

Hybrid Sol–Gel Membranes of Polyacrylonitrile–Tetraethoxysilane Composites for Gas Permselectivity

Minoru Iwata,¹ Takeharu Adachi,¹ Miwa Tomidokoro,¹ Michiyoshi Ohta,² Takaomi Kobayashi²

¹Material Engineering, Nagaoka Technical College, Nishi-kataikai, Nagaoka, Niigata, 940-8532, Japan

²Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata, 940-2188, Japan

Received 2 May 2002; accepted 1 July 2002

ABSTRACT: Sol–gel reaction of tetraethoxysilane (TEOS) with fumed silica–polyacrylonitrile (PAN) membrane was carried out to prepare hybrid gas permeable membranes for oxygen and nitrogen separation. Various amounts of fumed silica microparticles with a few μm diameters were compounded in PAN–dimethylsulfoxide (DMSO) solution. After casting of the viscous compound solution on a flat sheet with 100 μm thickness, DMSO was evacuated under vacuum at 80°C. Then, the silica–PAN composite membranes were treated with TEOS for 1 day at 40°C in methanol. Air permeation was examined and compared in silica–PAN composite membranes with and without TEOS treatment. The latter hybrid membranes showed selective oxygen per-

meability, which depended on amounts of fumed silica in the membrane. The TEOS hybrid PAN membranes have a high ability of oxygen permselectivity for O_2/N_2 gas mixture with $\alpha(\text{O}_2/\text{N}_2) = 13\text{--}17$, when the silica content was in the range of 13–20 wt %. This is attributed to siloxane network formation in hybrid silica–PAN composite membranes. Favorable siloxane network formation resulted in high oxygen permeability of the hybrid composite membranes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1752–1759, 2003

Key words: gas permeation; separation techniques; membranes; gas permeation; nanocomposites

INTRODUCTION

Widespread use of gas separation membranes has occurred within the last decade.¹ Gas separation through membranes is one of the most significant new processes; also, the technology has permeated into a wide range of industries and applications.^{2,3} For gas separation, membranes can remove gas-mixture components when they are passed across the membrane. Therefore, gas-separation membranes have been widely functionalized for several fields; such membranes are preferentially permeable by one component while another component gas can be retained. Usually, the pressure differential across the membrane provides the driving force for gas diffusion. Components that diffuse across the membrane depend on membrane materials. Thus, a gas-permeable membrane can separate the components; only the degree is governed by membrane properties. In polymeric membranes, there are some advantages specially chosen for functionality. To produce oxygen- or nitrogen-enriched gas (i.e., for separation of oxygen and nitro-

gen by gas-separation membranes), those membranes must be highly permeable to gases.⁴

It has been reported that chemical structural parameters of a polymer correlate with N_2/O_2 permeability. For example, a polymeric membrane with silane or siloxane groups shows a high gas permeability coefficient relative to that without such functional groups.⁵ For an oxygen permselective membrane, molecular design dictates a high free volume of the resultant polymer in combination with a rigid main chain.⁶ Other strategies for a permselective membrane for oxygen enrichments include addition of metal–ligand in the membrane^{7,8} and hybrid materials that consist of inorganic and organic components.⁹ The sol–gel process has been used in hybrid membranes.^{10,11} The processes have been convenient techniques for introduction and preparation of Si-containing membranes such as Si–O–Si linkages into the hybrid membrane. Silane coupling agents,¹⁰ which are characterized by Si–OR bonds (R is an alkyl group such as methyl or ethyl group), are very interesting reagents that increase the oxygen affinity of the treated polymeric membrane. In addition, treatments can improve the membranes' chemical and mechanical stability.¹² Therefore, sol–gel membranes have been made of inorganic materials for aluminum oxides,¹³ titanium oxides,¹⁴ and zirconium,¹⁵ although organic polymeric hybrid membranes have been seldom used for sol–gel composite membranes.

Correspondence to: T. Kobayashi (takaomi@nagaokaut.ac.jp).

Hybridization of organic polymer and sol-gel compounds was reported using imide-silicone membranes.¹⁶ Specific monomer units with sol-gel initiation components in the monomer were synthesized for obtaining imide-silicone hybrid membranes.¹⁷ The effect of silicon dioxide particles on the gas transport properties of 6FDA-IPDA thin films was investigated. Separation properties of the resulting membranes for an oxygen and nitrogen mixture were significantly improved in the hybrid SiO₂ composite polymer.^{18,19} This is attributed to restriction of chain segmental mobility resulting from possible adsorption of the polymer to the silica surface.¹⁹ Therefore, if silica particle surfaces become anchoring sites for sol-gel networks, which restrict molecular orientation of polymeric segments of separation membranes, the hybridization of polymer and sol-gel networks poses a novel strategy for gas-permeation membranes.

