The Permeability Characteristics of Non-Porous Membrane by C₇H₅F₃/SiH₄ Plasma Polymeric Membrane

The Permeability Characteristics of Non-Porous Membrane by $C_7H_5F_3/SiH_4$ Plasma Polymeric Membrane

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Abstract—Low temperature rf-plasma was used to test the changes in the chemical and physical properties of a plasma-treated polymeric membrane made from $C_7H_5F_3$ and SiH_4, two materials that are very thermally, chemically, and mechanically stable. $C_7H_5F_3$ and SiH_4 plasma polymers were efficiently deposited to an aluminum oxide substrate with a pore size of 0.02 µm. Even though the amount of the monomer $C_7H_5F_3$ increased, there was no significant change in the permeability of oxygen. However, selectivity of oxygen over nitrogen increased noticeably. Also, when the plate distance of the supporter from the cathode head within the reactor was 4 cm, the concentration gradients of $C_7H_5F_3$ and SiH_4 were the greatest. This resulted in the maximum value of permeability and selectivity and allowed the creation of a plasma-treated polymeric membrane with such characteristics when the composite permeation coefficient ranged from 4,500-7,500 GJ·s/kg.

Key words: Plasma Polymerization, $C_7H_5F_3$ and SiH_4, Permeability, Selectivity

INTRODUCTION

Gas separation using membranes requires a relatively small amount of energy with equipment that is rather simple and easy to operate. The fact that the equipment does not cause phase transition allows it to be used to separate thermally sensitive materials [Spillman, 1989]. Currently, research and implementation of this process is often used in waste treatment apparatus such as fermentation baths and also at landfills to separate CO_2/CH_4 from bio gas. H_2O/Air and O_2/N_2 are also separated to remove moisture from the air. There is great interest in the potential economical value of the process of separating oxygen and nitrogen being used not only in internal-combustion engines and incinerating systems, but also for medical and military purposes. O_2/N_2 separation involves transmitting air through a membrane to raise the purity of oxygen and could eventually allow for complete combustion and greater combustion efficiency in heating boilers and incinerators. It could also help to reduce incomplete combustion materials such as carbon monoxide from exhaust fumes. Oxygen condensed in this manner could also be used in medicine, fermentation, and fish farming. The creation of highly efficient membranes at normal temperatures and pressures could help us in various fields such as the environment, medicine, and national defense. For example, advances in medical equipment and in military gas masks could come out of gas membrane technology [Winston ho and Sirker, 1992].

The efficiency of a separation membrane relies upon the membrane's permeability and selectivity. However, permeability and selectivity counteract each other. If the permeability is increased by using a membrane with large pores, the selectivity will be decreased. On the other hand, if a membrane having small pores is used, the selectivity and the permeability will tend to reverse. As

a result, current research focuses on maximizing one of the two characteristics without greatly reducing the other [Mohr et al., 1991]. A composite membrane created by plasma polymerization is able to have a high selectivity towards small molecules thanks to the molecular sieve by the polymer's thin film. There still is, of course, a small loss in the selectivity of the membrane that results from the higher permeability. However, since the selectivity is inversely proportional to the thickness of the thin membrane, the decrease in selectivity can be minimized by making the membrane as thin as possible [Walker et al., 1997].

Recent methods for manufacturing of gas separation membranes by means of plasma polymerization often use silicon compounds because of their good selective qualities and fluorine compounds. This is mainly because they have been found to have a high selectivity of the gases to be separated. Research is being conducted to improve selective qualities by using fluorine compounds as monomers that are deposited to porous, inorganic materials such as silica or alumina, which are strong and have high resistance to chemicals. Thus, porous inorganic membranes have high permeability and low selectivity, but their selectivity can be improved by coating them with a fluorinated layer using plasma polymerization [Lin et al., 1994].

In the research conducted, $C_7H_5F_3$ was used because of its thermal and chemical stability during plasma polymerization. This allowed maximum implementation of the merits of the process. Also used in this research was SiH_4, which is known to have good permeability of permeated gases. A nonporous polymeric membrane was created by using rf-plasma on the chemically resistant substrate Al_2O_3. The relationship between the gas's rate of permeability and its selectivity was examined in order to identify the effects that varying the plasma polymerization time, the rf-power, the dilution ratio of the monomer, and the position of the plate had on the membrane's permeability and on the membrane's ability to separate O_2/N_2 gas.

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EXPERIMENT

The rf-plasma reactor used in this experiment had a frequency of 13.56 MHz, and a maximum electrical output of 600 W. The reactor was a stainless steel one of the bell-jar type and it used a rotary pump to create a pressure of up to 10 mTorr. Its diameter was 29 cm and it stood 24 cm high. It was designed to keep the levels of reflective waves to under 5%, thus preventing reproducibility problems. A convectron vacuum gauge was used to measure the pressure inside the plasma reactor and the gas flow was adjusted by using a mass flow controller (MFC, Hitachi Co.).

