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Gas Permeation of Pure CO_2 and N_2 through Plasma-Treated Polypropylene Membranes

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Abstract : The surface of polypropylene membrane was modified by plasma treatment using Ar, N_2, NH_3 and O_2. Permeabilities for CO_2, N_2 and separation factor for CO_2 relative to N_2 were measured. The permeation experiments were performed by a variable volume method at 25℃ and 0.303MPa. The effects of the plasma conditions such as treatment time, power input, gas flow rate and pressure in the reactor on the transport properties of modified membrane were investigated. The surface of the plasma treated membrane was analyzed by means of FTIR-ATR, XPS and AFM. The surface structure of the plasma treated membrane was fairly different from that of the untreated membrane. Although the permeation rates for both CO_2 and N_2 decreased with increasing plasma treatment time, the separation factor was found to be improved by the plasma treatment. The operating conditions of plasma treatment imposed on membranes had notable effect on the permeability and separation factor.

1. Introduction

The study on separation membranes can be divided into two areas : separation membrane manufacture and gas separation membrane process. The field of separation membrane manufacture was mainly performed for developing new separation membrane or studying separation membrane structure. In order to improve the efficiency of existing separation membranes, studies on a durability improvement of separation membrane and a prevention of dropping off in efficiency have been performed. Recently, surface modification of materials is a rapidly growing research field having applicability to many areas of materials science. Polypropylene is well-known for its excellent mechanical properties and chemical stability. The recent development of microporous polypropylene membrane has extended its applicability. Although these membranes have qualities that suit for use in a variety of filtration and separation process, the hydrophobic nature of polypropylene does not make the membranes have an enough permeability of gases. The study on improvement of the permeability and the selectivity through membrane surface modification, has performed with keeping mechanical properties and chemical stability [1,2]. Low temperature plasma processes have been more widely used as techniques of modifying surface layer, which results in a good separation efficiency [3,4]. The plasma process can be divided into a plasma polymerization and a plasma treatment. In the former, the organic vapor (monomer) is subjected to the electric discharge, and polymers are formed, whereas in the latter, gases that are introduced into the glow discharge are nonpolymerizable in nature. Compared with plasma polymerization, the plasma treatment process has advantages that the handling is simple and also that the monomer, which is usually expensive is not required. In spite of these advantages, the preparation of gas separation membrane by plasma treatment has hardly been reported except for several works [4]. Plasma treatment is a valuable means of modifying polymer surfaces without affecting the bulk properties of the polymer [1]. Ruoh-Chyu Ruaan reported oxygen/nitrogen separation by polybutadiene/polycarbonate composite membranes modified by ethylenediamine plasma [5]. Matsuyama et al. had studied the preparation of gas separation membranes by plasma treatment and the CO_2 permeation [6,7].

In this work, the surface of polypropylene membrane was modified by treatment using Ar, N_2, NH_3 and O_2 plasma. The effects of plasma conditions such as treatment time, power imput, gas flow rate and pressure in plasma reactor on the permeabilities for CO_2 and N_2 and separation factor for CO_2 to N_2 were investigated. The effect of the operating conditions of plasma treatment on the permeability and selectivity were discussed.

2. Experimental

2.1. Materials

Polypropylene (OPP, ρ=0.9, thickness=40 μm) was supplied from Hwa Seung Industry Co. The material was cleaned by supersonic washer for 1 min. Ar, N_2 and O_2 (99.999%) as a plasma gas were supplied from Dae Sung Co. and NH_3 (99.995%) was supplied from Seoul Special Gas Co.

2.2. Plasma Treatment

The plasma treatment was conducted using a plasma reactor, PLASMA SYSTEM440 (Tepla Co.). It consisted of reaction chamber made of Aluminium (35×35 cm) equipped with 2.45 GHz micro frequency generator. T2000 controller (Tepla Co.) was used to control the wave process. Microwave generator by Magretron had a maximum power of 600W and could maintain 0.05torr using 2-stage rotary pump. The inlet gas flow rate was controlled by MFC (5850 TR : Brooks Instrument Co.). Fig. 1 shows the apparatus and Table 1 lists experimental conditions of plasma treatment.

