# Preparation of Zeolite-Filled PDMS Membranes and It's Properties for Organic Vapor Separation

## Min Joung Kim[†] and Kyung Ho Youm[*]

School of Chemical Engineering, Chungbuk National University, Cheongju 361-763, Korea
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**Abstract** : In order to improve organic vapor separation efficiency of polydimethylsiloxane (PDMS) membrane, various zeolites (zeolite 4A, zeolite 13X and natural zeolite) were introduced into a thin PDMS film. The measurements of permeability and selectivity of zeolite-filled PDMS membranes were carried out with a $CO_2$ gas and a $CO_2$ gas/acetic acid vapor mixture, respectively. The $CO_2$ permeability of zeolite-filled membranes decreased with increasing zeolite content and then recovered up to 30 wt% content. The effect of zeolite type on the improvement of $CO_2$ permeability was found to be in the order of zeolite 13X > natural zeolite > zeolite 4A. The $CO_2$ selectivity of zeolite-filled membranes was enhanced up to 9 times compared with the selectivity of a pure (unfilled) PDMS membrane. The effect of zeolite type on the improvement of $CO_2$ selectivity was found to be in the order of natural zeolite > zeolite 13X > zeolite 4A.

## 1. Introduction

Gas separation using membranes have emerged as an important alternative to other gas separation technologies for many reasons. These reasons are higher energy efficiency, lower cost of operation and maintenance, and ease of scale-up. Many polymers and inorganic materials are used as a membrane material for gas separation. Usually, most polymers used as a membrane material have a converse relationship between the gas permeability and selectivity. For instance, elastomeric polymers, such as silicone rubber, have high permeabilities but poor selectivities. Adversely, glassy polymers, such as polyimides, are quite selective but they have low permeabilities [1].

Development of the additive-filled polymer membranes has studied in order to improve the permselectivity of polymer membranes in gas separation and pervaporation [2-9]. Jia and coworkers [5], and Duval and coworkers [6] prepared the zeolite-filled silicone rubber membranes and applied it for the separation of various gas molecules. They found that zeolite played the role of a molecular sieve in the membrane by facilitating the permeation of smaller molecules but hindering the permeation of larger ones. In this manner, zeolite improved the selectivity as well as the permeability of membranes. Duval and coworkers [7], and Te Hennepe and coworkers [8,9] prepared the heterogeneous membranes by introducing silicalite-1, a hydrophobic zeolite, into a PDMS film and applied it for the separation of alcohol by pervaporation. They showed that the selectivity and permeability of alcohol were improved by introducing silicalite-1 into a PDMS membrane.

As mentioned above, although many researchers studied the polymer membranes containing various additives, but its applications were limited only to gas separation ($O_2/N_2$, $CO_2/CH_4$ etc.) and pervaporation (alcohol/water etc.). Air pollution by

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[†] Present address: Membranes and Separation Research Center, KRICT, Taejon 305-606, Korea

organic vapors recently became serious environmental problem and removing (or retaining) organic vapors from (or in) the process gas is an important application of the membrane technology. In the membrane literature, very few applications of the additive-filled polymer membranes for organic vapor separation are reported.

We prepared the zeolite-filled PDMS membranes and determined its properties for organic vapor separation according as zeolite type and content into the membrane. This study is of interest in exhaust of fermentation gas from the sealed package of Kimchi, a Korean traditional food, by removing $CO_2$ gas and retaining organic vapors using the membrane attached on the outer surface of Kimchi package. In order to improve the permselectivity of organic vapor, various zeolites (zeolite 4A, zeolite 13X and natural zeolite) were introduced into a thin PDMS film. The morphology of these membranes was investigated with SEM, and the permeability and selectivity were determined with a $CO_2$ gas and a $CO_2$ gas/acetic acid vapor mixture, respectively.

## 2. Theory

The permissive and selective properties of gas molecule through a polymer membrane are governed by the interaction of gas molecule with membrane material. They depend on the size and condensability of gas molecule, the segmental mobility and intersegmental packing density of polymer [10].