The substrate used in the plasma polymerization was the widely used aluminum oxide membrane filter (0.02 μm, 47 mm, Whatman Co.). The experiment was divided into two parts: The first part involved plasma polymerization and the second dealt with gas permeation. In the plasma polymerization experiment, the pressure of the reactor was lowered to 30 mTorr by using a rotary pump, and then the remaining gases and moisture were removed by using argon gas for about 5 min. Then, the monomer $C_7H_5F_3$ (benzotrifluorid, Fluka Co., 99%) was injected through a ring near the plate, SiH_4 was injected from head, and plasma was generated in the reactor at a pressure of 90 mTorr. Polymerization time, rf-power, etc. were left as variables as $C_7H_5F_3$ and SiH_4 plasma-treated polymeric membranes were created.

To examine the functional group in the membrane, a KBr disc was created and treated by using the plasma polymers, and then it was analyzed by FT-IR (Shimadzu, 8501). Also, to examine the morphology of the polymeric surface according to different process variables of the plasma, SEM was used.

Gas was passed through a permeant section that maintained normal pressure. The variable volume method, which involves measuring the permeated gas by means of a flow meter that was set up on the permeant section, was used to measure the results. The permeated gases, pure oxygen and nitrogen, were sent from the gas cylinder by using a pressure controller. The pressure was then fixed to a constant value by using a pressure gauge. Gas that entered from high-pressure regions passed through the membrane of the permeant cell and came out though the permeant section, which maintained normal pressure. Fig. 1 shows, for this experiment, the apparatus of the bubble flow meter used for measuring the amount of permeated gas.

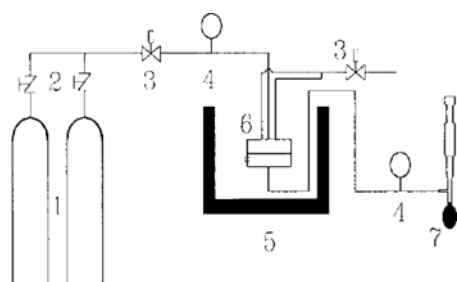A water bath was used to maintain a constant temperature with-

in the cell, and permeability was calculated according to the following formula.

$$P/l = \frac{1}{p_2 - p_1} \times \left[\frac{q/t}{A}\right]$$

where, P/l is the gas permeability [cm^3(STP)/cm^{2}s cmHg], q/t is the flow rate of the permeated gas [cm^3(STP)/s], l is the membrane thickness [cm], p_1 and p_2 are the pressures [cmHg] applied to the upstream and downstream part of the permeant cell, respectively, and A is the actual permeant surface area [cm^2] which is represented by the effective membrane area. Selectivity was calculated by using the ideal separation factor (P_{O_2}/P_{N_2}), which is a ratio of the permeability coefficients of the two gases. The permeant experiment was conducted at room temperature 25 °C by using a water bath, and measurement of the permeated gases was done after a sufficient amount of time had passed in order to get more accurate results. The permeant cell consisted of an inlet plate and an outlet plate, and a porous supporter was installed to prevent damage to the lower portion of the cell.

RESULTS AND DISCUSSION

Fig. 2 shows the FT-IR transmittance of the $C_7H_5F_3$ and SiH_4 plasma-treated polymeric membrane when the polymerization time was 60 min, the rf-power 120 W, the flow rate of $C_7H_5F_3$ was 12 sccm, and the flow rate of SiH_4 was 4 sccm. As shown in the results, the CF_x band reaches its peak at the 1,100 cm^{-1} interval. Generally, band broadening of plasma-treated polymers at the 950-1,250 cm^{-1} caused by fluorine monomers usually means that cross-linking has occurred in the CF_x band. The increase of cross-linking level results from the greater amount of fluorine in the fluorine compound. Therefore, high levels of cross-linking were confirmed in the created $C_7H_5F_3$ and SiH_4 plasma polymeric membrane. In addtion, OH bonding is shown in the 3,200-3,400 cm^{-1} band interval. This was caused by oxygen molecules in the atmosphere bonding with the free radical, activated species formed by the high activation energy released when the monomer
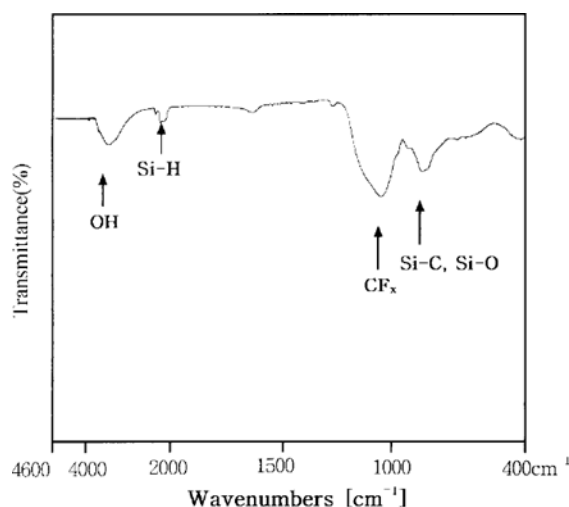

Fig. 1. Schematic diagram for experiment of gas permeation.

