Effects of Supercritical Carbon Dioxide Treatment Conditions on the Gas Separation Properties of Polydimethylsiloxane Hybrid Membrane Materials for Air Purification

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ABSTRACT: A siloxane/polydimethylsiloxane (PDMS) hybrid membrane containing fluorinated side chains was prepared by a convenient and mild sol–gel process and a crosslinking reaction. The effects of the supercritical carbon dioxide (scCO$_2$) conditions (i.e., treatment temperature, treatment time, and treatment pressure) on the permeation properties of fluorinated PDMS containing hybrid membrane were investigated. The chemical structure, microstructure, and physical performance of the membranes treated before and after were also discussed. The chemical structure of the PDMS membranes did not change with the scCO$_2$ treatment conditions. The membranes still retained better membrane-forming abilities, higher permeability, and selectivity than normal PDMS membranes. Compared to those of the membrane with membrane formation after scCO$_2$ treatment, the oxygen permeability coefficient and oxygen/nitrogen separation factor of the membrane with scCO$_2$ treatment before membrane formation were higher and were up to 7.11 $\times$ 10^{-8} cm^3 (STP) cm/(cm^2 s cmHg) and 3.27, respectively. The permeation properties of the hybrid membrane were obviously higher than those of Robeson's upper bound. The high air-purification performance of the hybrid membrane may have been due to the introduction of fluorine atoms into PDMS membrane, and the increase in free volume resulted from the plasticizing function of the scCO$_2$ treatment. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

For many years, polydimethylsiloxane (PDMS) has received considerable attention as a special membrane material for gas separation because of its intrinsically high permeation rate.[1,2] Therefore, PDMS has become one of the most important transport membranes for oxygen among commercially available polymeric membranes. However, its oxygen/nitrogen ideal separation factor is very low, and its membrane-forming ability is so poor that direct applications are limited. At present, organic–inorganic hybrid membranes have attracted considerable attention as potential next-generation membrane materials because such hybrid materials have the potential to combine the desired properties of organic and inorganic systems, for example, to improve the thermal properties of inorganic ones with the flexibility and selectivity of organic ones.[3–8] In a previous work,[9] we prepared a siloxane/(PDMS) hybrid membrane containing fluorinated side chains with a convenient and mild sol–gel process and a crosslinking reaction. The oxygen permeability coefficient was 6.02 $\times$ 10^{-8} cm^3 (STP) cm/(cm^2 s cmHg) and the oxygen/nitrogen separation factor was up to 3.47. The permeation

properties of the fluorinated hybrid membrane were obviously higher than those of Robeson's upper bound and normal PDMS membranes.

Supercritical carbon dioxide (scCO$_2$) is a clean and versatile solvent and a promising alternative to noxious organic solvents and chlorofluorocarbons. It has attracted particular attention as a supercritical fluid in chemical synthesis and in processing areas for polymers because of its appealing and unique properties. It is a green medium because of its nontoxic, nonflammable, chemically inert, inexpensive, and environmentally friendly properties.[10] In addition, scCO$_2$ has attracted a great deal of interest in both the academic and industrial fields for polymeric applications, such as polymer modification,[11] polymer blending,[12] the formation of polymer composites,[13] microcellular foaming,[14] particle production,[15] and polymerization,[16] where CO$_2$ plays the role of a plasticizer, solvent, or antisolvent.

scCO$_2$ is a good solvent for many nonpolar (and some polar) compounds with low molecular weight[17] and for a few polymers, such as certain amorphous fluoropolymers and silicon-containing polymers.[18–21] Only fluoropolymers and silicon-containing

polymers can be dissolved in $scCO_2$; carbon-chain polymers and heterochain polymers are indissoluble, but they can be swelled and plasticized. Thereby, $scCO_2$ may be used as a plasticizing agent and a swelling agent and can enhance the free volume of some carbon-chain polymers and heterochain polymers. Koros[22] reported that $scCO_2$ tends to plasticize glassy polymers and reduce the separating efficiency of the membrane. It is clear that the use of $scCO_2$ is becoming more prevalent and that polymeric membranes can play an important role in the purification and reuse of CO_2 in the supercritical state. Nevertheless, few studies have explored the application of $scCO_2$ conditions in the field of high-performance rubber polymer membranes for gas separation.[23,24]

The objective of this study was to improve the air-purification performance of PDMS membrane materials by means of $scCO_2$. In this study, a PDMS hybrid membrane containing fluorinated side chains was first prepared, and the effects of the $scCO_2$ conditions on the permeation properties of the PDMS hybrid membrane were investigated.

EXPERIMENTAL

Materials

PDMS, polymethylhydrosiloxane, and chloroplatinic acid solution (as a catalyst) were purchased from the Research Center of Organic Silicone (Chengdu, China). The number-average molecular weight of PDMS was 500,000, and the vinyl content was 10 mol %. The hydrogen content of polymethylhydrosiloxane was 1.5 mass %. Vinyl trimethoxysilane and 13-fluorinated triethoxysilane were supplied by Fine Chemical Institute of Silicone and Fluoride (Guangzhou, China). All other solvents and chemical agents were analytical grade and were used without further purification. Pure gases, O_2 and N_2, were purchased from Guangzhou Gas, Ltd., China. All of the gases used had a minimum purity of 99.9%.