Under steady-state, the following equation (Fick's law) can be used to describe gas flux through a nonporous membrane such as PDMS [11]:

$$J = \frac{D(C_1 - C_2)}{l} \tag{1}$$

Where $J$ (cm$^3$/cm$^2 \cdot$ s) is the flux through a membrane, $D$ (cm$^2$/s) is the diffusion coefficient, $C_1$ and $C_2$ are the concentration (cm$^3$/cm$^3$) of feed and permeate side and $l$ (cm) is the membrane thickness.

In Equation (1), the concentrations ($C_1$ and $C_2$) are related the partial pressure, $p$ (cmHg), by Henry's law, which states that linear relationship

between the concentration inside the membrane and the partial pressure outside the membrane.

$$C = S \cdot p \tag{2}$$

Where $S$ (cm$^3$/cm$^3 \cdot$ cmHg) is the solubility coefficient. Combing Equations (1) and (2) gives:

$$J = \frac{P(P_1 - P_2)}{l} \tag{3}$$

Where $P$ is defined as the product of diffusion coefficient, $D$, and solubility coefficient, $S$, ($P = D \cdot S$), and is called the gas permeability. The unit of permeability, $P$, at standard condition (1 atm, 25℃) is expressed in barrer (1 barrer = $1 \times 10^{10}$ [cm$^3$(STP) $\cdot$ cm/cm$^2 \cdot$ s $\cdot$ cmHg] ).

The selectivity (or separation factor), $\alpha_{AB}$, is defined as the ratio of concentration fraction of gas $A$ and $B$ at feed and permeate side [12]:

$$\alpha_{AB} = \frac{Y_A/Y_B}{X_A/X_B} \tag{4}$$

Where $X_A$ and $X_B$ are the concentration fractions of gas $A$ and $B$ at feed side, $Y_A$ and $Y_B$ are those at permeate side.

## 3. Experimental

### 3.1. Materials

PDMS (RTV 615A and RTV615B, General Electric Co., USA) was used as a membrane matrix. RTV 615A is a component of PDMS prepolymer, and RTV 615B is a component of curing agent containing the cross-linker and platinum catalyst. Zeolite 4A (Cosmo Co., Korea), zeolite 13X (Aldrich Co., USA) and natural zeolite (from Kampo area in Korea) were used as the additives filled into a PDMS membrane. Table 1 gives the properties of these different zeolites. The size of zeolite particles, which was measured with a particle size analyzer (Model Elzone 280PC, PDI Co., USA), was typically in the range 1.3~7.7 $\mu$m. To remove the water molecule and impurities in the pore of zeolites, zeolite 4A was calcinated at 600℃ for 30 minutes

**Table 1.** Properties of zelolites

| Zeolite | Pore size[a] | Mean particle size[b] | Si/Al ratio[a] |
|---|---|---|---|
| Zeolite 4A | 4.0 Å | 3.0 $\mu$m | 1.0 |
| Zeolite 13X | 7.2 Å | 1.3 $\mu$m | 1.2 |
| Natural Zeolite | 4~55 Å | 7.7 $\mu$m | 5.0 |

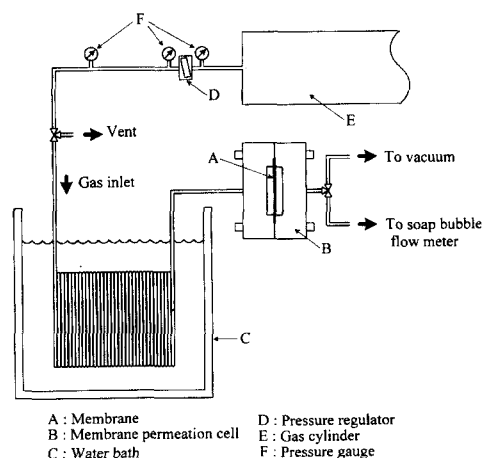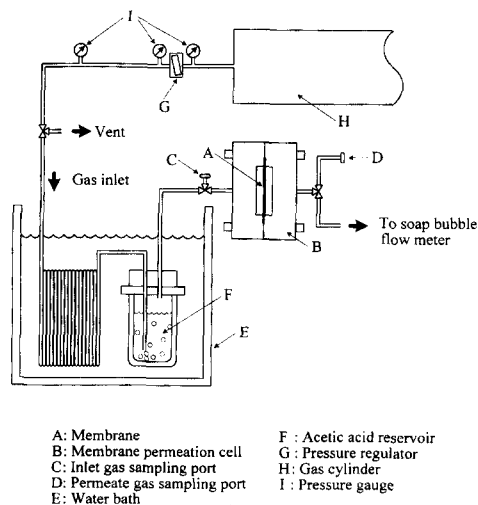a) from reference 17
b) measured by particle size analyzer
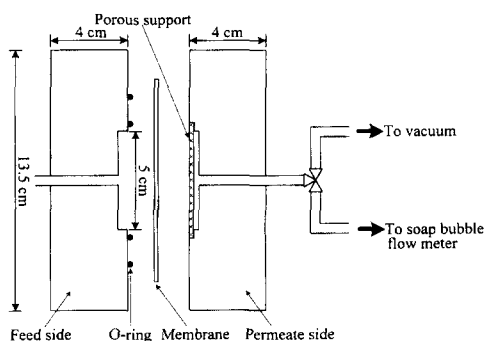