1. Gas cylinder	5. Water bath
2. Pressure regulator	6. Permeation cell
3. Micro valve	7. Bubble flow meter
4. Pressure gauge	

Fig. 2. Typical FT-IR spectra of plasma polymerized $C_7H_5F_3$ & SiH_4 on KBr (60 min, 120 W, $C_7H_5F_3$=12 sccm, SiH_4=4 sccm).
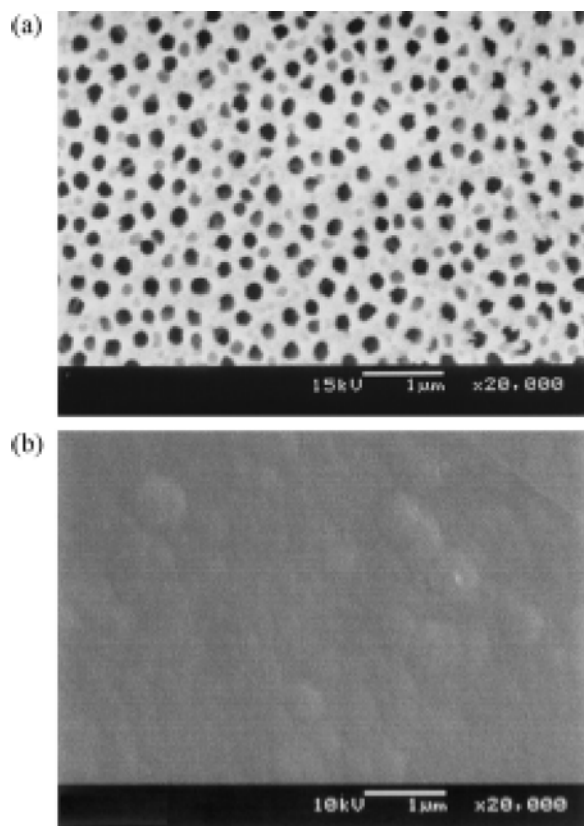
Fig. 3. SEM pictures of the plasma polymer of $C_7H_5F_3$ & SiH$_4$ deposited on porous aluminum oxide membranes.
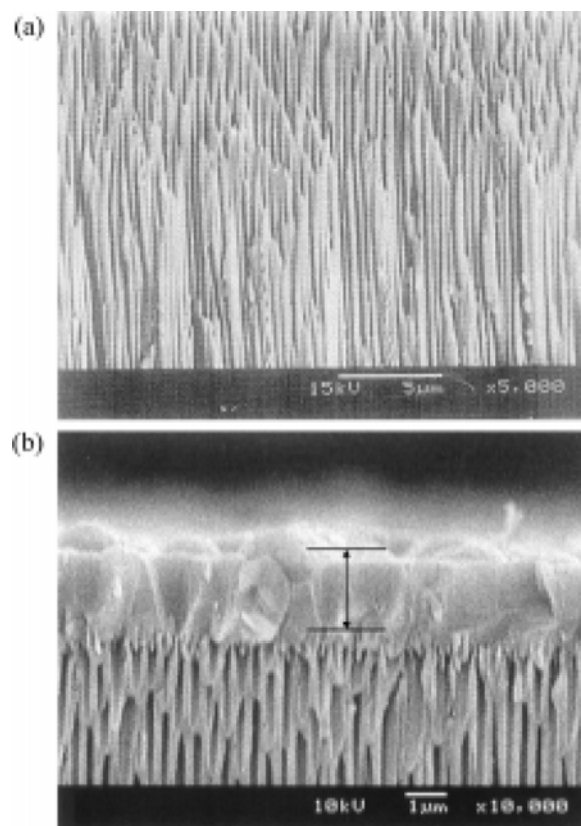(a) aluminum oxide surface, (b) plasma polymerized surface

Fig. 4. SEM pictures of the plasma polymer of $C_7H_5F_3$ & SiH$_4$ deposited on porous aluminum oxide membranes.
(a) aluminum oxide cross-section, (b) plasma polymerized cross-section

$C_7H_5F_3$ was treated by using plasma, after the reaction had been completed.

Cross-linking as a result of the plasma treatment of SiH$_4$ could be confirmed by using the Si-C and Si-O bands in the 840-870 cm^{-1} interval and Si-H bonding at 2,120 cm^{-1} as evidence. In conclusion, bonding between deposited fluorine and Si in the $C_7H_5F_3$ and SiH$_4$ plasma polymeric membrane was confirmed.

Figs. 3 and 4 show the SEM results of the surface and cross-sectioned inner structure of a $C_7H_5F_3$ and SiH$_4$ plasma polymeric membrane (polymerization time 60 min, rf-power 120 W, flow rate of $C_7H_5F_3$ 12 sccm, flow rate of SiH$_4$ 4 sccm) placed on an aluminum oxide substrate with a pore size of 0.02 μm. As shown in Fig. 3(a), the aluminum oxide used as the substrate had uniform pores. Fig. 3(b) shows that the surface of the membrane was effectively deposited into a fine structure as a result of plasma polymerization, and that the pores of the aluminum oxide used as the supporter were completely clogged off. As in the research results of Huber and others [1997], the membrane surface deposited by plasma-treating $C_7H_5F_3$ and SiH$_4$ in this experiment also had hemispherical structures of various sizes. Also, from the SEM results shown in Fig. 4(a), it is obvious that the cross-section of aluminum oxide used in the experiment had well-organized, conical straight pores. SEM results, in Fig. 4(b), from a cross-section of the $C_7H_5F_3$ and SiH$_4$ plasma polymeric membrane show that the plasma polymers were uniformly deposited to the aluminum oxide's surface barrier in layers that were approximately 2-2.1 μm thickness.

