

Effects of Plasma Treatment on CO₂ Plasticization of Poly(methyl methacrylate) Gas-Separation Membranes

Chien-Chieh Hu,¹ Chen-Yuan Tu,¹ Yi-Chieh Wang,² Chi-Lan Li,² Kueir-Rarn Lee,² Juin-Yih Lai¹

¹R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan University, Chung Li 32023, Taiwan, Republic of China

²Department of Chemical Engineering, Nanya Institute of Technology, Chung Li 32034, Taiwan, Republic of China

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ABSTRACT: To suppress undesirable plasticization effects of condensable gas (CO₂) in high pressure gas-separation process, a surface-modified poly(methyl methacrylate) (PMMA) membrane prepared by a plasma treatment was synthesized in this study. The pressure dependencies of permeability were analyzed to characterize the plasticization phenomenon and how it can be controlled by the plasma modification. FTIR-ATR and TGA results suggest that the plasma treatment leads to surface crosslinking of PMMA membrane. Thus, the plasticization effect resulting from

sorbed CO₂ on the Ar-plasma-treated PMMA membrane was significantly reduced, but the reduction in permeability was lower than that of other crosslinking modification methods. The reduction of the CO₂ permeability contributes to a major part to the selectivity of He/CO₂ for the Ar-plasma-treated PMMA membranes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 395–401, 2004

Key words: crosslinking; gas separation; membranes; plasticization; thermogravimetric analysis (TGA)

INTRODUCTION

Gas separation by membrane is nowadays considered to be a proven technology, which has gained an important place in chemical technology and has been used in a broad range of applications. For polymers used as gas-separation membranes, both high permeability and high selectivity are essential to minimize capital and operation costs.¹ High-performance polyimides have excellent gas-separation properties at low pressures for several gas pairs, but they cannot maintain this performance at high pressures in the presence of highly sorbed components.^{2–5} In membrane studies, plasticization is defined as an increase in the segmental motion of polymer chains, attributed to the polymer matrix swollen upon sorption of one or more sorbates, such that the permeabilities of both components increase and the selectivity decreases.⁶ It is well known that the plasticization is the major problem faced by CO₂-selective polymeric membranes.^{7–10} Because glassy polymer is used in commercial separations involving CO₂, it is very important to understand the plasticization process and assess its effect on membrane performance.^{11–15}

A membrane system for natural gas treatment offers significant advantages, but the operation at high permeate pressures is desirable from the perspective of CO₂ sequestration. Moreover, as the CO₂ concentration in the feed increases, the membrane economics become more favorable, assuming that the membrane remains stable. These two considerations emphasize the importance of developing plasticization-resistant membranes. Work has been carried out on the suppression of CO₂ plasticization of ester derivatives of bisphenol A, which contain different amounts of polar groups and aromatic rings on PC.¹⁶ Makaruk et al.¹⁶ observed that the plasticization suppression effect becomes more significant when the intermolecular distances and the polarity of the additive molecules increase simultaneously.

Many investigations have shown that the crosslinking of polymeric gas-separation membranes might be a useful method for improving separation characteristics by decreasing plasticization at high CO₂ pressures.^{17,18} To suppress undesirable plasticization effects in CO₂/CH₄ separation, crosslinkable 6FDA-based copolyimides were synthesized by Wind et al.¹⁷ They concluded that the covalent crosslinking appears most promising for the purpose of plasticization suppression in practical polyimide membranes. Bos et al.¹⁹ studied the heat treatment of polyimide membranes. They showed that the thermal annealing of membranes at 350°C for 15–30 min significantly reduced CO₂ plasticization in pure gas and mixed gas permeation experiments. However, the heat treatment significantly reduced the CO₂ permeability (loss

Correspondence to: K.-R. Lee (krlee@nanya.edu.tw).