In the present work, we prepared silica-polymer composite membranes for O₂/N₂ separation. Fumed silica-polyacrylonitrile (PAN) composite membranes were treated with tetraethoxysilane (TEOS) by sol-gel reaction. Because the composite membrane physically contained silica microparticles that became anchoring sites of the sol-gel networks in the polymeric membranes, sol-gel hybridization formed a nonporous network membrane for gas separation. Therefore, development of novel gas-permeable membranes would be convenient, given that a number of polymer advantages are available as sol-gel supports. This report describes membrane preparation and properties of sol-gel hybrid PAN membranes for gas permselectivity of O₂/N₂ permeability.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN, 70,000 Da) was purchased from Aldrich (Milwaukee, WI). Aerosil of fumed silica (Degussa #380, 380 m²/g surface area) powder was produced by Japan Aerosil Co. Tetraethoxysilane (TEOS) and all other reagents used in the present experiments were of reagent grade unless otherwise described. Dimethylsulfoxide (DMSO) was distilled in reduced pressure before use for PAN-fumed silica compounding.

Membrane preparation

Figure 1 shows the schematic procedure of preparation of fumed silica-PAN compounds and sol-gel reaction for hybrid PAN membranes. Detailed procedures of silica-PAN composite membranes were followed. PAN was dissolved in DMSO overnight at 50°C; then, fumed silica powder was mixed for 1 day

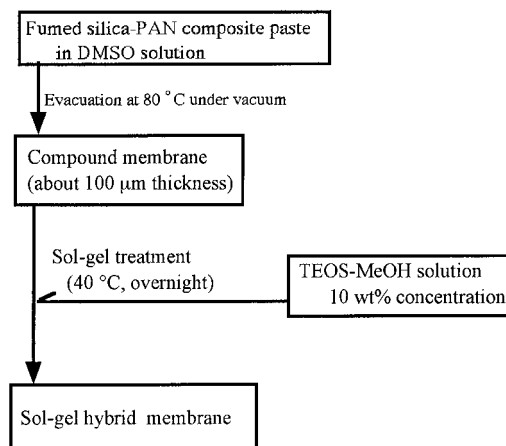


Figure 1 Schematic procedure of preparation of fumed silica-PAN compounds and sol-gel reaction for TEOS-treated silica-PAN hybrid membranes.

at room temperature. The obtained PAN-silica-DMSO paste solution was then mixed with 10 wt % of PAN-DMSO solution to produce 1.3–20 wt % concentration of fumed silica content. After degassing, the silica-PAN DMSO solution was spread on a flat sheet with about 100 μm thickness and DMSO was evacuated at 80°C for membrane formation.

The resulting membrane sheets (60–110 μm thickness) were cut into 10-mm-diameter disks before sol-gel processes. TEOS treatment of the PAN-silica composites was carried out in 10 wt % of TEOS methanol solution in the presence of 0.1M HCl concentration. The sol-gel reaction continued during the day at 40°C, after which glassed-composite PAN membranes were obtained. After sol-gel treatment, unreacted TEOS was washed with an excess of methanol; then, the obtained membranes were dried *in vacuo*.

Permeation experiments

The apparatus for gas permeation consisted of a disc-type membrane sample (10 mm diameter and 60–100 μm thickness) that was installed in a membrane folder (GTR-10; Yanagimoto, Japan). The effective membrane area for permeation was $A = 3.14 \text{ cm}^2$. Air (99.99% purity) was supplied at 1 atm pressure difference (ΔP) between the upstream and downstream sides of the membrane at 30°C. On the upper side of the membrane, pressure was applied to permeable gas components across the membrane. Permeated gas was analyzed by gas chromatography (G1880T; Yanagimoto) with a 5-Å molecular sieve at 80°C. The permeability coefficient P (cm³ cm/cm² s cmHg) was calculated for oxygen and nitrogen according to the following equation:

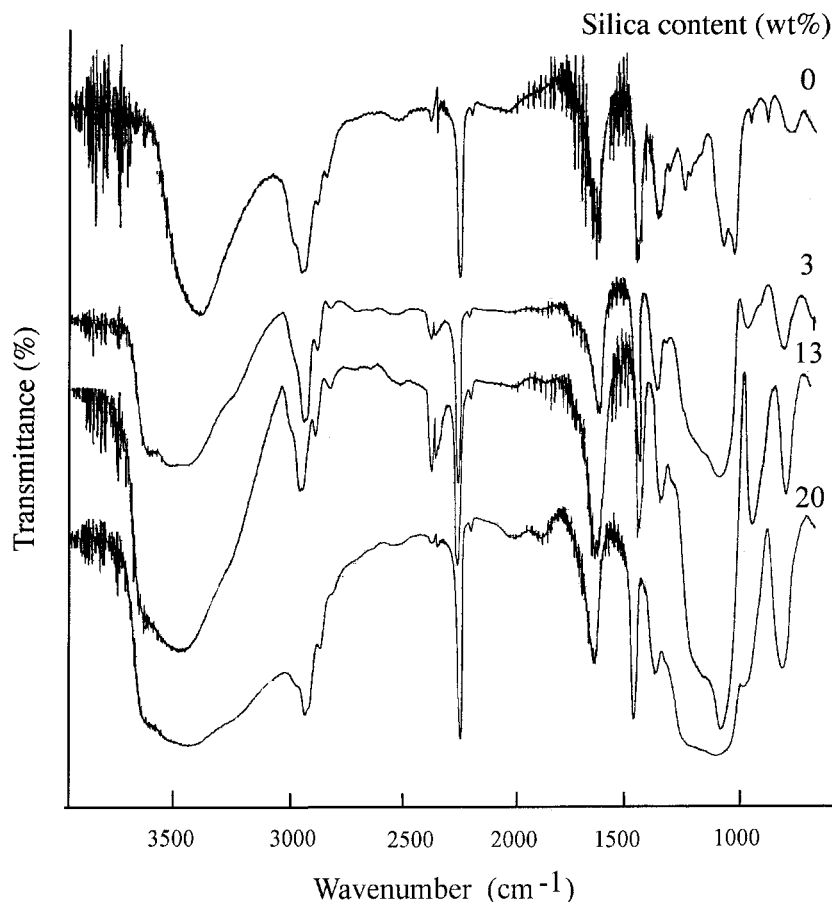


Figure 2 FTIR spectra of fumed silica-PAN composite membranes.

$$P = (\kappa l / \Delta P A)(q / t) \quad (1)$$

where κ is the apparatus constant for the GTR-10 ($\kappa = 1.65[-]$) and l (cm) and ΔP (cmHg) are the membrane thickness and pressure difference between both sides of the membrane, respectively. From gas chromatography data, the gas permeation volume q (dm^3) per unit time t (s) was determined for each gas.

Membrane characterization

IR spectra of hybrid sol-gel membranes were measured with Shimadzu FTIR 8100 spectrometer (Shimadzu, Kyoto, Japan) by transmittance mode with 40 times integration under nitrogen atmosphere.

Surface topography was characterized by atomic force microscopy (AFM) using Nanoptics 1000 (Seiko Instruments, Tokyo, Japan). All imaging was performed in the tapping mode using silicon tips. Image analysis was performed with the supplied software (Nanoptics 1000 data analysis program for three dimensions, version 1.2). Before measurement of the AFM image, the sample was carefully lyophilized.

RESULTS AND DISCUSSION

Membrane characteristics

Figure 2 shows IR spectra of silica-PAN composite membranes containing various amounts of fumed silica. It is known that PAN has characteristic IR peaks at 1450 and 2250 cm^{-1} for CH bending and CN stretching.²⁰⁻²² Also, peaks near 2900–3000 cm^{-1} were for CH stretching. As shown, the silica-PAN composite membranes have Si-O-Si stretching near 1100 cm^{-1} and a Si-OH bonding peak in the range of 3100–3700 cm^{-1} .²³ These peaks are attributed to the fumed silica powder added to the PAN membrane. When fumed silica amounts in the membrane were increased, these characteristic IR peaks of Si-O-Si and Si-OH stretching broadened radically. Also, it is notable that the IR peak intensity of the silanol stretch band increases with lower silica content of 1.3 wt %. The Si-O-Si stretching band was also present in high IR intensity at 1095 cm^{-1} when the content was 13 wt %. However, these IR peaks became broad when fumed silica content was 20 wt %. The discrepancy between silica content and IR band intensity suggests that the added silica powder mutually interacts in the PAN mem-