The effect of plasma polymerization time on the permeability and selectivity of the membrane was examined with $C_7H_5F_3$ and SiH$_4$. Membranes were deposited by using different polymerization times ranging from 30-120 min. Fig. 5 shows the effects of
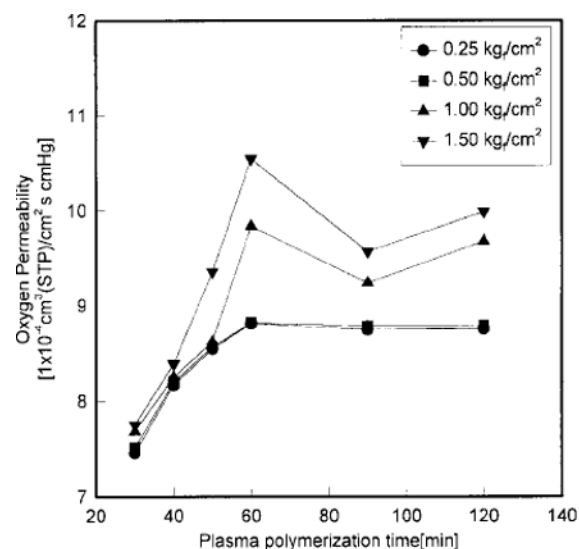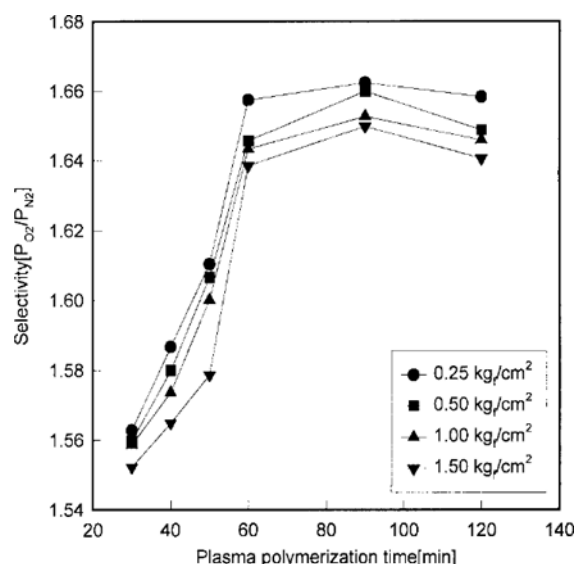

Fig. 5. Plasma polymerization time dependence of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH$_4$ (120 W, $C_7H_5F_3$=12 sccm, SiH$_4$=4 sccm).
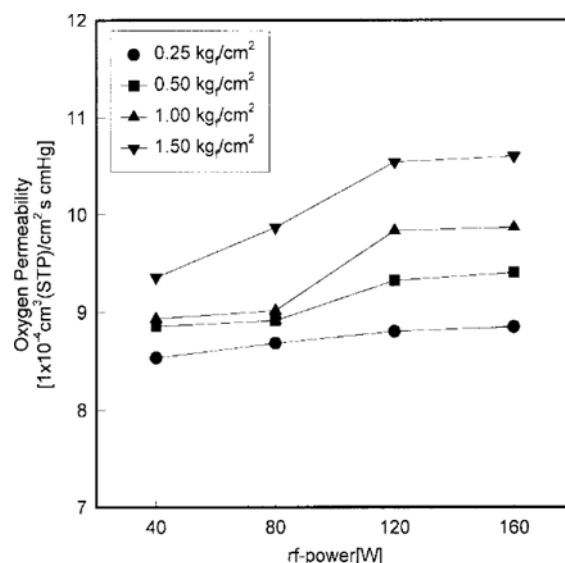
Fig. 6. Plasma polymerization time dependence of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (120 W, $C_7H_5F_3$=12 sccm, SiH_4=4 sccm).

Fig. 7. rf-power dependence of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, $C_7H_5F_3$=12 sccm, SiH_4=4 sccm).

Fig. 8. rf-power dependence of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, $C_7H_5F_3$=12 sccm, SiH_4=4 sccm).

polymerization time on the permeability of oxygen by $C_7H_5F_3$ and SiH_4 plasma polymeric membrane (rf-power 120 W, flow rate of $C_7H_5F_3$ 12 sccm, flow rate of SiH_4 4 sccm). In case of films prepared by plasma CVD, the membrane's permeability of oxygen generally increases with reaction time. However, the permeability was especially good at 60 min but it decreased at 90 min and increased at 120 min. The highest level of permeability occurred when the pressure of the permeated gas was 1.5 kg/cm².

Fig. 6 shows the selectivity of oxygen over nitrogen by a $C_7H_5F_3$ and SiH_4 plasma polymeric membrane having the same conditions as the membrane in Fig. 5. The selectivity rapidly increases for 60 min, but moderately increases from 60 min to 90 min. Until 60 min, the content of $C_7H_5F_3$ and SiH_4 increases because more of the activation species was generated in the plasma as the polymerization time increased. On the other hand, after 60 min passed, there was relatively little increase in the content of the monomers. In general, a variety of other reactions occur in plasma during plasma polymerization. In this experiment, the occurrence of sputtering and chemical etching resulted in removing and ablating polymeric material that was already attached to the thin membrane. After a certain point, the thin membrane's growth rate becomes as slow as the chemical etching rate rather than the macromolecule polymerization rate. Therefore, the membrane's permeability and selectivity towards oxygen for 60 min is dominated by chemical etching, not macromolecule polymerization.