**Fig. 1.** Gas permeation cell.

and stored in a desiccator. In the case of zeolite 13X and natural zeolite, calcination was carried out at 350℃ for 2 hours.

## 3.2. Apparatus

Detail of the membrane permeation cell is shown in Figure 1. The effective membrane area of this cell was 21.01 cm². A porous metal plate was installed in the cell to support the membrane, and the two viton o-rings were used to prevent gas leakage.

An apparatus to measure the permeability of zeolite-filled PDMS membrane is shown in Figure 2. The test gas ($CO_2$) was fed to the membrane cell through the feed line immersed in a water bath controlled at 30℃. The permeation rate of $CO_2$ gas through the membrane was measured using the soap bubble flow meter. An apparatus to measure the selectivity of zeolite-filled PDMS membrane is shown in Figure 3. To prepare $CO_2$ gas/ acetic acid vapor mixture, $CO_2$ gas was introduced into a reservoir containing acetic acid solution. Sampling ports were installed in both feed and permeate side to measure the concentration fractions of gas mixture.



A : Membrane            D : Pressure regulator
B : Membrane permeation cell   E : Gas cylinder
C : Water bath          F : Pressure gauge

**Fig. 2.** System set up for the measurement of the $CO_2$ permeability of the zeolite-filled PDMS membranes.



A: Membrane               F : Acetic acid reservoir
B: Membrane permeation cell    G : Pressure regulator
C: Inlet gas sampling port     H: Gas cylinder
D: Permeate gas sampling port   I : Pressure gauge
E: Water bath

**Fig. 3.** System set up for the measurement of the $CO_2$ selectivity of the zeolite-filled PDMS membrane.

## 3.3. Membrane Preparation

The zeolite-filled PDMS membranes were prepared by dispersion of various zeolites in the PDMS solution, followed by a casting on a glass plate and a crosslinking reaction. Two components of RTV 615 were mixed in a 10 : 1 ratio and this solution was stirred for 1 hour. The zeolite fine powder was added in this solution and thoroughly mixed until a homogeneous dispersion was obtained. After removal of air bubbles, the dispersion mixture was cast on a glass plate using a Gardener knife. The crosslinking reaction was carried out at 80℃ for 16 hours. The resulting membrane was removed from a glass plate and then kept in a desiccator until it was used. Zeolite content was varied from 0 to 50 wt%. Membrane thickness was measured with a micrometer (Model SM-112, Teclock Co., Japan). The morphology of zeolite-filled PDMS membranes was investigated by a scanning electron microscopy (SEM, Model S570, Hitachi Co., Japan).