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~ 50%). It was hypothesized that the heat treatment leads to polymeric membrane crosslinking because the treated films were insoluble in strong solvents. Another approach for improving the plasticization resistance of polymeric membranes is the formation of semi-interpenetrating polymer networks. Bos et al.²⁰ observed that the semi-interpenetrating networks derived from blends of commercial polyimide matrimid and the acetylinic oligomer Thermid FA-700 also showed high plasticization resistance, but the permeability was reduced. As seen from the majority of reports in the literature, the plasticization effect on the properties of gas-separation membranes has been studied intensively. Very little has been reported on plasticization suppression because it is hard to find a method that can improve the selectivity of the membrane without an unacceptable loss in permeability.

A variety of treatments including chemical crosslinking, heat treatment, and formation of interpenetrating polymer network have been applied to improve the plasticization resistance of the polymeric membrane. However, these applications are hampered in many cases because of their higher energy consumption and long treatment time. Plasma treatment, as the most promising one, can overcome these problems. The plasma technique was mainly applied in the field of the surface modification of solid materials.^{21–24} To our knowledge, there is no documentation regarding the plasma treatment method for developing a plasticization-resistant membrane that has been reported and thus is the main objective of the present study. Electrons, atoms, and radicals in the plasma attack the surface of the polymeric membranes and then remove atoms from the polymeric surface to form radical sites at the surface, and finally, the radicals react with other radicals to form crosslinked chains.²⁵ The crosslinked membrane surface results in a reduction of chain mobility and simultaneously prevents membrane plasticization. Furthermore, the reduction of permeability for argon (Ar)-plasma-treated membrane was lower than that of other crosslinked membranes, attributed to a very thin crosslinked skin layer of the membrane. In this article, the effect of argon plasma inducing membrane crosslinking on the plasticization resistance of the poly(methyl methacrylate) (PMMA) membranes is tested by pure gas permeation experiments. The separation performance of an untreated and a crosslinked membrane is compared.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) [PMMA, MW: 996,000 (GPC)] was supplied by Aldrich Chemical Co. (Mil-

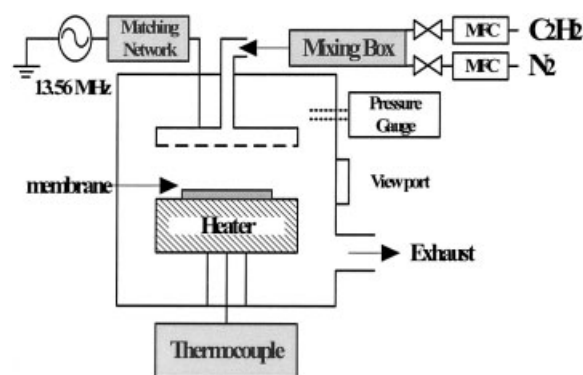


Figure 1 Schematic diagram of the plasma reactor system.

waukee, WI). Commercially available dichloromethane was used as a solvent without further purification. Carbon dioxide and helium with high purity (99.9%) were used in the pure gas permeation experiments.

Membrane formation and modification

A 14.3% (w/w) dichloromethane solution of PMMA was cast onto a glass plate to a predetermined thickness using a Gardner knife. The solvent was then allowed to evaporate slowly under ambient conditions. After 24 h, the solid membranes were dried in a vacuum oven at 110°C for 24 h to remove traces of residual solvent. The mean thickness of the membrane was measured using a micrometer and was based on the average of at least 25 points on the membrane. The resulting thickness was in the range of 60–70 μm .

Plasma treatment was carried out in a plasma reactor system with two internal electrodes, pressure gauge, vacuum system, and matching network for capacity coupling of a 13.56 MHz radio frequency source. The schematic diagram of the plasma reactor system is shown in Figure 1. The vacuum reactor system was evacuated to 20 mTorr with a rotary pump before plasma treatment. The argon was introduced with controlled flow rates by a mass flow controller system. The argon mass flow rate was fixed at 10 sccm (standard cm^3/min). The operating pressure and power were fixed at 300 mTorr and 100–300 W, respectively. The plasma treatment time was in the range of 1–10 min.