Fig. 7 shows the $C_7H_5F_3$ and SiH_4 plasma polymeric membrane's (polymerization time 60 min, flow rate of $C_7H_5F_3$ 12 sccm, flow rate of SiH_4 4 sccm) permeability of oxygen at different levels of rf-power. The permeability level tended to increase as the rf-power increased, but there was no great change overall. Fig. 8 shows the selectivity of oxygen over nitrogen by a $C_7H_5F_3$ and SiH_4 plasma polymeric membrane having the same conditions as the membrane in Fig. 7. As shown in the diagram, permeability increased when rf-power increased. Generally, an increase in rf-power
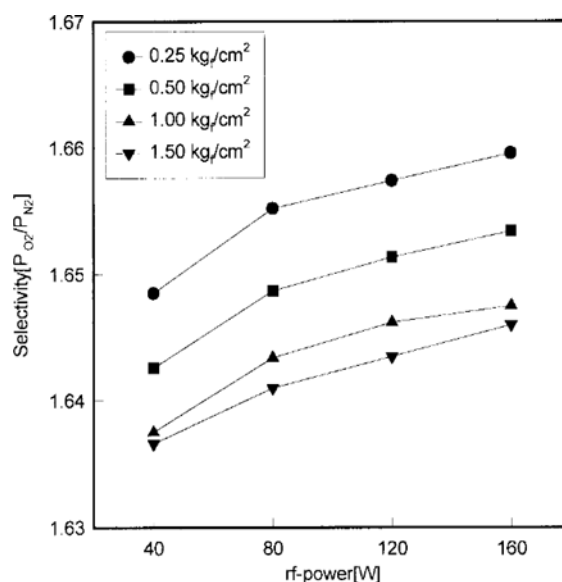
increases the electrical energy and the density inside the plasma. Monomers collide with high-energy particles such as electrons, ions, and photons inside the plasma and increase the energy-absorbing activation specimens. This results in a large increase in the amount of fluorine and silicon contained in the plasma polymers coated on the substrate. An increase in the fluorine content caused selectivity to increase, and an increase in the silicon content raised the permeability level towards oxygen. In this experiment, it was confirmed that permeability and selectivity increases with rf-power.

Figs. 9 and 10 show the $C_7H_5F_3$ and SiH_4 plasma polymeric membrane's (polymerization time 60 min, rf-power 120 W, flow rate of SiH_4 4 sccm) permeability of oxygen and its selectivity of
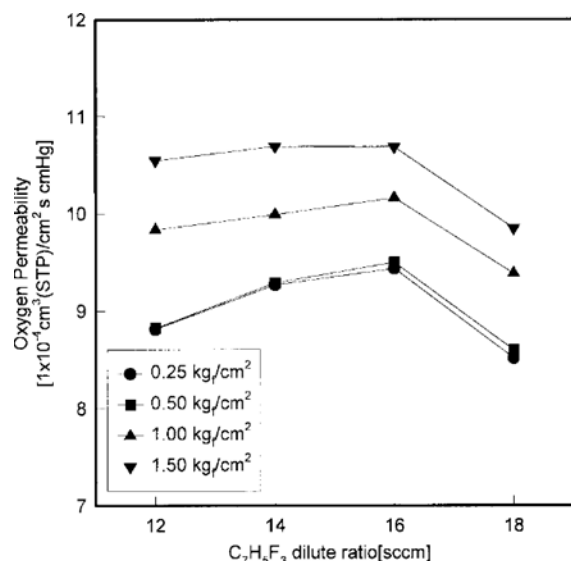
Fig. 9. $C_7H_5F_3$ dilute ratio dependence of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, 120 W, SiH_4=4 sccm).
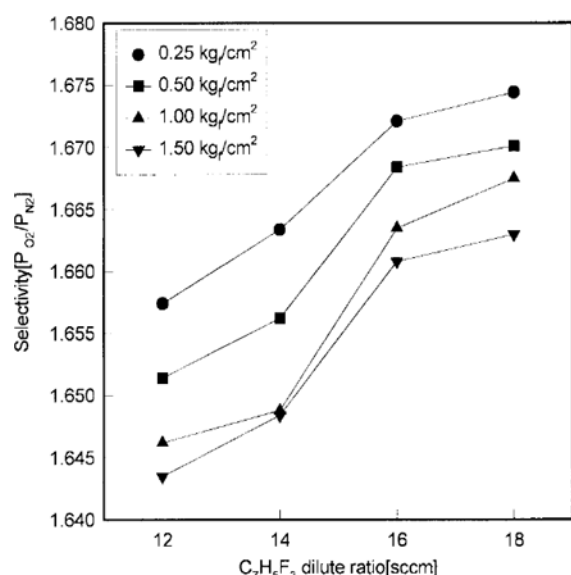

Fig. 10. $C_7H_5F_3$ dilute ratio dependence of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, 120 W, SiH_4=4 sccm).

oxygen over nitrogen when the flow rate of $C_7H_5F_3$ was ranging from 12 sccm to 18 sccm. As shown in Fig. 9, the permeability of oxygen don't almost changed in.