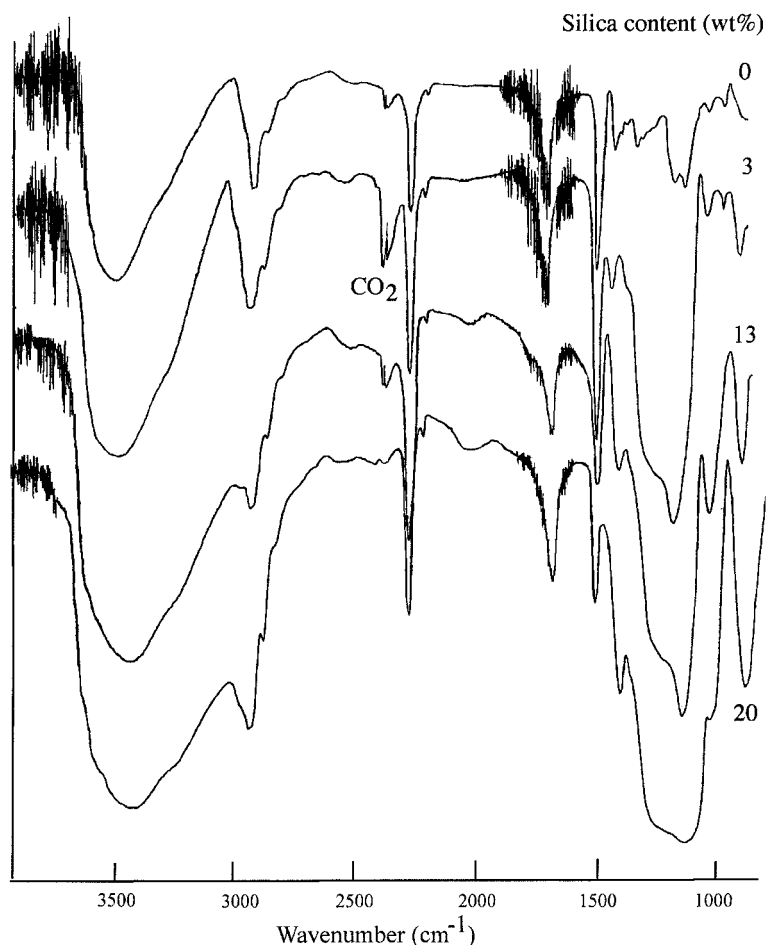


Figure 3 FTIR spectra of TEOS-treated silica-PAN membranes containing various amounts of silica contents (wt %).

brane; thus, interaction between silica powders was increased in high silica content in the PAN membrane.

Figure 3 compares IR spectra of TEOS-treated membranes containing various amounts of fumed silica. The TEOS-PAN hybrid membranes show characteristic IR peaks of silanol and Si-O-Si stretching at 3500 and 1100–1400 cm^{-1} , respectively. The IR peaks of CN stretching and CH bending at 2300 and 1450 cm^{-1} for PAN segments also remained. The observation indicates that PAN segments were not influenced by the sol-gel reaction in the acidic methanol solution. Compared with IR spectra for the TEOS-treated silica-PAN membranes with 1.3 and 20 wt % of silica content (designated in 1.3 and 20), Si-O-Si stretching near 3500 cm^{-1} became much stronger relative to CN stretching of PAN at 2300 cm^{-1} with the 20 wt % silica content. Similarly, the approximate 1100 cm^{-1} peak intensity became strong relative to that of CH bending at 1450 cm^{-1} . Here, rigid Si-O-Si networks were developed by the TEOS sol-gel reaction within the silica-PAN composite membranes. Comparison of IR spectra between Figures 2 and 3 for corresponding silica contents demonstrates similar results. In Figure 4, peak ratios of 2300 cm^{-1} CN stretching and 1100

