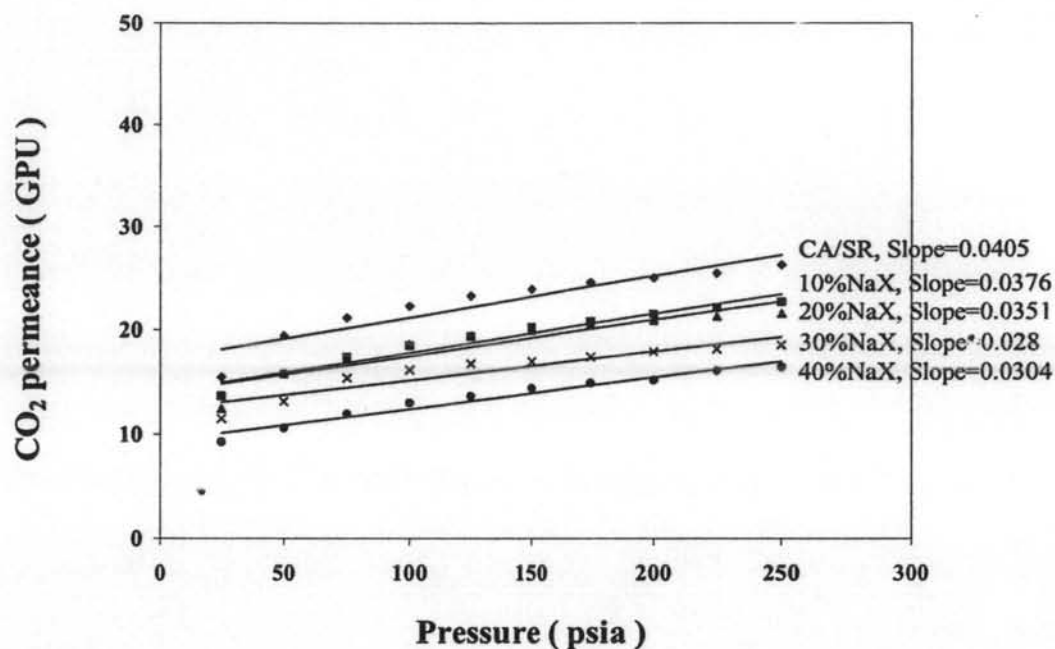


Figure 4.12 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/ SR/ dense supporting CA at 170 °C.

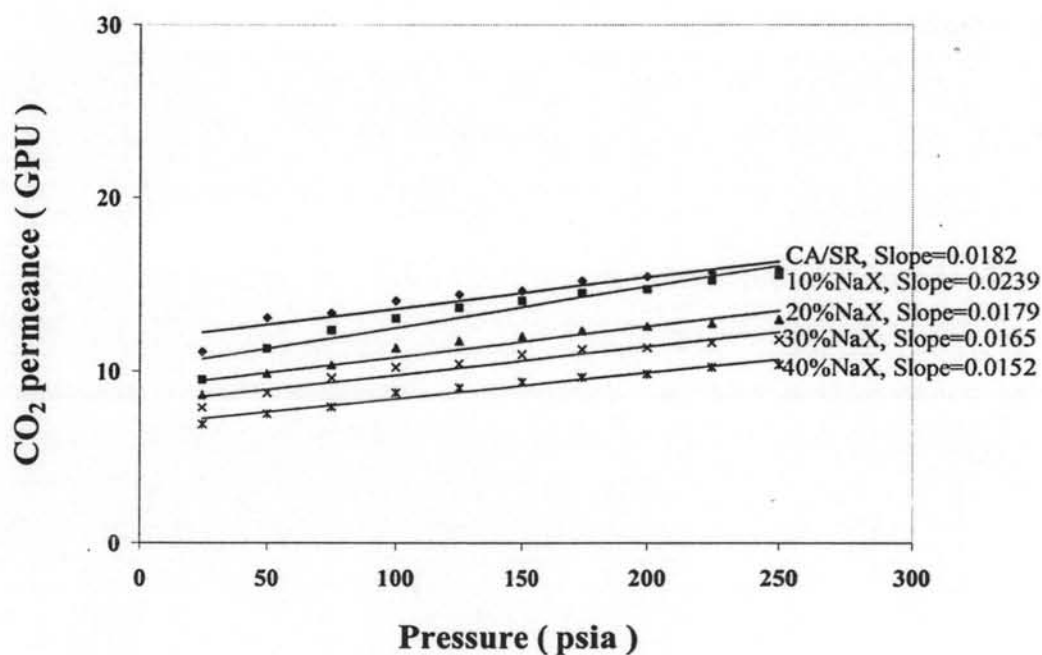


Figure 4.13 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/ SR/ dense supporting CA at 190 °C.

4.3.2 Mixed Matrix Membranes from Cellulose Acetate Powder

The thermal treatment at 170°C and 190°C were applied to the NaX/CA powder MMMs. The obtained result was shown in Figure 4.14 - 4.15. The slope of the treated NaX/CA powder MMMs at 170°C was lower than that of the untreated membrane and slopes were further decrease with increasing heat treating temperature to 190 °C. The reason is because the densification of membrane by the thermal treatment as described in section 4.2.