Characterization

ATR-FTIR measurements were carried out using a Perkin-Elmer FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Thermogravimetric analysis was performed using a Perkin-Elmer TGA 7 at a heating rate of 10°C/min in nitrogen. Mechanical properties were measured according to ASTM D638-

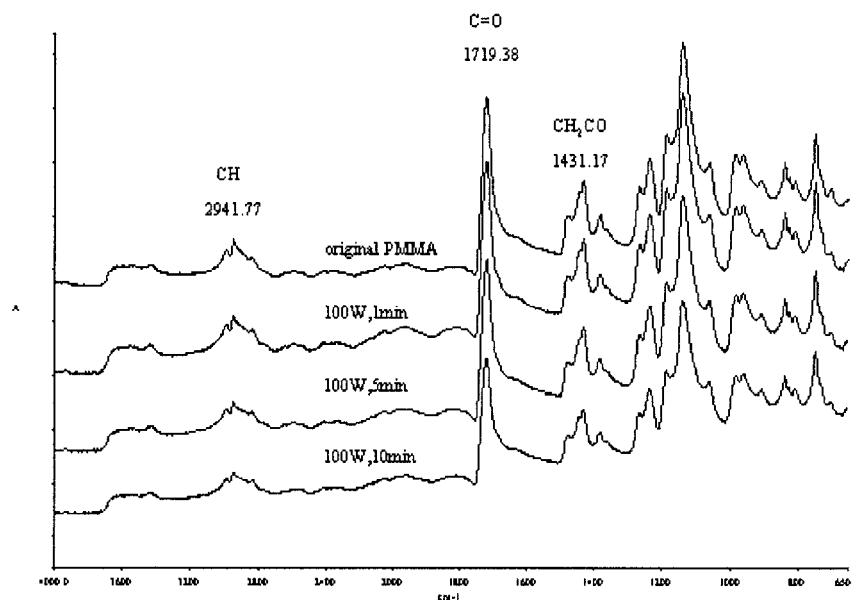


Figure 2 Comparison of ATR-FTIR spectra of PMMA membranes.

97. Tensile tests were carried out on an Instron (Canton, MA) 5544 tensile machine (5 mm/min). The surface roughness of the PMMA membrane was investigated using an atomic force microscope (AFM). All images were collected in air using a tapping mode under a constant force.

Permeation study

A gas permeation analyzer (Model GTR10, Yanaco, Kyoto, Japan) was used to measure the pure gas permeability coefficients for the polymeric membranes to He and CO₂. All experiments were carried out under isothermal conditions at 35 ± 0.5°C. Permeability is usually expressed as barrer [10⁻¹⁰ (cm³ (STP) cm)/(cm² s cmHg)]. The ideal selectivity was calculated based on the ratio of permeability coefficients

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (1)$$

where P_A and P_B are the permeability coefficient for pure gases A and B.

RESULTS AND DISCUSSION

Identification of the crosslinking of PMMA membrane

In general, the major observations of the membrane treated with Ar-plasma are formation of crosslink and densification. The degree of membrane crosslinking may be controlled by varying the plasma treatment time or changing the power of plasma. The FTIR tech-

nique is known as a simple and rapid method of confirming the change in chemical and physical properties of polymers. In this study, ATR-FTIR was used to monitor the surface crosslinking of PMMA dense membranes treated with argon plasma. Figure 2 shows the typical results of untreated and plasma-treated PMMA dense membranes. No appreciable difference was observed between the spectra of the untreated and plasma-treated membranes in the 1000–1500 cm⁻¹ region, suggesting that the main chain composition of PMMA remained unchanged. The crosslinking of the membranes was characterized by a well-defined peak at 1719 cm⁻¹. As the plasma treatment time increased, the adsorption at 1719 cm⁻¹ continuously decreased. This result may be attributed to the occurrence of crosslinking through the plasma treatment.

In general, the thermal stability of membrane is directly related to the degree of crosslinking. To investigate the thermal decomposition properties of the PMMA membranes, the thermogravimetric analyses for the original and Ar-plasma-treated PMMA membranes are presented in Figure 3, which shows that the loss of mass of the untreated PMMA membrane commences at the lower temperature, whereas the plasma-treated membrane begins at the higher temperature. These curves certainly indicated that the PMMA membrane is stabilized by the treatment of plasma, and one may also conclude that the PMMA membrane is crosslinked in the plasma treatment process. Observation of thermogravimetric curves and ATR-FTIR spectra confirms that the crosslinking of PMMA dense membrane can be induced by using argon-plasma treatment.