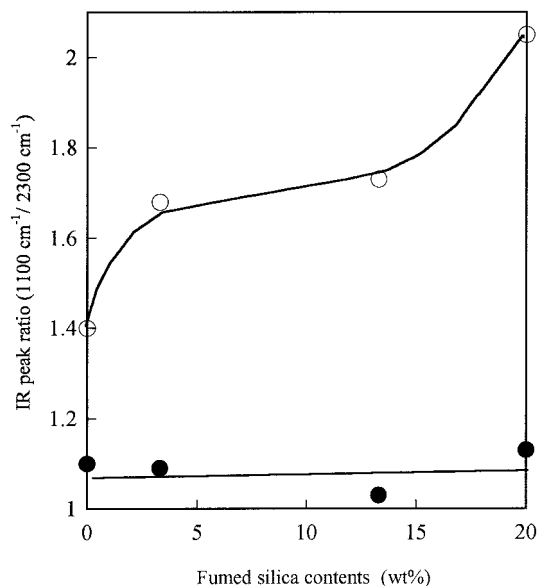
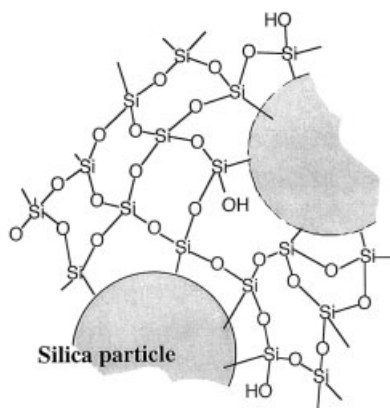


Figure 4 IR peak ratio of the 1100 to 2300 cm^{-1} for IR spectra of silica-PAN membranes obtained without (●) and with TEOS treatment (○).



Scheme 1 Illustration of sol-gel networks between anchoring silica particles fixed in the PAN membrane.

cm^{-1} Si-O-Si stretching were plotted against fumed silica content. The figure shows that values of TEOS-treated membranes were higher than those for untreated membranes. In addition, the peak ratio value increases with increasing silica content in the membranes. These facts indicate that the sol-gel process for Si-O-Si formation in the PAN membrane was enhanced in the presence of fumed silica. This is because the fumed silica particles contain silanol on the surface, thus providing anchoring sites for the TEOS sol-gel reaction.²⁴⁻²⁶

Furthermore, we note that the Si-O-Si stretching band for the 20 wt % silica content becomes highly broadened in the TEOS membrane. This suggests that the highly crosslinked networks^{23,27,28} of TEOS were formed in the 20 wt % membrane. As a result, when the silica content was high in the membrane, network formation occurred easily by the sol-gel reaction. This is caused by the crucial role of fixed silica microparticles in the PAN membrane in providing anchoring sites to the sol-gel networks (**Scheme 1**).

Figure 5 presents AFM topography of the silica-PAN composite membrane surface before (a) and after (b) the TEOS sol-gel reaction. As seen in Figure 5(a) for a membrane without TEOS treatment, surface roughness increases with increased silica content. We noted that the surface grain size was increased by adding silica to the membrane. The values of mean surface roughness R_a (nm) were 6.8, 24.9, and 67.8 for 0, 3, and 20 wt % of fumed silica content in the PAN membranes, respectively. Figure 5(b) shows AFM images for the surface of the TEOS-treated membranes having 0, 3, and 20 wt % of fumed silica contents. It is obvious from the topography of 0 wt % of fumed silica content that the resulting membrane has small grains with $R_a = 56.7$ nm. When comparison was made between Figure 5(a) and 5(b) for no fumed silica membranes, it is clear that grain size was increased by the TEOS reaction. This indicates that the TEOS layer containing large size grains was formed on the mem-

brane surface, given that no silica was present in the PAN membrane. This was also indicated from FTIR data in Figure 4. That is, the value of the peak ratio at 0 wt % was high in the TEOS-treated membrane, indicating that the sol-gel reaction of TEOS proceeded in the PAN membrane. On the other hand, AFM images show that addition of silica powder to the membrane can increase formation of the TEOS layer near the silica microparticle aggregates. That is, TEOS layer grains were developed near the fumed-silica aggregates in the PAN membrane. For instance, Figure 5(b) shows 20 wt % contents. In addition, when silica content was increased from 3 to 20 wt %, the resulting value of R_a increased from 584 to 929 nm, respectively [Fig. 5(b)]. The AFM image for the 20 wt % content apparently indicates that the formed TEOS layer was developed on silica aggregates in composite membranes. It seems reasonable to infer **Scheme 1** from this evidence that the TEOS sol-gel process occurs in the silica composite PAN membrane.

