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단 신

고분자 분리막을 이용하여 SF_6/N_2 혼합 기체에서 SF_6 분리

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Separation of SF_6 from SF_6/N_2 Mixtures Using Polymeric Membranes

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요　약: 육불화황(SF_6)은 매우 큰 지구 온난화 효과를 가진다. 따라서, SF_6의 사용을 줄이고 이것을 대기 중으로 방출하는 것을 억제하기 위한 노력이 있어 왔다. 전기 기구에서 SF_6의 사용량을 줄이는 한 가지 방법은 SF_6/N_2 혼합 기체를 사용하는 것이다. 혼합 기체에서 SF_6의 농도는 10~60%까지 변화가 가능하다. 그러나, 기구를 분해하거나 수리할 경우에 혼합 기체에서 SF_6를 회수하여야 한다. SF_6의 끓는점이 -60°C 정도로 매우 낮으므로 액화법은 적용하기가 어렵다. 한 가지 가능한 대안은 분리막을 사용하는 것이다. 본 연구에서는 5가지 고분자에 대해서 육불화황과 질소의 투과 성질에 대해서 조사하였다. 예를 들면 25°C에서 이축연신 폴리프로필렌(BOPP)에 대한 질소의 투과도는 0.19 barrer인 반면에 육불화황의 투과도는 0.0012 barrer로써 선택도는 158이었다. SF_6/N_2 혼합기체에 대한 upper bound가 처음으로 제안되었는데 n = -1.33 and k = 160 (barrer)이었다.

Abstract: SF_6 has an extremely high global worming potential (GWP). Therefore, there has been an effort to reduce the use of SF_6 and its emission into atmosphere. One possible solution for minimizing the use of SF_6 in electrical equipments is utilization of gas mixtures such as SF_6/N_2. The SF_6 concentration in the gas mixture varies from 10 to 60%. However, when the apparatus is repaired or dismantled, we have to recover SF_6 from the gas mixture. Since the boiling point of SF_6 is low (~-60°C), the liquefaction method is difficult to apply. One possible alternative is the membrane separation technology. In this study, we investigated the SF_6 and N_2 permeation properties of 5 polymeric membranes. For example, permeability of N_2 in BOPP membrane at 25°C was 0.19 barrer, whereas that of SF_6 was only 0.0012 barrer, resulting in the selectivity of 158. An upper bound for SF_6/N_2 gas pair was suggested for the first time with n = -1.33 and k = 160 (barrer).

Keywords: *polymer membrane, global warming potential, upper bound,* SF_6/N_2

1. Intoroduction

Due to its very good insulation (dielectric constant of SF_6 is 1.0021 at 20°C, 1.0133 bar, 23.340 MHz) and cut-off properties, pure SF_6 gas has been widely used as an insulation or arc quenching medium in electrical power apparatus working under high voltages. For example, in the electric power industries, pure SF_6 gas is used in gas insulated switchgears (GIS), gas insulated lines (GIL), and gas circuit breakers (GCB). However, SF_6 has an extremely high global worming potential (GWP). When we set GWP of CO_2 as 1, that of SF_6 is 23,900 [1]. Therefore, there has been an effort to reduce the use of SF_6 and its emission into atmosphere. One possible solution for minimizing the

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use of SF_6 in electrical equipments is utilization of gas mixtures such as SF_6/N_2 [2]. The SF_6 concentration in the gas mixture varies from 10 to 60%. However, when the apparatus is repaired or dismantled, we have to recover SF_6 from the gas mixture. Since the boiling point of SF_6 is low (~-60°C), the liquefaction method is difficult to apply [3,4]. One possible alternative is the membrane separation technology [5-7]. There have been little reports on the separation of SF_6/N_2 mixture using polymeric membranes. Yamamoto et al. used polyimide hollow fiber membranes to separate SF_6 from SF_6/N_2 mixtures [8,9], whereas Pittroff and Vondenhof utilized polycarbonate hollow fiber membranes for the separation [10]. Lee et al. also studied the separation chracteristics of SF_6/N_2 mixtures using polysulfone, tetra-bromo polycarbonate, and polyimide hollow fiber membranes [11]. However, all of them used hollow fiber membranes and the upper bound of this gas pair has never been reported.

In this study, we investigated the SF_6 and N_2 permeation properties of 5 polymeric membranes and proposed the trade-off curve for SF_6/N_2 gas mixture for the first time.