From Figure 4.14 and Figure 4.15, the increase amount of NaX-zeolite in MMMs was not substantially effect the slope of graphs. The possible explanation was due to the effect of thermal treatment was more obvious than the effect of NaX-zeolite.

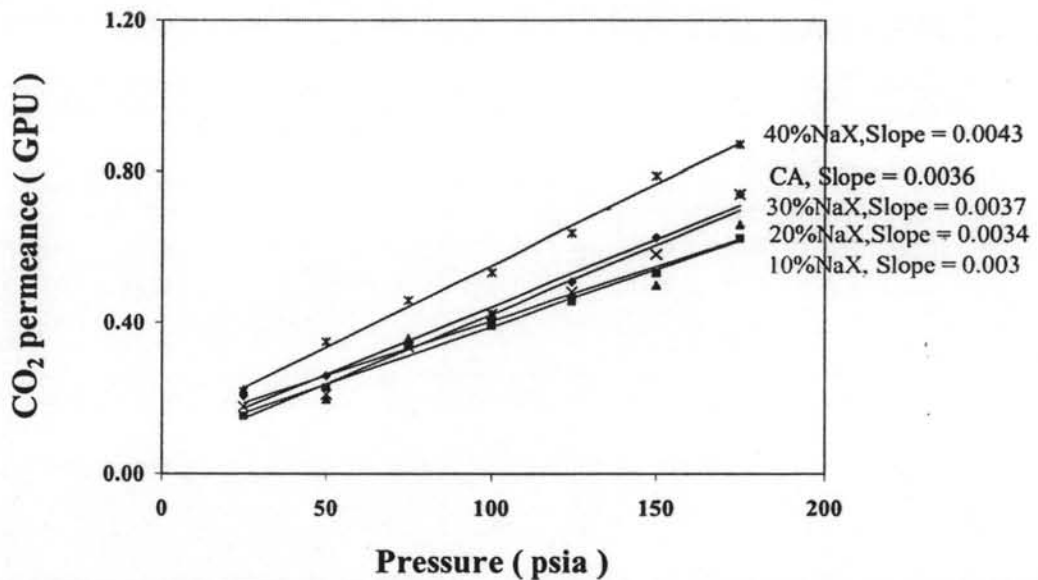


Figure 4.14 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/CA powder at 170 °C.

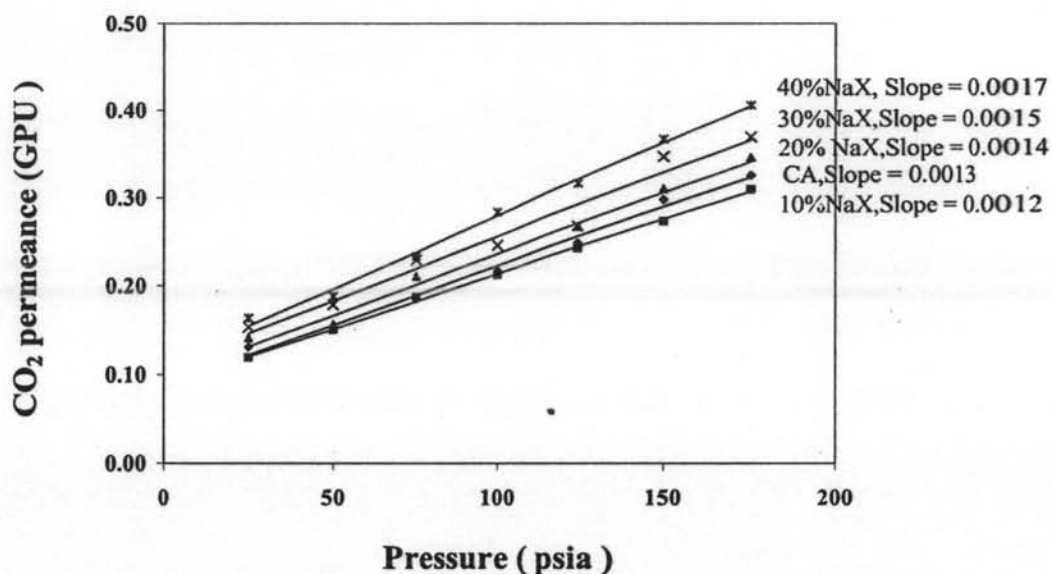


Figure 4.15 Relations between pressure and CO₂ permeation rate in treated 10, 20, 30, 40%NaX/CA powder at 190 °C.

4.5 Combined Effect of the PEG Treated NaX and Thermal Treatment on CO₂ Permeation Rate

In this section, liquid PEG was additionally incorporated into MMMs to study the plasticization suppression. 30%PEG/15%NaX/SR/supporting CA was selected because it provided the best CO₂/CH₄ selectivity (Soontraratpong, 2005). The selected MMMs were treated at 170°C and 190°C. The obtained results are shown in Figure 4.16 and Figure 4.17.