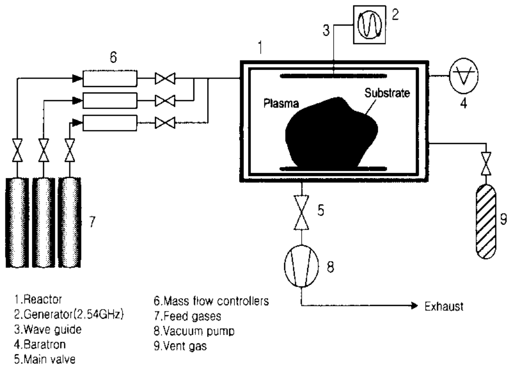


Fig. 1. Schematic diagram of plasma treatment system.

Table 1. Experimental Conditions of Plasma Treatment

Vaccum (torr)	Power (W)	Flow rate (ml/min)	Time (min)
0.05/40	40/80	20/40	2~10

2.3. Surface Analysis

FTIR-ATR (Bio-RAD FTS6000) was applied to observe chemical structure change of the surface after plasma treatment. XPS was used to analyze the chemical structure, atomic composition and chemical bond into the membrane surface. XPS spectra were measured with X-ray Photoelectron Spectroscopy (PHI5700) employing Al X-ray source, at take-off angle 45°. To observe the topography and roughness, Atomic Force Microscopy (TopoMetrix Co. : ACCUREX) was used.

2.4. Gas Permeation

The gas permeation experiments were performed by a variable volume method and Fig. 2 shows the schematic diagram of the apparatus [8]. The gas which was injected into a downstream side of permeation cell penetrated into the membrane through porous steel. The permeated gas flowed into a capillary tube connected to the upstream side to measure the volumetric flow rate, and into a GC (Shimadsu 14-B packing material : porapak Q) to

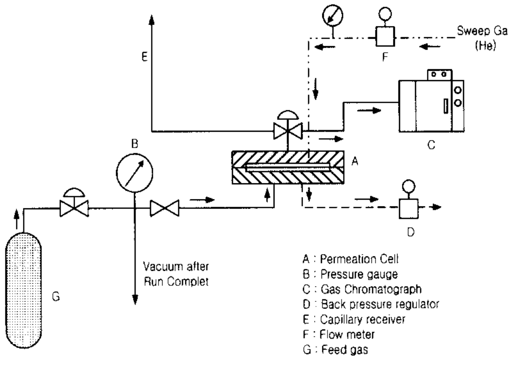


Fig. 2. Schematic diagram of gas permeation apparatus.

measure the composition of permeated gas. He was used as the carrier gas. The temperature of the column and the TCD was maintained at 70℃ and 75℃, respectively. The permeation area in this cell was 19.6 cm^{2}. The back pressure regulator was connected to keep a preassure [9]. The permeation experiment was performed at upstream preassure of 0.303 MPa and 25℃.

3. Result and Discussion

3.1. Confirmation of Surface Structure Changes

Analysis of ATR was calibrated in 4-5 hours after plasma treatment. Substrates were kept with silica gel in a vacuum desiccator before the analysis. In the case of plasma deposition or some of plasma treatment, we could assay the changes of hydroxyl, carboxyl, and amine groups with ATR [10,11], but we confirmed that there was little difference between the phase of spectrums before and after plasma treatment in this experiment. The peaks of Fig. 3 displayed that the 2900-3000 cm^{1} was C-H stretching, 1450-1370 cm^{1}was vibration of CH_3, 1250 cm^{1} was twist of CH_2, 1160 cm^{1} was C-C stretching and rocking of CH_3, and 996 cm^{1} and 840 cm^{1} were rocking of CH_3 and CH_2, espectively. The result was the almost same as the typical spectrum of polypropylene. It was believed that the plasma treatment did not affect the surface chemical structures of polypropylene.