Gas permselectivity of hybrid sol-gel membranes

In Figure 6, results of air mixture permeability for silica-PAN composite (closed symbol) and TEOS-PAN hybrid membranes (open symbol) were plotted against the membranes' silica content. Before TEOS treatment, values of O_2 and N_2 permeability were in the range of 1×10^{-11} to 5×10^{-11} ($\text{cm}^3 \text{ cm/cm}^2 \text{ s cmHg}$). Oxygen permeability of silica-PAN composite membranes was somewhat higher than that of nitrogen. On the other hand, oxygen permeability was enhanced effectively in the TEOS-PAN hybrid membranes. The data suggest that oxygen permeability strongly depends on the membranes' silica content. Below 13 wt % of silica content, values were in the range of 4×10^{-11} – 1×10^{-10} ($\text{cm}^3 \text{ cm/cm}^2 \text{ s cmHg}$). However, when the silica content was greater than 13 wt %, the oxygen permeability value increased significantly in the range of 1.75×10^{-10} to 2.7×10^{-10} ($\text{cm}^3 \text{ cm/cm}^2 \text{ s cmHg}$). Furthermore, in the silica content range, nitrogen permeability was apparently lowered. To compare oxygen and nitrogen permselectivity, $\alpha(\text{O}_2/\text{N}_2)$ was defined as the ratio of oxygen permeability [$P(\text{O}_2)$] to nitrogen one [$P(\text{N}_2)$] as in the following:

$$\alpha(\text{O}_2/\text{N}_2) = P(\text{O}_2)/P(\text{N}_2) \quad (2)$$

Figure 7 shows plots of $\alpha(\text{O}_2/\text{N}_2)$ against fumed silica contents for untreated and TEOS-treated membranes. The value of $\alpha(\text{O}_2/\text{N}_2)$ for an untreated PAN membrane was 1.7 because no silica was added. In the range between 0 and 20 wt %, the change of the $\alpha(\text{O}_2/\text{N}_2)$ value was insignificant for the untreated membrane. On the other hand, TEOS-treated membranes showed a notable difference of $\alpha(\text{O}_2/\text{N}_2)$ with