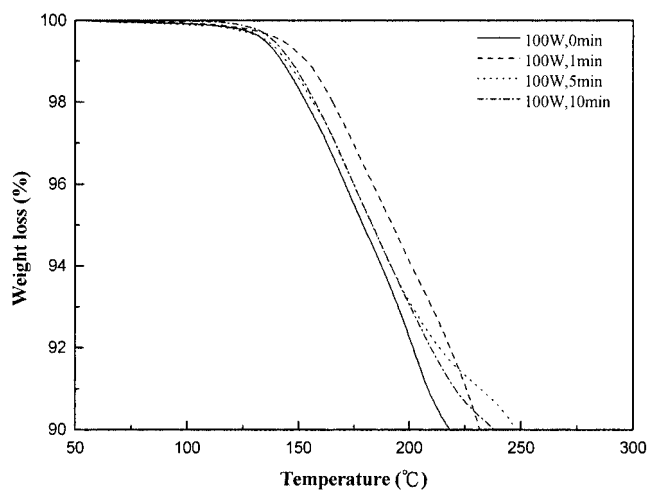


Figure 3 Thermogravimetric analysis of PMMA membranes treated with argon plasma.

Effects of plasma treatment on mechanical properties and morphology of the PMMA membranes

The mechanical properties of membrane may be one of the most important parameters for membrane practical application. The induced crosslinking by plasma treatment may enhance the mechanical properties of the PMMA membrane. Analysis of mechanical properties analysis was used to confirm the above hypothesis. Table I summarizes the tensile strength at break and Young's modulus of PMMA dense membranes. It can be observed that the Young's modulus of plasma-treated membrane is higher than that of the untreated membrane regardless of (long or short) treatment time because the chain mobility was inhibited as a result of the surface crosslinking. In addition, the tensile strain is also related to the mobility of molecular chains. Table I also shows that the membranes with longer plasma treatment time have smaller tensile strain (i.e., crosslinking decreases polymer chain mobility). Surprisingly, Table I clearly indicates that the tensile strength of plasma-treated membrane was less than that of the untreated one. There are probably two dominant mechanisms to change the tensile strength of the membrane during plasma treatment. One is attributed to the crosslinking and the other to the etching. Figure 4 shows the AFM image of the plasma-treated side of the PMMA membrane, in a scan range of 1 μm . There is a noticeable difference between the untreated membrane and the plasma-treated membrane. A smooth surface can be seen in the untreated membrane, whereas an obvious etching trace can be observed in the plasma-treated membrane. Table II summarizes the roughness parameter of the top surface in the 1- μm scan range. It shows that the roughness of the membrane surface increases with increasing plasma treatment time, which means that the etch-

ing effect may dramatically influence the final membrane properties. The above results suggest that the etching of the membrane results in a membrane with smaller tensile strength. Additionally, it should be pointed out that the tensile strength of the plasma-treated membrane increases with increasing plasma treatment time (Table I). This is attributed to the fact that polymer chains undergo crosslinking during the plasma treatment procedure.

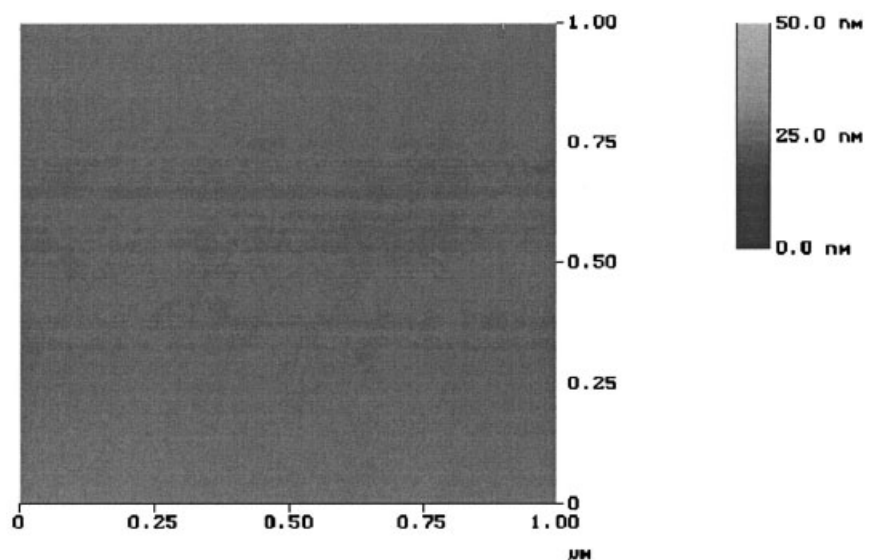
Effect of plasma treatment on the plasticization resistance of the PMMA membranes