2. Theory

For a given pair of gases, the parameters characterizing membrane separation performance are the permeability coefficient, P_A, and the permeation selectivity, $\alpha_{A/B}$. The permeability coefficient is the product of solubility coefficient and diffusivity. The permeation selectivity is the ratio between composition ratio at the permeate side and composition ratio at the feed side. In addition, the permeation selectivity is a product of solubility selectivity and diffusivity selectivity. For the effective and efficient separations, both high permeability and selectivity are desirable since higher permeability decreases the size of the membrane area required to treat agiven amount of gas and higher selectivity results in a higher purity in the product gas.

However, it has been known that there is a reverse relation between permeability and selectivity and so called "upper bound" exists for each gas pair. According to Robeson [12], the upper bound performance characteristics can be described by an empirical equation; $P_A = k\alpha^n$, where n is the slope of the log P_A versus log $\alpha_{A/B}$ plot and n < 0. In other words, as the selectivity of the polymer for gas A over gas B, $\alpha_{A/B}$, increases, permeability of an upper bound polymer to gas A, P_A, decreases. Freeman showed that the empirical upper bound relationship can be theoretically predicted [13]. For example, the value of 1/n can be predicted from activation energy theory as follows

$$1/n = 1 - (d_B/d_A)^2 \quad (1)$$

where d_B and d_A are molecular diameters of B (less permeable) and A (more permeable) gas molecules, respectively.

3. Experimental

Biaxially oriented polypropylene (BOPP) and linear low density polyethylene (LDPE) are obtained from Samyoung Chemiclas (Korea), while nitrile rubber, natural rubber, and chloroprene are obtained from Alliance Rubber Products (Malaysia). Mixture of SF_6/N_2 (50 : 50) (Special Gas Co., 99.9%) was used as a permeation gas.

Mixed gas permeability coefficients were measured using a GTR-W30 gas permeation apparatus equipped with a gas chromatography (Yanaco, Japan). The description about the apparatus is shown in detail elsewhere [14]. The effective area of membranes was 28 cm^2. The measuring temperature range was 35~45°C and the feed pressure was 4 bar. The composition of SF_6 and N_2 was 50 : 50. SF_6 and N_2 concentrations were detected using a thermal conductivity detector. Preliminary experimental results indicated that the permeation coefficients of gases from single and mixture experiments are the same. By measuring the permeate gas concentration, the selec-

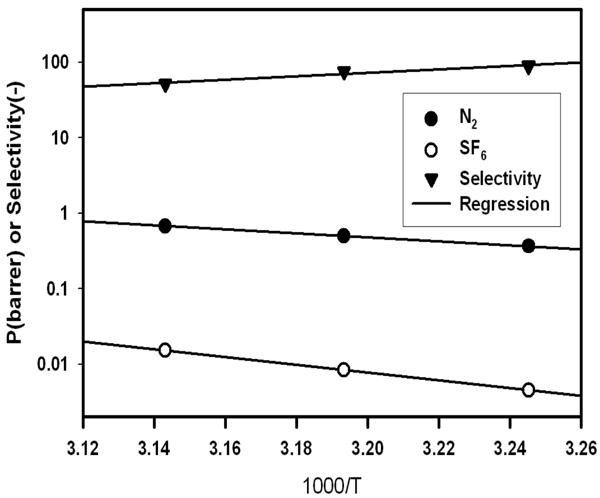

Fig. 1. Temperature dependence of gas permeabilities and selectivity of BOPP film.

Table 1. SF_6 Permeability, N_2 Permeability and Permeation Selectivity of Polymeric Membranes at 25°C. Data were Extrapolated from Permeation Experimental Results at 35～45°C using a SF_6/N_2 (1/1) Mixture. 1 Barrer = 1 × 10^{-10} cm^3(STP)-cm/cm^2-s-cmHg

	P (N_2) (Barrer)	P (SF_6) (Barrer)	α (N_2/SF_6)	Activation energy (kJ/mol)	
				N_2	SF_6
BOPP	0.19	0.0012	158.3	50.1	90.2
Nitrile rubber	0.68	0.012	56.7	47.5	64.8
Chloroprene	1.44	0.14	10.3	45.5	58.7
LDPE	1.31	0.14	9.4	41.8	58.2
Natural rubber	13.8	4.2	3.3	34.1	40.0

tivity was calculated as a ratio of SF_6 mole fraction to N_2 mole fraction of a permeate gas.