Generally, fluorine compounds had almost no effect on the membrane's permeability levels of the permeated gas. The decrease in permeability from 16 sccm to 18 sccm was affected by chemical etching more than it was by plasma treatment. The decrease in permeability is seen as being a result of changes in the deposited Si bonding within the plasma polymer. Fig. 10 shows that the selectivity increased as the flow rate of $C_7H_5F_3$ increased. The results were what they had been predicted to be. However, when the flow rate of $C_7H_5F_3$ is 16-18 sccm, the increase in the membrane's permeability of oxygen abates. Monomers in the plasma

state become excited because of the plasma. However, most of them fail to participate in the reaction and are simply released, since they are in the vacuum state. Therefore, there is a limit on the number of monomers that can participate in a reaction at any certain polymerization time and rf-power.

In the experiment conducted, an increase in selectivity was observed when the number of $C_7H_5F_3$ monomers was increased, and the plasma polymerization time and rf-power were set at certain values. However, it was also confirmed that the degree of increase grew smaller when the $C_7H_5F_3$ value passed 16 sccm.

Figs. 11 and 12 show the effect of varying the plate distance between the supporter and the cathode head within the reactor.
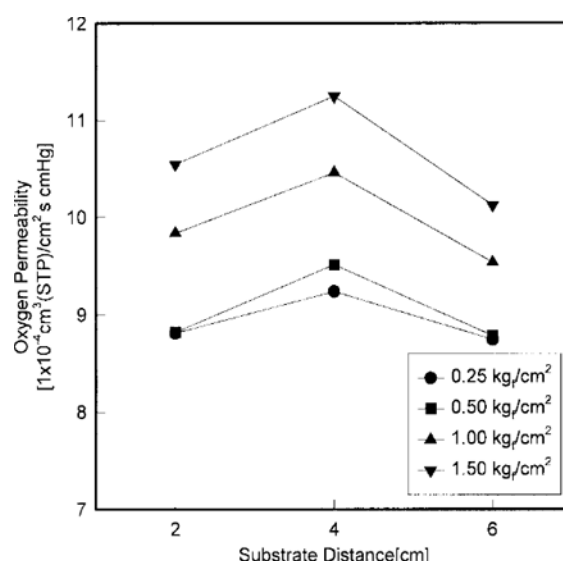

Fig. 11. Substrate distance of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, 120 W, $C_7H_5F_3$=12 sccm, SiH_4=4 sccm).
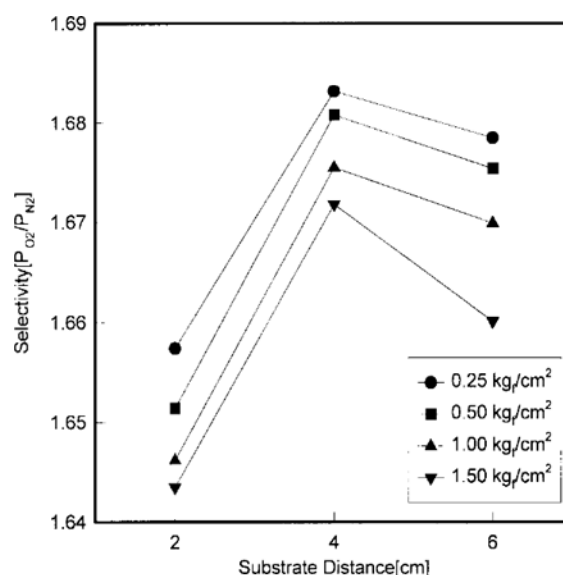

Fig. 12. Substrate distance of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4 (60 min, 120 W, $C_7H_5F_3$=12 sccm, SiH_4= 4 sccm).

The conditions of the $C_7H_5F_3$ and SiH_4 plasma polymeric membrane were as follows: polymerization time 60 min, rf-power 120 W, flow rate of $C_7H_5F_3$ 12 sccm, SiH_4 4 sccm. The experiment was conducted with plate distance ranging from 2 cm to 6 cm. Fig. 11 shows that the permeability was the greatest when the plate distance was 4 cm, and it also shows that the permeability was higher when the distance was 2 cm than 6 cm. This is seen as a result of the SiH_4 gradient being concentrated towards the head within the reactor, and the gradient being especially high at 4 cm. In Fig. 12, it is shown that the selectivity of oxygen was also the greatest when the distance was 4 cm, and that there was a slight decrease when the distance was 6 cm. It was confirmed that the concentration gradient of $C_7H_5F_3$ was the greatest in the plasma reactor when the distance from the head was 4 cm, and for distances greater than 4 cm, the concentration of F^- decreased.

In the experiment conducted, we found that the concentration gradients of $C_7H_5F_3$ and SiH_4 monomers were the greatest when the plate distance was 4 cm.