Recently, several investigations show that the plasticization of polyimide membranes for gas separation at high CO_2 pressures can be prevented using a crosslinking technique. The motivation of this work was to develop a fundamental database of plasticization-resistance properties of plasma-treated polymeric membrane. Sanders et al.²⁶ observed that CO_2 is extremely effective in inducing plasticized permeation behavior in PMMA, but the plasticization resistance of PMMA has not been investigated. This is the reason that we chose PMMA in our work.

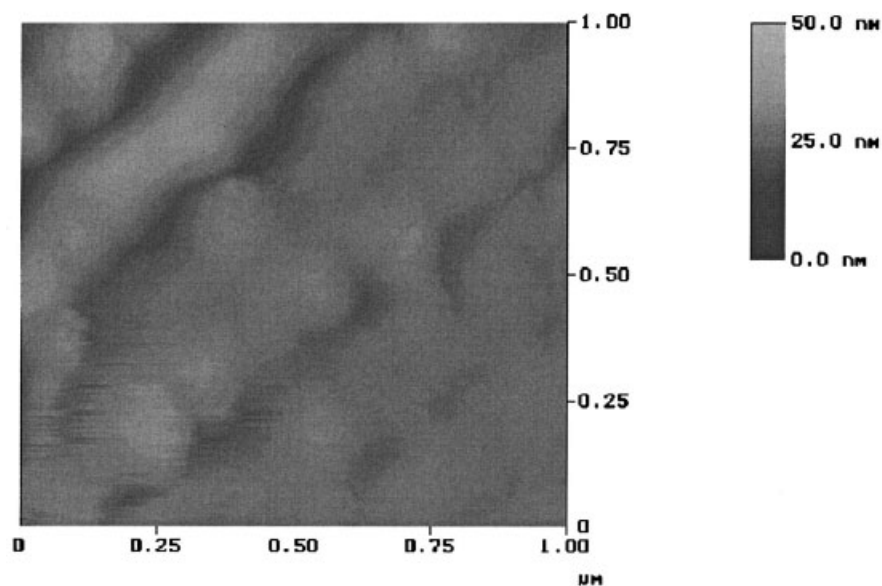
The effect of plasma treatment conditions and operating pressure on the CO_2 permeability of the PMMA membrane is shown in Figure 5. It shows that the CO_2 permeability decreases with increasing plasma treatment time. Compared with the unmodified PMMA membrane, the CO_2 permeability of the plasma-treated membrane (100 W, 10 min) decreased by about 24%. These phenomena imply that the membrane with long treatment time has small permeability (i.e., becomes more dense in terms of crosslinking compared to that of the membrane treated for a short time). It is worth noting that the loss of permeability for the plasma-treated membrane is lower than that of crosslinked membranes prepared by other methods.¹⁹ Moreover, the CO_2 permeability of the plasma-treated membrane increases slowly at an operating pressure higher than 4 atm (plasticization pressure of untreated PMMA membrane). In addition, compared with the untreated PMMA membrane, the plasma-treated PMMA membrane has higher plasticization pressure. From the above information, it can be concluded that

TABLE I
Mechanical Properties of PMMA Membranes Treated with 100 W Argon Plasma

| Treatment time (min) | Tensile strength (MPa) | Young's modulus (GPa) | Tensile strain (%) |
|----------------------|------------------------|-----------------------|--------------------|
| 0 | 43.7 | 1.75 | 4 |
| 1 | 33.0 | 1.92 | 2 |
| 5 | 40.7 | 2.05 | 2 |
| 10 | 41.0 | 2.01 | 3 |



(a)



(b)

Figure 4 AFM image of the top surface of the PMMA membranes: (a) original membrane; (b) Ar-plasma-treated membrane obtained by 100 W plasma treatment for 10 min.

simple plasma treatment of the PMMA membrane is sufficient to suppress CO₂ plasticization.