## 3.4. Measurements of Permeability and Selectivity

The $CO_2$ permeability of zeolite-filled PDMS membranes was measured according to ASTM D1434-82 [13]. Measurements of the $CO_2$ permeability typically involved pumping down the membrane permeation cell shown in Figure 2 and degassing the membrane from both sides for 1 hr. The test gas was then introduced into the inlet side of the membrane at 1 bar and 30℃ for 20 minutes while the permeate side of the cell was still under vacuum. The vacuum was then cut off and the permeation rate of $CO_2$ gas was measured by the soap bubble flow meter at 30-minute intervals. Using the steady state value of permeation rate, the $CO_2$ permeability, $P$, at standard condition was calculated by the following equation:

$$P = \frac{Q \cdot l}{(P_1 - P_2) \cdot A} \qquad (5)$$

Where, $Q$ ($cm^3/s$) is the permeation rate of $CO_2$ gas through the membrane at standard condition and $A$ ($cm^2$) is the effective membrane area. Also

using the time-lag method [14,15], the diffusion coefficient, $D$, and solubility coefficient, $S$, of $CO_2$ gas in the zeolite-filled PDMS membranes were calculated.

Measurements of the $CO_2$ selectivity were carried out with a mixture of $CO_2$ gas and acetic acid vapor at 1 bar and 30℃ using the apparatus shown in Figure 3. Gas samples in the feed and permeate side were collected at 1.5-hr intervals and analyzed the compositions using a gas chromatography (Model 5890 Ⅱ, Hewlett Packard Co., USA). The $CO_2$ selectivity was calculated according to the ratio of gas compositions in the feed and permeate side after steady state being reached:

$$\alpha_{CO_2 / CH_3 COOH} = \frac{Y_{CO_2} / Y_{CH_3 COOH}}{X_{CO_2} / X_{CH_3 COOH}} \qquad (6)$$

# 4. Results and Discussion

The zeolite-filled PDMS membranes were prepared to maximum 50 wt% content, because it was not possible to prepare the membrane above 50 wt% content due to zeolite rich phase was formed. Membrane thickness is increased with increasing zeolite size and content, and it ranges from 150 to 400 $\mu m$. Surface and cross-sectional SEM photographs of the zeolite-filled PDMS membranes are represented in Figure 4. Figure 4 shows that zeolite particles are uniformly dispersed in the polymer phase.

## 4.1. $CO_2$ Permeability

The $CO_2$ permeability of zeolite-filled PDMS membrane with change of zeolite type and content is given in Figure 5 comparing with that of a pure PDMS membrane. Figure 5 shows that the $CO_2$ permeability of zeolite-filled membranes decreases with increasing zeolite content up to 30 wt% and then increases above this content. These trends are similar to the results of Ser and coworkers [16], which had been obtained using the zeolite-filled polyethersulfone (PES) membrane. Furthermore, it is worth noting that
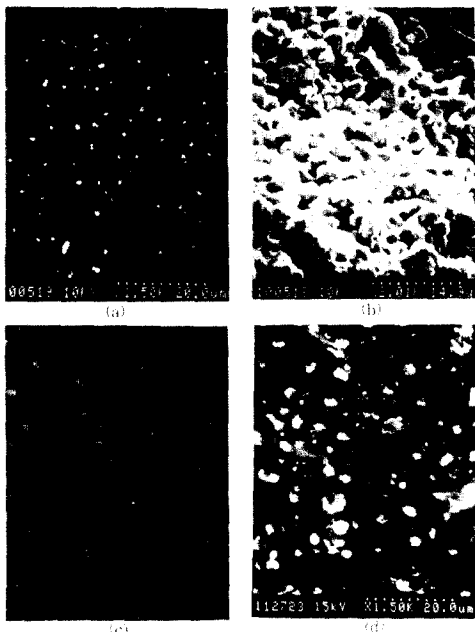
Fig. 4. SEM photographs of the various zeolite-filled PDMS membranes. (a) surface of 50 wt% zeolite 4A-filled membrane, (b) cross section of 50 wt% zeolite 4A-filled membrane, (c) surface of 50 wt% zeolite 13X-filled membrane and (d) cross section of 50 wt% zeolite 13X-filled membrane.
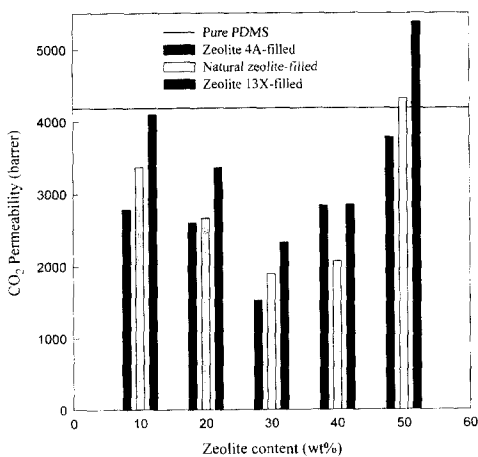