It is clearly seen in these figures that PEG reduced the CO₂ permeation rate and results in the increment in the plasticization suppression of MMMs. The reason was probably because PEG filled up the transient gap between polymer chains and caused the densification of MMMs. Obviously, the thermal treatment yielded a significant decrease in slope of graphs especially when treated at 190°C. Therefore, the treated 30%PEG/15%NaX/SR/supporting CA can further improve the ability of MMMs in plasticization suppression.

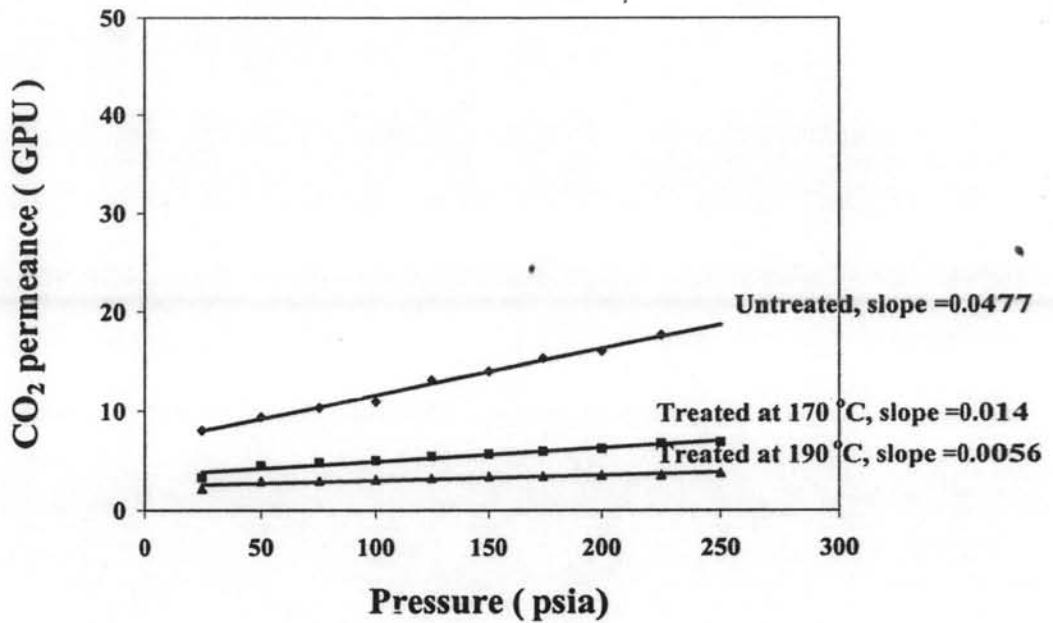


Figure 4.16 Relations between pressure and CO₂ permeation rate of 30%PEG/15%NaX/ SR/ porous supporting CA.

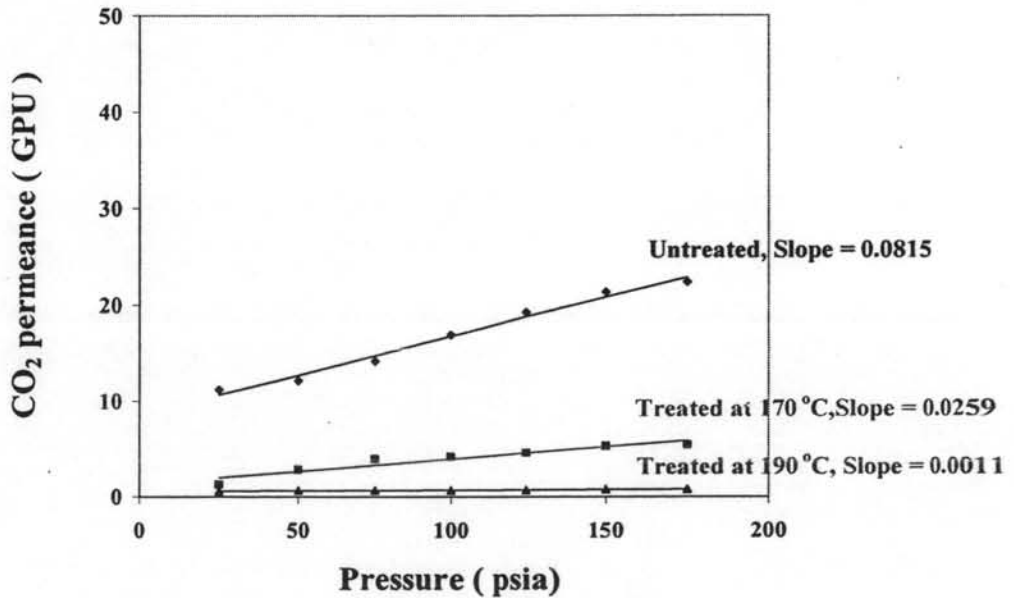


Figure 4.17 Relations between pressure and CO₂ permeation rate of 30%PEG/15%NaX/ SR/ dense supporting CA.