The effect of power of plasma treatment on the gas permeability of PMMA membranes is shown in Figure 6. The higher power of plasma possibly increases the formation of crosslinking on the surface of PMMA

membrane and leads to a decrease in CO₂ permeability, but the etching effect becomes stronger when the power of plasma exceeds 200 W, after which the permeability increases. Additionally, an opposite phenomenon was observed in the permeation test of helium. The helium permeability increased with increas-

TABLE II
Summary of the Roughness of the Top Surface of the PMMA Membrane Treated with 100 W Argon Plasma

| Treatment time (min) | R_q^a (nm) | R_a^b (nm) | R_{max}^c (nm) |
|----------------------|--------------|--------------|------------------|
| 0 | 0.21 | 0.16 | 1.01 |
| 1 | 0.54 | 0.42 | 2.28 |
| 5 | 0.80 | 0.56 | 3.08 |
| 10 | 1.54 | 1.35 | 4.59 |

^a Root mean square (RMS) of z values.

^b Mean roughness.

^c Mean difference between five highest peaks and five lowest values.

ing power of plasma, as shown in Figure 7. Both the crosslinking and etching induced by plasma treatment contributed to the change of permeability of the membrane. Meanwhile, the stronger crosslinking decreases the permeability coefficient, but stronger etching results in an increase of the permeability. Figure 7 indicates that the effect of etching on the permeability of He is higher than that of the crosslinking. The permeability and ideal selectivity of the PMMA membranes are tabulated in Table III. The plasma treatment significantly reduces the CO_2 permeability.

As listed in Table III, except for the 100-W treatment, the decreased permeability of CO_2 is the main factor responsible for yielding improved ideal selectivities of He/ CO_2 for the plasma-treated membranes. The stronger plasma treatment (longer time or higher power) possibly promotes the etching of the membrane and leads to a loose packing of polymer chains. Therefore, it facilitates the permeation of gas molecules of smaller Lennard-Jones diameter (e.g., He, compared with that of the larger CO_2).

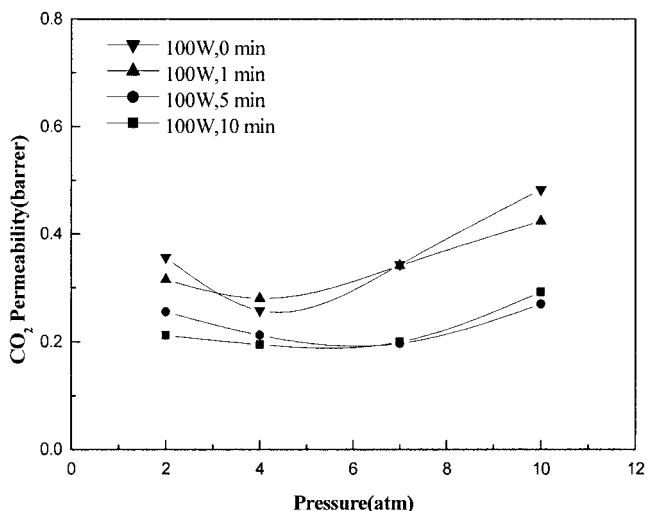


Figure 5 Pressure dependency of CO_2 permeabilities in PMMA membrane treated with argon plasma at 35°C.