Fig. 5. $CO_2$ permeabilities of zeolite-filled PDMS membranes as a function of zeolite content.
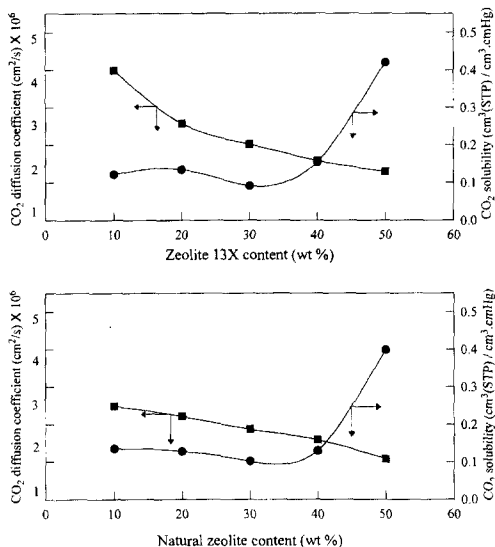
$CO_2$ permeability of the membrane containing



Fig. 6. Diffusion coefficient and solubility of $CO_2$ gas for zeolite 13X and natural zeolite-filled PDMS membrane as a function of zeolite content.

zeolite 13X is always higher than that of zeolite 4A and natural zeolite-filled membranes.

The diffusion coefficient, $D$, and solubility coefficient, $S$, of $CO_2$ gas in the zeolite 13X and natural zeolite-filled PDMS membranes with change of zeolite content are represented in Figure 6. These values are calculated using the data obtained by the time-lag method.

In Figure 6, the diffusion coefficient of $CO_2$ gas is gradually decreased with increasing zeolite content because $CO_2$ gas can be easily diffuse through PDMS matrix than zeolite pore. However the solubility of $CO_2$ gas is slowly decreased with increasing zeolite content up to 30 wt% and then rapidly increased above this content. It is clear that the increase of $CO_2$ permeability above 30 wt% contents mainly due to the increase of $CO_2$ solubility. The magnified cross-sectional SEM image of natural zeolite-filled membrane at 50 wt% content is shown in Figure 7. This image indicates a homogeneous distribution of zeolites in the PDMS matrix, and shows that the void spaces are created around zeolite particles. The void space may be believed to arise from
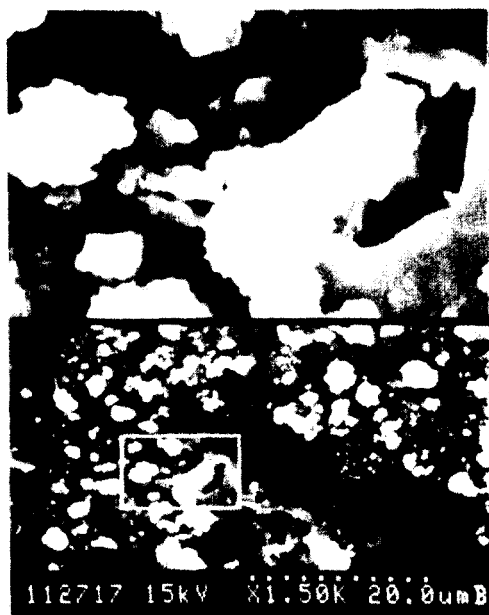
**Fig. 7.** SEM photographs of the surface for 50 wt% natural zeolite-filled PDMS membrane.



**Fig. 8.** $CO_2$ selectivities of zeolite-filled PDMS membranes as a function of zeolite content.

the partial incompatibility between PDMS chains and zeolite crystals, implying that the PDMS interacts weakly with the zeolite framework at high zeolite content. These void spaces, which are acting like a free volume, may be inducing the rapid increasing of $CO_2$ solubility above 30 wt% contents.