Fig. 13 shows permeability of oxygen in relation to activation energy. It shows the permeability of oxygen for different variables when the temperature was 20 °C, and the permeant pressure was 1 kg_f/cm^2 in relation to activation energy. Gas permeability can be represented by the following formula, and the formula can be used to calculated the activation energy of the permeability of oxygen.

$$Q=Q_0E^{-E_a/RT}$$

where, Q is the rate of gas permeation, E_a is the activation energy, R is the ideal gas constant, and T is the temperature. Fig. 13 shows that as the activation energy increased, the permeability generally increased. Fig. 14 shows the selectivity values against the activation energy. The selectivity increased up until the activation energy value reached approximately 4.0×10^{-2} J/mol, but after that it decreased. Generally, the permeability and selectivity were high when the activation energy was 3.2-4.0×10^{-2} J/mol.
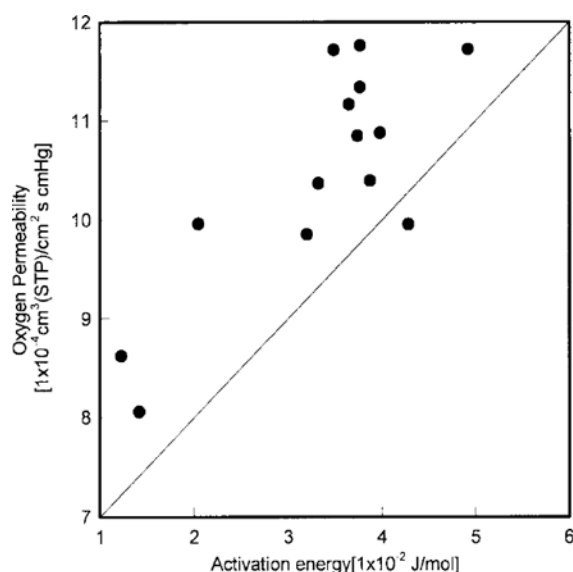
Fig. 13. Effect of activation energy of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4.
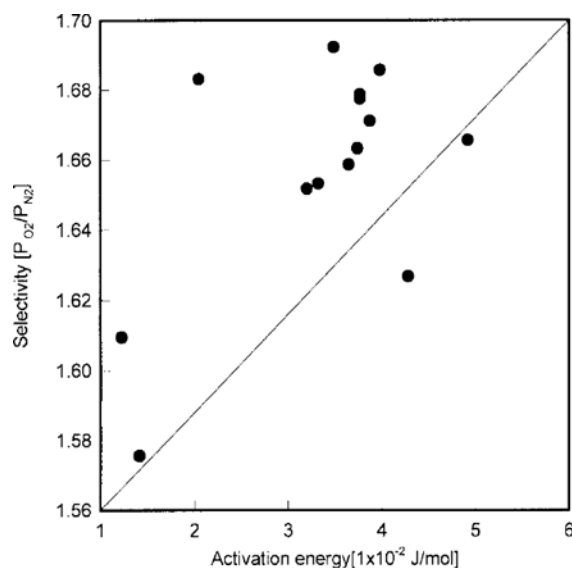
Fig. 14. Effect of activation energy of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH_4.

Diffusion of gas molecules through a nonporous membrane generally occurs because of consecutive jumps by the permeated molecules between the polymer molecules. Mutual interaction in the polymer chain is the dominant force behind these jumps. If the flux of energy is under a certain level, the distance between the polymer chains is not sufficient for jumping to occur. Therefore, resistance forms against the permeability of gases through the polymeric membrane and this results in a lower quantity of permeated gas.

In the experiment that was conducted, as the activation energy increased, the permeability and the selectivity generally had high values. It was confirmed that permeability and selectivity had especially high values when the activation energy was in the 3.2 -4.0×10^{-2} J/mol range.

Figs. 15 and 16 show the overall permeability of gas by the $C_7H_5F_3$ and SiH_4 plasma polymeric membrane in relation to (W/ FM)/t, the composite permeability coefficient representing the inflow of energy in the reactor per every unit of gas inflow. Here W, F, M, t are the rf-power, the flow rate of the monomers, the molecular weight of the monomers, and the polymerization time, respectively. In Figs. 15 and 16, permeability and selectivity do not increase simultaneously with the increase in (W/FM)/t. However, we can see that permeability and selectivity generally have high values when the value of (W/FM)/t was high. From this, it can be said that in the experiment most of the energy that flowed in was consumed in the plasma polymeric reaction of $C_7H_5F_3$ and SiH_4. Plasma polymers are created by a combination of things such as excite monomers, their participation in reactions, and various reactions such as etching. Therefore, plasma polymers rely on the degree to which those reactions occur. The composite permeability coefficient represents the overall flow of energy involved in all the reactions within the plasma. Low composite permeation coefficients result in plasma polymerization playing a dominant role, while high coefficients result in the etching process playing a dominant role.
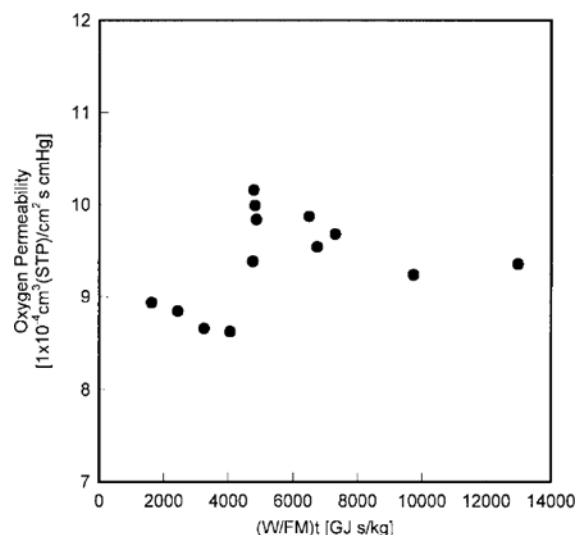
Fig. 15. Effect of (W/FM)t of gas permeation of oxygen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH$_4$.
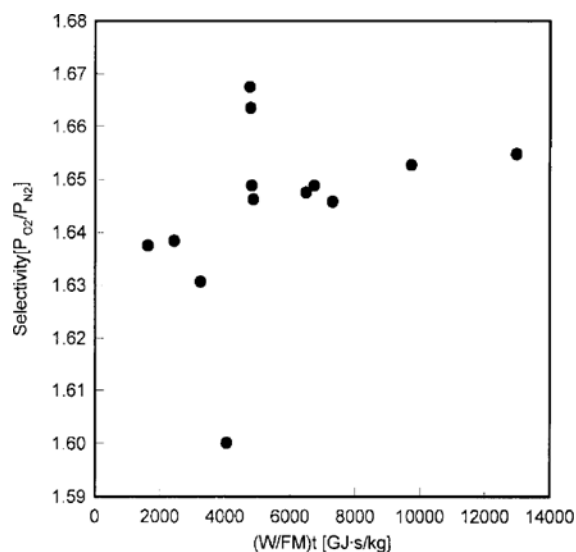