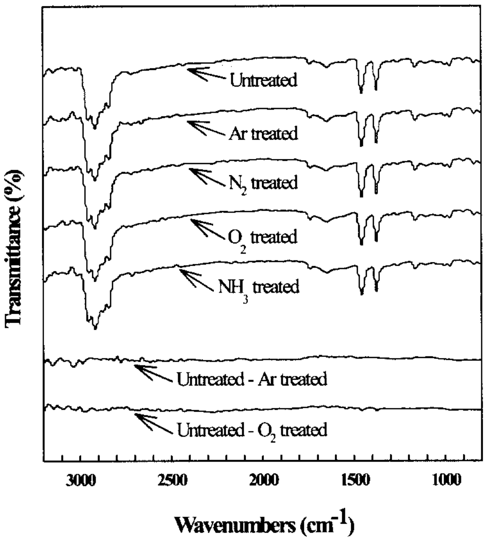


Fig. 3. FTIR-ATR spectra of plasma treated polypropylene at 40 W, for 4 min.

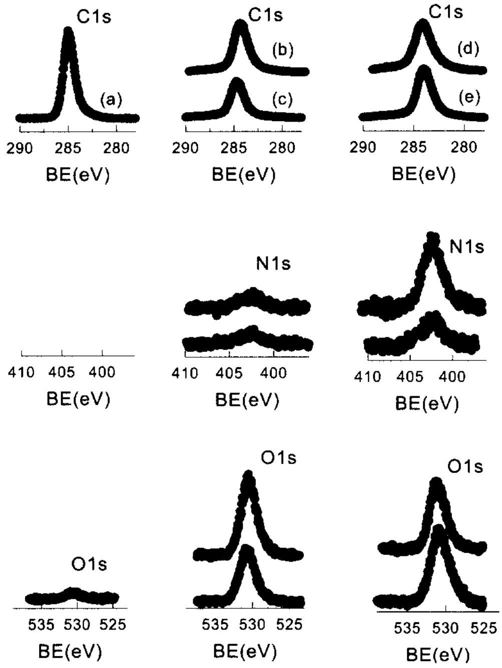


Fig. 4. XPS spectra (C1s, O1s, N1s) of polypropylene with treated Ar, O_2, NH_3 and N_2 plasma. a) Untreated, b) O_2 plasma treated, c) Ar plasma treated, d) NH_3 plasma treated, e) N_2 plasma treated

Table 2. Summary of Changes of Composition of Elements in Plasma Modified Polypropylene Membranes

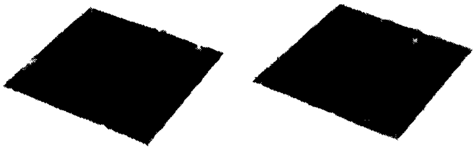
Treatment	C (%)	O (%)	N (%)	O/C
Untreated	99.38	0.62	-	0.0062
O_2 plasma	85.28	12.82	1.90	0.150
N_2 Plasma	85.31	11.15	3.55	0.130
Ar plasma	87.12	12.15	0.74	0.139
NH_3 plasma	86.97	7.92	5.11	0.091

Table 3. Effect of Plasma Treatment on XPS Spectra of Polypropylene Membranes with and without Plasma Treatment (Given by Peak Heights in Counts Per Second)

Treatment	Cls (284.8eV)	Ols (531.0eV)	Nls (402.0eV)
Untreated	30249	412	-
O_2 plasma	16794	5405	435
N_2 Plasma	16124	4880	850
Ar plasma	11992	3554	360
NH_3 plasma	19847	4288	1488

Table 4. AFM Measurements

	RMS roughness (nm)	No. of grinds per (nm^2)
untreated	14.5841	538
O_2 plasma	19.6687	930
N_2 plasma	16.9034	840
Ar plasma	15.9981	765
NH_3 plasma	18.7327	864

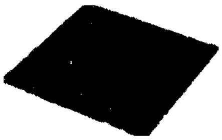


x=100 nm, z=300 nm
(a) Untreated

x=100 nm, z=300 nm
(b) Argon

x=100 nm, z=300 nm
(c) Nitrogen

x=100 nm, z=300 nm
(d) Ammonia



x=100 nm, z=300 nm
(e) Oxygen

Fig. 5. Atomic force micrographs of polypropylene.