It is well known that the transport of gas molecules through a zeolite framework depends on the pore size of zeolite, and the affinity between gas molecule and zeolite [17]. Generally, zeolites have the open pores, which are composed of microcrystalline voids and channels, so a gas molecule whose kinetic diameter is smaller than zeolite pore is able to enter and diffuse through a zeolite framework. Also, a Si/Al ratio of zeolite, which determines the number of cation and the hydrophilicity of zeolite framework, dominates the affinity between gas molecule and zeolite. Zeolites with a low Si/Al ratio are hydrophilic and cause strong interaction with polar gas molecules such as water, $NH_3$, $CO_2$ etc. This means that polar gas molecules are more strongly adsorbed on zeolites with a low Si/Al ratio than non-polar
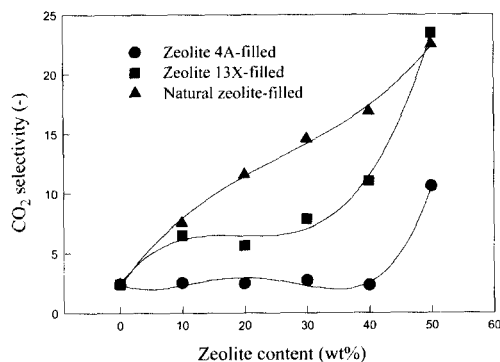
ones of comparable molecular weight, so the diffusion of polar gases through zeolites with a low Si/Al ratio is suppressed.

As shown in Table 1, the pore size of zeolite 4A and natural zeolite is similar to the kinetic diameter of $CO_2$ molecule (3.3Å), but the pore size of zeolite 13X is larger than that. Hence the convective transport of $CO_2$ molecule through the pore of zeolite 4A and natural zeolite may be hindered, so the $CO_2$ permeability of the membrane containing zeolite 13X is higher than that of the membrane containing zeolite 4A and natural zeolite. For zeolite 4A and natural zeolite, two zeolites have the similar pore size but natural zeolite has a higher Si/Al ratio. Hence the membrane containing natural zeolite has a higher $CO_2$ permeability compared with zeolite 4A-filled membrane. The $CO_2$ permeability of zeolite 4A-filled membrane is lowest than any other membrane because zeolite 4A has lowest pore size and strong interaction with $CO_2$ gas.

## 4.2. $CO_2$ Selectivity

The $CO_2$ selectivities ($\alpha_{CO_2/CH_3COOH}$) of various zeolite-filled PDMS membranes for $CO_2$ gas/acetic acid vapor mixture are represented in Figure 8 as a function of zeolite content.

The pure PDMS membrane shows a low $CO_2$ selectivity of 2.43. The acetic acid vapor has a larger molecule size than $CO_2$ gas, so its diffusive permeation through PDMS matrix is lower than

that of $CO_2$ gas. However the acetic acid vapor is very soluble in PDMS, because which is an organophilic polymer, so its sorptive permeation is higher than that of $CO_2$ gas. Above characteristics clearly indicate that the overall permeation rate of acetic acid vapor is comparable to that of $CO_2$ gas, resulting that the selectivity of pure PDMS membrane for $CO_2$ gas/acetic acid vapor mixture is low.

The $CO_2$ selectivity of zeolite 4A-filled membrane is similar to that of pure PDMS membrane up to 40 wt% content, but significantly increases to 10.6 at 50 wt% content. The small pore size of zeolite 4A hinders both $CO_2$ gas and acetic acid vapor transport through the pore of zeolite 4A, so the $CO_2$ selectivities of zeolite 4A-filled membrane up to 40 wt% content are low. The reason that a high $CO_2$ selectivity of 10.6 for the membrane containing 50 wt% zeolite 4A is thought to be due to higher diffusion selectivity of $CO_2$. For zeolite 13X-filled membrane, $CO_2$ selectivity increases with increasing zeolite content and significantly enhanced when zeolite content is above 30 wt%. The result for natural zeolite-filled membrane is similar to that of zeolite 13X-filled membrane and it is due to increasing $CO_2$ permeation compared with that of acetic acid vapor.