Fig. 16. Effect of (W/FM)t of selectivity of oxygen for a nitrogen on composite membrane by the plasma polymer of $C_7H_5F_3$ & SiH$_4$.

Therefore, in this experiment, $C_7H_5F_3$ and SiH$_4$ plasma polymeric membranes that had the highest levels of permeability and selectivity were created when (W/FM)/t was in the 4,500-7,500 GJ·s/kg range.

CONCLUSIONS

The following conclusions have been made from the conducted experiments involving the creation of a $C_7H_5F_3$ and SiH$_4$ plasma polymeric membrane with different process variables. Low temperature rf-plasma was used to create the membrane, and the physical and chemical properties of the membrane were examined.

1. The placing of a $C_7H_5F_3$ and SiH$_4$ plasma polymeric mem-

brane (polymerization time 60 min, rf-power 120 W, flow rate of $C_7H_5F_3$ 12 sccm, flow rate of SiH$_4$ 4 sccm) on an aluminum oxide substrate with a pore size of 0.02 μm resulted in the plasma polymers being uniformly deposited to the aluminum oxide's surface barrier in layers that were approximately 2-2.1 μm thick.

2. As the number of $C_7H_5F_3$ monomers used in the creation of the $C_7H_5F_3$ and SiH$_4$ plasma polymeric membrane was increased, there was no significant change in the permeability of oxygen, but there was an increase in the selectivity of oxygen over nitrogen.

3. The $C_7H_5F_3$ and SiH$_4$ monomers had the greatest concentrations when their distance in the plasma reactor from the cathode head was 4 cm. This is also when they had the highest values of permeability and selectivity.

4. $C_7H_5F_3$ and SiH$_4$ plasma polymeric membranes that had the highest levels of permeability and selectivity were created when (W/FM)/t, the composite permeability coefficient representing the inflow of energy in the reactor per every unit of gas inflow, was in the 4,500-7,500 GJ·s/kg range.

NOMENCLATURE

A : actual permeant surface area [cm^2]
E_a : the activation energy
F : gas flow rate [sccm]
l : membrane thickness [cm]
M : gas molecular weight [kg/kg mol]
p_1, p_2 : pressures [cmHg]
P/l : gas permeability [cm^3(STP)/cm^2·s·cmHg]
P_{O_2}/P_{N_2} : ideal separation factor
Q : rate of gas permeation
R : ideal gas constant
q/t : flow rate of the permeated gas [cm^3(STP)/s]
T : temperature
t : polymerization and treatment time [min]
W : rf-power [W]
(W/FM)t : the composite parameter [kJ·s/kg]

REFERENCES

Huber, F., Springer, J. and Muhler, M., "Studies on the Surface Free Energy and Surface Struture of PTFE Film Treated with Low Temperature Plasma," *J. Appl. Polym. Sci.*, **63**, 1517 (1997).

Lin, X., Chen, J. and Xu, J., "Improvement of Oxygen/Nitrogen Permselectivity of Poly[1-(Trimethylsilyl)-1-Propyne] Membrane by Plasma Polymerization," *J. Mem. Sci.*, **90**, 81 (1994).

Mohr, J. M., Paul, D. R., Mlsna, T. E. and Lagow, R. J., "Surface Fluorination of Composite Membranes. Part 1. Transport Properties," *J. Mem. Sci.*, **55**, 131 (1991).

Spillman, R. W., "Economics of Gas Separation Membrane," *Chem. Eng. Prog.*, **85**(1), 41 (1989).

Walker, M., Baumgartner, K. M., Ruckh, M., Kaiser, M., Schock, H. W. and Rauchle, E., "XPS and IR Analysis of Thin Barrier Films Polymerized from C_2H_4/CHF$_3$ ECR-Plasma," *J. Appl. Polym. Sci.*, **64**, 717(1997).

Winston ho, W. S. and Sirker, K., "Membrane Handbook," Van Nostrand Reinhold (1992).