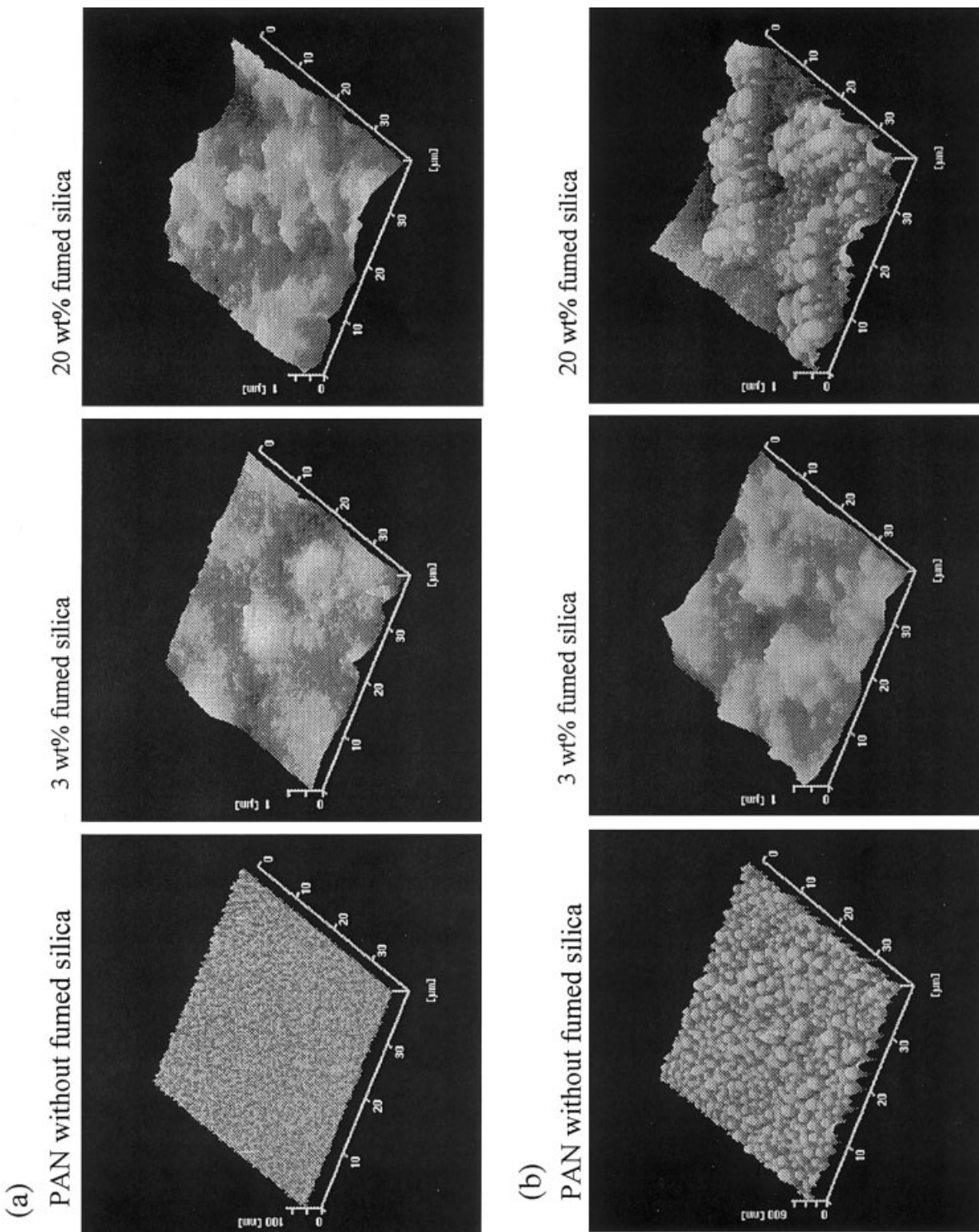


Figure 5 AFM images of (a) fumed silica-PAN composite membranes and (b) TEOS-treated silica-PAN hybrid membranes containing 0, 3, and 20 wt % of silica contents.

high silica content. Higher than 13 wt %, significant oxygen permeation was observed: $\alpha(O_2/N_2) = 13\text{--}17$ for the TEOS-PAN hybrid membranes. With the same silica content, $\alpha(O_2/N_2) = 1.6\text{--}3$ was shown for silica-PAN composite membranes. These observations indicate that the oxygen permeation rate across TEOS-treated PAN membranes was about 10 times faster than that of the membrane untreated with TEOS.

In this study, two hybrid membrane types were used for gas permeation experiments. One was a silica-compounded PAN membrane without TEOS treatment. Another was a silica-compounded TEOS-treated membrane. As mentioned in IR data for the latter system, Si-O-Si networks in the PAN membrane highly formed when the silica content was 20 wt %. Therefore, TEOS treatments also enhanced membrane rigidity because highly crosslinked networks were formed by the sol-gel reaction near anchoring sites of silica aggregates. As a result, N_2 permeability was lowered when TEOS networks were dense in the high silica content samples. As shown in **Scheme 1**, TEOS anchoring sites were embedded within the PAN membrane and Si-O-Si networks were developed among silica sites. This was supported by both IR and AFM results; TEOS-silica hybridization for a high-separation N_2/O_2 membrane system was effective for high silica aggregates in the PAN membrane. Hence, resistance to oxygen permeation may be determined by segmental restriction of networks to nitrogen. On the contrary, IR data suggested that silanol segments were present in the TEOS-treated membrane. In particular, the silanol concentration increased in cases of high silica content. Consequently, oxygen molecules may interact easily with silanol residue in Si-O-Si networks. That is, residual silanol segments may act ef-

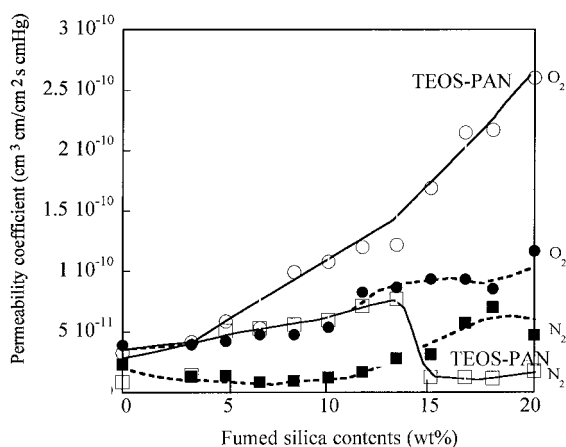


Figure 6 Permeability coefficients of oxygen and nitrogen of silica-PAN composite membranes and TEOS-treated silica-PAN hybrid membranes containing various amounts of silica contents. Closed symbols are for silica-PAN composite membranes and open symbols for the TEOS hybrid membranes.