4. Results and Discussion

The performance test was done for SF_6/N_2 separation using 5 polymeric membranes, which presents the greatest challenge for membrane systems due to the green house effect of SF_6. The temperature dependence of gas permeabilities and selectivity of the biaxially oriented polypropylene (BOPP) membrane is shown in

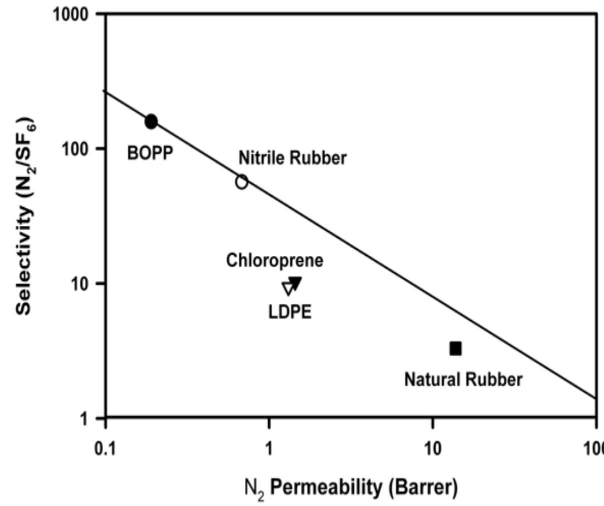

Fig. 2. The relationship between the N_2 permeability and the N_2/SF_6 selectivity for polymer films. The solid line is an suggested upper bound relation. Numerical values are provided in the Table 1.

Fig. 1. Since gas permeabilities follow the Arrehnius behavior very well, i.e., plot of log*P* vs. 1/T is linear, the gas permeabilities at 25°C and activation energies are calculated from the plot and reported in Table 1.

Permeability of N_2 in BOPP membrane at 25°C is 0.19 barrer, whereas that of SF_6 is only 0.0012 barrer, resulting in the selectivity of 158. Permeabilities of N_2 and SF_6 in nitrile rubber membrane at 25°C are 0.68 and 0.012 barrers, respectively, while the selectivity is 57. Selectivities of other membranes are about or less than 10. For all membranes, activation energy of less permeable SF_6 is higher than that of more permeable N_2. For both gases, as the permeability increases, the activation energy decreases. These results agree well with previous experimental data using other gas pairs [15]. Permeabilities and selectivities of 5 polymeric membranes are plotted in Fig. 2. The solid line in the figure is suggested trade off curve for the SF_6/N_2 gas pair using an empirical equation: $P_A = k\alpha^n$. The experimentalresults indicate that BOPP and nitrile rubber show interesting permeation behaviors for SF_6/N_2 separation. The slope of the solid line was estimated from the Eq. (1). To estimate the slope n, kinetic diameter values of 4.9 Å and 3.7 Å were used

Table 2. Values of upper Bound Slope n and the Front Factor k[12].

Gas pair	n	k (Barrer)
O_2/N_2	-5.666	1,396,000
N_2/CH_4	-4.507	2,570
CO_2/N_2	-2.888	30,967,000
CO_2/CH_4	-2.636	5,369,140
H_2/CO_2	-2.302	4,515
H_2/N2	-1.484	97,650
N_2/SF_6	-1.33	160
H_2/CH_4	-1.107	19,890

for SF_6 and N_2, respectively [16]. The n value was determined as -1.33. In Table 2, n and k values of several gas pairs are presented [12]. n value for the SF_6/N_2 gas pair is similar to the value for the H_2/CH_4. In the literature, the kinetic diameter for SF_6 was reported as high as 5.4 Å [17]. If we use this value, the n value can be -0.88. The front factor k value of 160 (barrer) was used to draw the upper bound. To get better trade off relationship between permeability of N_2 and selectivity for SF_6/N_2 gas pairs, more permeation experiments are needed.

5. Conclusions

In this study, we investigated the SF_6 and N_2 permeation properties of 5 polymeric membranes. Permeability of N_2 in BOPP membrane at 25°C was 0.19 barrer, whereas that of SF_6 was only 0.0012 barrer, resulting in the selectivity of 158. An upper bound for SF_6/N_2 gas pair was suggested for the first time with n = -1.33 and k = 160 barrer. To get better relationship between permeability of N_2 and selectivity for SF_6/N_2 gas pairs, more permeation experiments are needed.

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