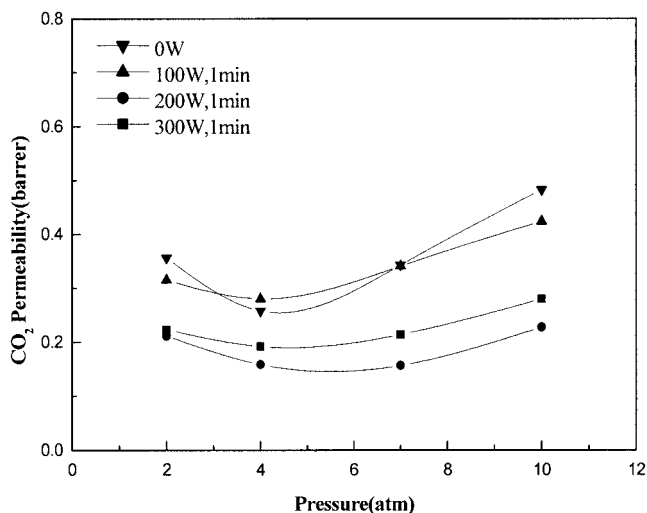


Figure 6 Pressure dependency of CO_2 permeabilities in PMMA membrane treated with argon plasma at 35°C.

CONCLUSIONS

The CO_2 plasticization-resistance of PMMA was achieved by treating the dense membranes with argon plasma for a certain period of time for various powers of plasma. The CO_2 permeability increased slowly at elevated pressures and the plasticization pressure shifted to higher pressure. It was questioned whether the suppression was attributed to a result of crosslinking of the PMMA membrane. From the FTIR-ATR and TGA observations, it was found that the crosslinking of the PMMA membrane caused the suppression of plasticization. The plasma treatment significantly lowered the gas permeability for all the membranes studied. However, the effects of plasma treatment on ideal

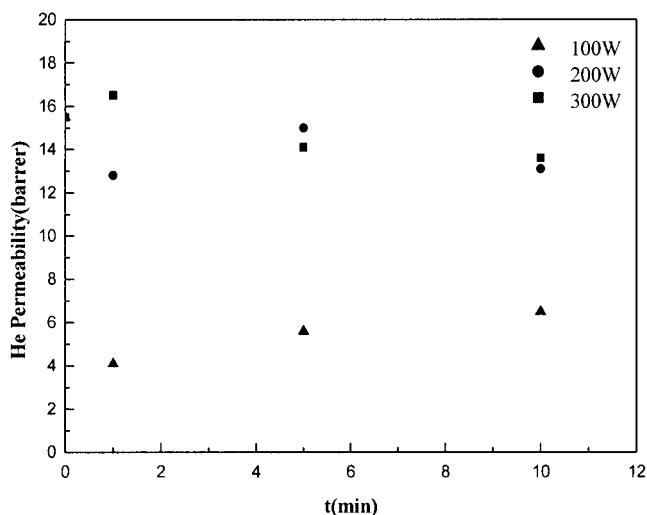


Figure 7 Helium permeabilities as a function of treatment time in PMMA membranes treated with argon plasma at 35°C.

TABLE III
Gas Permeability and Ideal Selectivity of PMMA
Membranes Treated with Argon Plasma^a

| Power (W) | P_{CO_2} (barrer) | | | | $P_{\text{He}}/P_{\text{CO}_2}$ | | | |
|--------------|----------------------------|----------|----------|-----------|---------------------------------|----------|----------|-----------|
| | 0 min | 1 min | 5 min | 10 min | 0 min | 1 min | 5 min | 10 min |
| 100 | 0.36 | 0.32 | 0.26 | 0.21 | 43 | 13 | 22 | 32 |
| 200 | 0.36 | 0.21 | 0.24 | 0.24 | 43 | 61 | 63 | 55 |
| 300 | 0.36 | 0.22 | 0.08 | 0.12 | 43 | 75 | 176 | 105 |

^a Gas permeation experiments were carried out under 2 atm and $35 \pm 0.5^\circ\text{C}$.

selectivity of He/CO₂ depended on the plasma treatment conditions. This study indicates that the plasma treatment had less of an impact on gas-separation properties of polymeric membranes compared to that of other crosslinking modification methods. Meanwhile, the result of this work is just a concept for suppressing CO₂ plasticization. For practical membrane applications, a further study will be necessary.

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