Analysis of XPS was calibrated in 24 hours. Substrates were kept in a vacuum desiccator. Fig. 4 shows the XPS spectra of the modified membranes. The Cls peak at 284.8 eV was decreased more than before treatment due to surface ablation exerted by plasma treatment, and its binding energy is quite little different from that before treatment. In N_2 and NH_3 plasma's cases, we could confirmed the big change in Nls on 402.0 eV after treatment, and a little change in Nls peak after Ar and O_2 plasma treatment did not detected clearly. Table 2 shows that the result of elemental composition which was obtained by integral calculus of Cls, Ols, and Nls peak intensity. From the result, the oxygen content before treatment was 0.62%, but the surface oxygen content after treatment were generally increased. In case of Ar and O_2 plasma treatment, it was largely increased to 12.15% and 12.85% respectively. Also we could confirmed the most numerous nitrogen content after the NH_3 plasma treatment. The introduction of the oxygen atoms to the substrate's surface after Ar plasma treatment was caused by the effect of reaction between the free radicals which emitted from an activated membrane surface by plasma and oxygen in the air. Also the introduction of the oxygen atoms to the substrate's surface after O_2 plasma treatment was caused not only by contact with oxygen in the air, but also by direct reaction between the oxygen plasma activated elements and the surface of polypropylene. In N_2 and NH_3 plasma's cases, also the same reason will be involved [4,12]. Table 3 shows each peak's intensity which reveals the change of peak height (counts/second) after treatment and the coincidence of the change in element composition ratio.

After treatment by a kind of plasma gas, output intensity and reaction time, the chemical structure of polymer had influence on the change of surface morphology. And it is widely believed that the oxygen-containing plasma has more marked effect on the plasma etching effect and surface roughness than non-oxygen plasmas [12,13], In this experiment, we confirmed that the O_2 plasma had a great effect on the surface than other plasmas. Table 4 lists the surface roughness and the number of particle in a fixed area, where the O_2 plasma exhibited the biggest change after treatment. Also, Fig. 5 shows that the topography of membrane's surface changed more by active gas plasma than non-active gas plasma.

3.2. Pure Gas Permeation through Modified Membranes by Plasma Treatment

3.2.1. Influence of Plasma Treatment Gas and Power Input

Tables 5 and 6 show that dependencies on permeabilities for CO_2 and N_2 and ideal separation factor (α) in a various experimental conditions, such as sort of gas, treatment time, and power input at 20 ㎖/min of gas flow rate and pressure of 0.05 torr in plasma reactor, when the ideal separation factor is defined as the ratio of permeability for CO_2 to that for N_2.

The ideal separation factor of treated membrane increased regardless of the sort of plasma gas, and the membrane had higher selectivity at 80W of power input. Generally, the increase of power input tends to cause an increase of the reaction rate on the polymer surface. Because the number of active species increase with rising input power, also the raised input power makes reactive elements more energetic. But an excessive increase of input power preferably tends to cause some surface etching which results in a decrease in the selectivity [12]. The selectivity of modified membrane by Ar plasma (non-active gas) was higher than the selectivity of modified membrane by other active gas plasma. This experimental evidence seems to be explained by a CASING (Crosslinked by Activated Species of Inlet Gases) effect which has widely been

Table 5. Effects of Sort of Gas and Exposure Time of Plasma Treatment on Pure Gas Permeability and α in Ar, O_2, N_2, and NH_3 Plasma Treatment at 40W of Power Input

Plasma Gas	Permeability and α	Treatment time [min]						
		0	2	3	4	6	8	10
Ar	CO_2 [Barrer]	86.19	83.55	83.14	83.00	82.89	82.60	82.36
	N_2 [Barrer]	2.047	1.469	1.325	1.423	1.410	1.435	1.548
	α [CO_2/N_2]	42.11	56.87	62.73	58.32	58.76	57.54	56.87
O_2	CO_2 [Barrer]	86.19	82.88	81.76	81.64	81.69	81.48	81.39
	N_2 [Barrer]	2.047	1.774	1.734	1.748	1.749	1.752	1.761
	α [CO_2/N_2]	42.11	46.71	47.15	46.70	46.70	46.50	46.21
N_2	CO_2 [Barrer]	86.19	80.43	79.34	79.02	79.09	79.64	79.76
	N_2 [Barrer]	2.047	1.699	1.721	1.727	1.800	1.814	1.839
	α [CO_2/N_2]	42.11	47.59	46.10	45.75	43.93	43.90	43.37
NH_3	CO_2 [Barrer]	86.19	82.42	82.12	82.24	82.21	82.64	81.98
	N_2 [Barrer]	2.047	1.766	1.681	1.540	1.597	1.610	1.650
	α [CO_2/N_2]	42.11	46.65	48.85	53.40	51.47	51.32	49.68