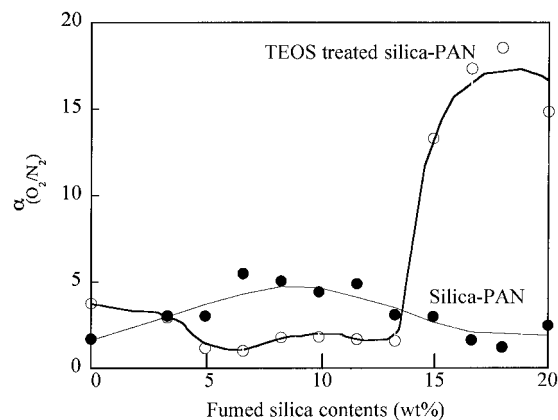


Figure 7 Plots of $\alpha(\text{oxygen/nitrogen})$ versus silica contents in membranes without (●) and with TEOS treatment (○).

ficiently on facilitated transport of oxygen.²⁹ Results for gas separation with higher permeability suggest the possibility of application of silica-PAN hybrid membrane to oxygen-enriched processes.

CONCLUSIONS

Hybrid silica PAN membranes treated with TEOS were prepared by sol-gel reaction. Fumed silica contents were changed in the range from 1.3 to 20 wt % in the PAN membranes. Then, these membranes were treated with TEOS for Si-O-Si network formation. We examined the effect of silica content in the PAN cast solution on membrane properties and O_2/N_2 permeability. We demonstrated efficient separation of the O_2/N_2 mixture when a dense Si-O-Si network was present in silica-PAN composite membranes that had high fumed silica content. Permselective oxygen by TEOS-treated silica-PAN hybrid membranes was demonstrated in gas-separation systems.

References

- Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic: Dordrecht, 1991.
- Winston Ho, W. S.; Sirkar, K. K. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992.
- Noble, R. D.; Stern, S. A. *Membrane Separations Technology. Principles and Applications*; Elsevier: Amsterdam, 1995; and references cited therein.
- Matsuura, T. *Synthetic Membranes and Membrane Separation Processes*; CRC Press: Boca Raton, FL, 1994; p. 412.
- Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic: Dordrecht, 1991; p. 39.
- Aoki, T.; Nakahara, H.; Hayakawa, Y.; Kokai, M.; Oikawa, E. *J Polym Sci Part A: Polym Chem* 1994, 32, 849.
- Aoki, T.; Shin, K.; Oikawa, E. *Polym J* 1996, 28, 106.
- Shin, K.; Aoki, T.; Oikawa, E. *Macromol Rapid Commun* 1995, 16, 599.
- Morikawa, A.; Yamaguchi, H.; Kakimoto, M.; Imai, Y. *Chem Mater* 1994, 6, 913.
- Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum Press: New York, 1991.

11. Sanchez, C.; Ribot, F. *New J Chem* 1994, 18, 1007.
12. Clark, H. A.; Plueddemann, E. P. *Mod Plast* 1963, 40, 133.
13. Brinker, C. J.; Sehgal, R.; Raman, N.; Schunk, P. R.; Headley, T. J. *J Sol-Gel Sci Technol* 1994, 2, 469.
14. Anderson, M. A.; Gieselmann, M. J.; Xu, Q.; *J Membr Sci* 1988, 39, 243; *Polymer* 1984, 25, 963.
15. Lai, J. Y.; Chou, C. C. *J Appl Polym Sci* 1989, 37, 1465.
16. Changrong, X.; Huaqiqng, C.; Hong, W.; Pinghug, Y.; Guangyao, M.; Dingkun, P. *J Membr Sci* 1999, 162, 181.
17. Smahi, M.; Schrotter, J.-C.; Lesimple, C.; Prevost, I.; Guizard, C. *J Membr Sci* 1999, 161, 157.
18. Moaddeb, M.; Koros, W. J. *J Membr Sci* 1996, 111, 283.
19. Moaddeb, M.; Koros, W. J. *J Membr Sci* 1997, 125, 143.
20. Yamadera, R. *Koubunshikagaku* 1964, 230, 362.
21. Stupp, S. I.; Carr, S. H. *J Polym Sci Polym Phys Ed* 1977, 15, 485.
22. Coleman, M. M.; Petcavich, R. J. *J Polym Sci Polym Phys Ed* 1978, 16, 821.
23. Smith, A. L. *Analysis of Silicone*; Wiley: New York, 1974; p. 247.
24. Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum Press: New York, 1991; p. 72.
25. Merrill, R. C.; Spencer, R. W. *J Phys Colloid Chem* 1950, 54, 506.
26. Plueddemann, E. P. U.S. Pat. 4,370,255, 1983.
27. Alvic, T.; Dale, J. *Acta Chem Scand* 1971, 25, 2142.
28. Kobayashi, T.; Takahashi, S.; Fujii, N. *J Appl Polym Sci* 1993, 49, 417.
29. Winston Ho, W. S.; Sirkar, K. K. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992; p. 842.