The effect of zeolite type on the improvement of $CO_2$ selectivity is found to be in the order of natural zeolite > zeolite 13X > zeolite 4A. The $CO_2$ selectivity of zeolite 4A-filled membrane is lower than any other membrane because of the smaller pore size of zeolite 4A. For zeolite 13X-filled membrane, $CO_2$ selectivity is higher than that of zeolite 4A-filled membrane. For the membrane containing natural zeolite, of which pore size is similar to zeolite 4A but has a higher Si/Al ratio than any other zeolite, its $CO_2$ selectivity is highest and is enhanced up to 9 times compared with the selectivity of a pure (unfilled) PDMS membrane. We conclude that the PDMS membranes containing zeolite 13X and natural zeolite are effective to remove a polar gas such as $CO_2$ from the mixture of polar gas/organic vapor. Also the above results indicate that both the molecular sieving effect (zeolite pore size) and the interaction between gas molecules and zeolite framework (hydropilicity of zeolite) play a major role to the permselectivity of a PDMS membrane containing zeolite particles.

## 5. Conclusions

The heterogeneous membranes were prepared by introducing various zeolite particles (zeolite 4A, 13X and natural zeolite) into a thin PDMS film. The $CO_2$ permeability of zeolite-filled PDMS membranes was decreased with increasing zeolite content and then recovered above 30 wt% content. The effect of zeolite type on the improvement of $CO_2$ permeability was found to be in the order zeolite 13X > natural zeolite > zeolite 4A. The separation properties of zeolite-filled PDMS membrane for a mixture of $CO_2$ gas/acetic acid vapor were significantly enhanced up to 9 times compared with the pure PDMS membrane. The effect of zeolite type on the improvement of $CO_2$ selectivity was found to be in the order of natural zeolite > zeolite 13X > zeolite 4A. The PDMS membranes containing zeolite 13X and natural zeolite are effective to remove a polar gas such as $CO_2$ from the mixture of polar gas/organic vapor. Both the pore size and Si/Al ratio of zeolite may be control to the permselectivity of a PDMS membrane containing zeolite particles.

## References

1. T. M. Gr, *J. Memb. Sci.*, **93**, 283 (1994).
2. D. R. Paul, and D. R. Kemp, *J. Polym. Sci. Symp.*, **41**, 79 (1973).
3. M. Goldman, Fraenkel, D. and G. Levin, *J. Appl. Polym. Sci.*, **37**, 1791 (1989).
4. W. Ji, S. K. Sikdar, and S. T. Hwang, *J. Memb. Sci.*, **103**, 243 (1995).
5. M. Jia, K.-V. Peinemann, and R.-D. Behling, *J. Memb. Sci.*, **57**, 289 (1991).
6. J.-M. Duval, B. Folkers, M. H. V. Mulder, G. Desgrandchamps, and C. A. Smolders, *J. Memb. Sci.*, **80**, 189 (1993).

7. J.-M. Duval, B. Folkers, M. H. V. Mulder, G. Desgrandchamps, and C. A. Smolders, *Sep. Sci. & Technol.*, **29**(3), 357 (1994).

8. Te H. J. C. Hennepe, C. A. Smolders, D. Bargeman, and M. H. V. Mulder, *Sep. Sci. & Technol.*, **26**(4), 585 (1991).

9. Te Hennepe H. J. C., W. B. F. Boswerger, D. Bargeman, M. H. V. Mulder, and C. A. Smolders, *J. Memb. Sci.*, **89**, 185 (1994).

10. R. E. Kesting, and A. K. Fritzsche, Polymic Gas Separation Membranes, John Wiley & Sons, New York (1993).

11. D. R. Paul, and Y. P. Yampol'skii, Polymeric Gas Separation Membranes, CRC Press, Boca Raton (1994).

12. R. R. Zolandz, and G. K. Fleming, in Membrane Handbook, W. S. W. Ho, and K. K. Sirkar, Eds., Van Nostrand Reinhold Publishing, New York (1992).

13. ASTM, D1434-82(1991).

14. M. Mulder, Basic Principles of Membrane Technology, 2$^{nd}$ Ed., Kluwer Academic Publishers, Dordrecht (1996).

15. J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford (1975).

16. M. G. Ser, N. Bac, and L. Yilmaz, *J. Memb. Sci.*, **91**, 77 (1994).

17. D. W. Breck, Zeolites Molecular Sieves, John Wiley & Sons, New York (1974).