Table 6. Effects of Sort of Gas and Exposure Time of Plasma Treatment on Pure Gas Permeability and α in Ar, O_2, N_2, and NH_3 Plasma Treatment at 80W of Power Input

Plasma Gas	Permeability and α	Treatment time [min]						
		0	2	3	4	6	8	10
Ar	CO_2 [Barrer]	86.19	81.76	81.61	81.87	81.30	82.00	82.47
	N_2 [Barrer]	2.047	1.130	1.200	1.287	1.316	1.342	1.493
	α [CO_2/N_2]	42.11	72.32	67.93	63.61	61.76	61.11	59.32
O_2	CO_2 [Barrer]	86.19	79.97	80.68	80.56	80.41	80.03	80.98
	N_2 [Barrer]	2.047	1.688	1.674	1.654	1.671	1.684	1.726
	α [CO_2/N_2]	42.11	47.35	48.19	48.70	48.12	47.52	46.91
N_2	CO_2 [Barrer]	86.19	80.39	78.02	78.53	78.45	78.12	78.70
	N_2 [Barrer]	2.047	1.621	1.570	1.534	1.527	1.621	1.636
	α [CO_2/N_2]	42.11	49.64	49.69	51.19	51.37	48.19	48.10
NH_3	CO_2 [Barrer]	86.19	79.95	79.62	79.50	78.98	79.24	79.54
	N_2 [Barrer]	2.047	1.320	1.380	1.470	1.530	1.520	1.540
	α [CO_2/N_2]	42.11	60.56	57.69	54.08	51.62	52.13	51.64

recognized and known [14].

3.2.2. Effect of Plasma Treatment Time

Generally, the selectivity and permeability of the modified membrane by plasma were affected by two definite processes : crosslinking and etching. The increased gas selectivity by the formation of crosslinking decreased with increasing plasma treatment time. It was due to the surface etching by plasma and the surface crack by the inside cohesive power [15]. From the result of the XPS analysis, the surface carbon content decreased irrespective of the kinds of plasma treatment gas. This may be due to the etching effect during the plasma treatment.

Generally, a polymer reacts with plasma on the surface, and generates a volatile product which can be removed by a vacuum pump. As the plasma treatment time extends, there is some surface degradation which affected through which both the selectivity and permeability for the gas by excessive reactions on the surface [4,12].

3.2.3. Influence of Inlet Gas Flux and Reactor Pressure

In the case of plasma reactions, if the pressure in the reactor is high (>1 torr), it has widely been recognized and known that the decomposition of the surface is promoted by the ascension of the gas temperature [12].

But, Fig. 6 shows that there was little influence on the permeation for CO_2 in the range of reactor pressure of 0.05 torr to 4.0 torr. And in the case of the plasma polymerization, the gas permeation rate is actually influenced by the inlet monomer flow rate which affects thin membrane's layer, but we could confirmed that the inlet gas flow rate had negligible influence on the CO_2 permeation rate at this plasma treatment as shown in Fig. 7. Fig. 8 shows the relationships between the permeability for CO_2 and CO_2/N_2 separation factor in various polymer membranes. In this figure, the same relationship in the present PP membranes with and without plasma treatment is also plotted as full and half-filled circles, respectively. It is apparent that the plasma treatment can improve the relationship between these factors. And these figures shows

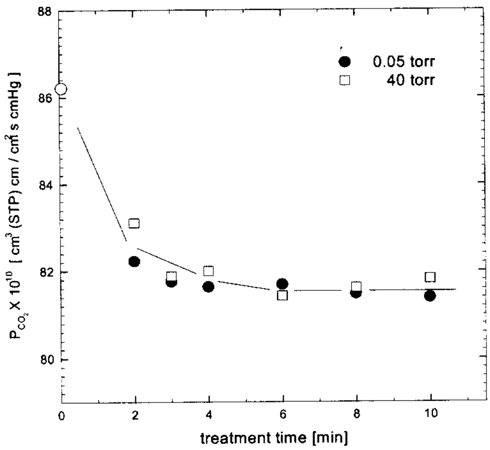


Fig. 6. Treatment time dependencies of CO_2 permeabilities through O_2 plasma treated polypropylene at 0.05 torr and 40 torr.

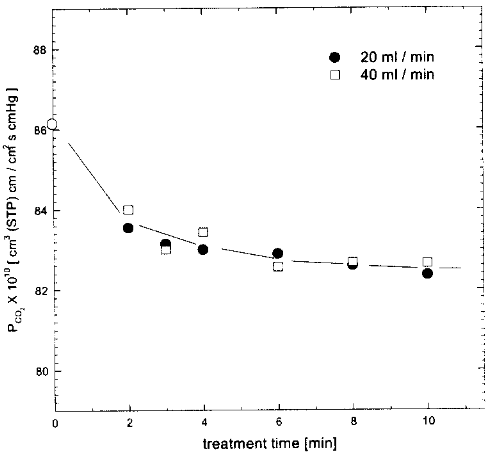


Fig. 7. Treatment time dependencies of CO_2 permeabilities through Ar plasma treated polypropylene at 20 ml/min and 40 ml/min.

the comparison between the result of CO_2 and CO_2/N_2 permeation rate in this experience and the usual polymer membrane's case which refer to literature [16].

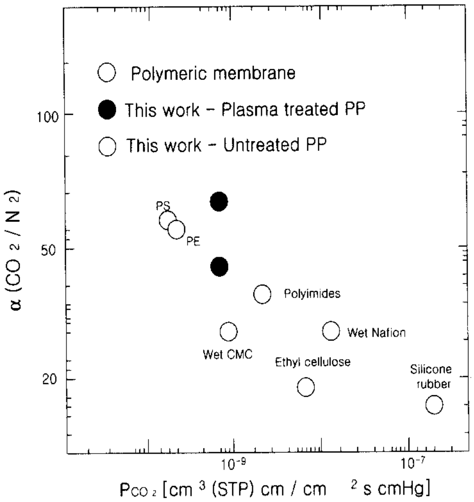


Fig. 8. Comparison of separation factor of polymeric membranes and this work for CO_2/N_2 separation.

4. Conclusion

The permeabilities for CO_2 and N_2 through polypropylene membrane modified by plasma were measured. Also the surface changes was measured before and after the treatment. The topography of membrane's surface after treatment was changed more by active gas plasma such as O_2, H_2 and NH_3 plasma than by non-active gas plasma such as Ar plasma. The O/C ratio on the surface was increased by the introduction of oxygen after all plasma treatments. Especially, after NH_3 plasma treatment, the highest nitrogen content ratio (%) was yielded. After plasma treatment, the changes of membrane surface were all subtly linked with both cross-linking and etching effects, and these kind of phenomenon had an influence on the gas permeation rate and the separation capacity of the membrane. The inlet flow rate of the plasma gas and the pressure in the reactor had negligible influence on the gas permeation rate of the modified membrane, but the selectivity of CO_2 relative to N_2 was directly affected by power input, treatment time and flow rate of plasma gas. The ideal separation factor for CO_2 relative to N_2 was as a whole increased by the influence of cross-linking on the surface, and the modified membrane at 80W of power input exhibited higher selectivity. Especially, the membrane treated with Ar plasma for 2 min at 80W power input revealed the largest ideal separation factor (α) of : 72.32, while the CO_2 permeability was 81.76×10^{-10} [cm^3(STP) cm/cm^2 s cmHg]. But, the separation factor gradually decreased owing to the plasma etching effect on the membrane surface with increasing plasma treatment time.

It is confirmed that the gas permeation capacity of the modified membrane with plasma could be improved by an appropriate control of the plasma conditions such as treatment time, the power input and sort of plasma gas.

Nomenclature

P_{CO_2} : Permeability of CO_2, [cm^3 (STP) cm/cm^2 s cmHg]
P_{N_2} : Permeability of N_2, [cm^3 (STP) cm/cm^2 s cmHg]
x : mole fraction at upstream feed side [-]
y : mole fraction at downstream (permeate) side [-]
α : Ideal separation factor for CO_2 relative to N_2 defined as P_{CO_2}/P_{N_2}[-]

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