Preparation of the Crosslinking Agent and the Hybrid Solution

The preparation of the crosslinking agent and the hybrid solution were reported in our previous work.[9]

Preparation of the Crosslinking Agent

According to a molar ratio of 1:1, polymethylhydrosiloxane and vinyl trimethoxysilane were mixed in an ice bath under vigorous mechanical stirring. Proper chloroplatinic acid solutions were added slowly to the mixed solution under a nitrogen inlet. The reaction times continued for 2 h at room temperature, for 2 h at 40°C, and for 12 h at 60°C under mechanical stirring. A straw-yellow transparent crosslinking agent was obtained.

Preparation of the Hybrid Solution

PDMS (1.0 g) was dissolved in 25 mL of tetrahydrofuran (THF) under continuous mechanical agitation to form a PDMS solution. The previous crosslinking agent (0.265 g) and appropriate chloroplatinic acid solutions were dropped slowly into the PDMS solution and stirred for 1 h at room temperature. The mass percentages (10 wt %) of 13-fluorinated triethoxysilane were added to the PDMS solution. The solutions were hydrolyzed in the presence of an acid catalyst by the addition of an appropriate amount of 0.5 M HCl, and the pH values of the sol

Table I. $scCO_2$ Treatment Conditions of the PDMS Solutions

No.	Treatment temperature (°C)	Treatment pressure (MPa)	Treatment time (h)
1	30	10	2–3
2	40	10	2–3
3	50	10	2–3
4	60	10	2–3
5	60	15	2–3
6	60	20	2–3
7	60	25	2–3
8	60	15	4–5
9	60	15	1–2

were adjusted to 4 at room temperature. After 1 h, the solutions with various proportions of 13-fluorinated triethoxysilane sol were obtained.

$scCO_2$ Treatment Conditions and Membrane Preparation

The $scCO_2$ treatment conditions of the previous PDMS solutions are listed in Table I. We prepared the PDMS hybrid membranes by casting the sol onto a poly(ethylene terephthalate) sheet at room temperature. The resulting membranes were easily removed after 12 h, and then, they were dried in a vacuum for 24 h at 65°C to remove any residual solvent. The flexible and transparent hybrid membranes were approximately 40 μm thick; this was roughly calculated by the determination of the thickness of more than five locations on any of the membranes.

To further determine the effects of the $scCO_2$ conditions on the permeation properties of the PDMS hybrid membrane, a series of membranes were prepared by $scCO_2$ treatment after membrane formation; that is, the hybrid membrane was prepared first with the PDMS hybrid solutions, and then, the hybrid membrane was treated according to previous $scCO_2$ treatment conditions.

Characterizations

Fourier Transform Infrared (FTIR) Spectroscopy Measurement. FTIR spectra of the membrane samples with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation were obtained with a Bruker EQUINX 55 (Ettlingen, Germany). Each sample was vacuum-dried at 80°C for 24 h to remove the absorbed water in the membranes.

Scanning Electron Microscopy (SEM) Observation. The substrate-facing surface (SFS) and the fracture surface (FS) of the hybrid membrane samples with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation were coated with gold and observed with a scanning electron microscope (JEOL JSM-T300, München, Germany).

Swelling Testing. To determine the relationship between the physical performance and the chemical crosslinking degree, the swelling behavior of the hybrid membranes with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation were studied. The swelling index (SI), which is the slope of the rebound curve of the void ratio versus the
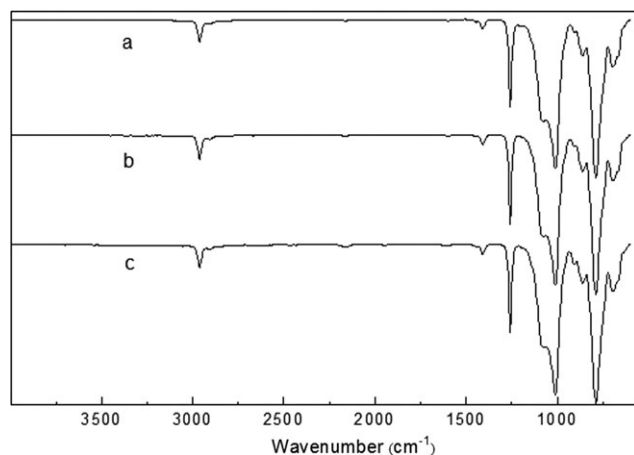
Figure 1. FTIR spectra of the membrane samples with (a) no treatment, (b) membrane formation after $scCO_2$ treatment, and (c) $scCO_2$ treatment after membrane formation.

logarithm of the effective pressure curve, was used to estimate the consolidation settlement of overconsolidated fine grained soils. The membranes were dipped in THF, xylene, toluene, and chloroform, respectively, for 4 h at room temperature. The SI was calculated by the following equation:

$$SI\,(\%) = (W_2 - W_1)/W_1 \times 100 \qquad (1)$$

where W_1 and W_2 are the initial and final (swollen) weights of the sample, respectively.[25]

Mechanical Properties. The mechanical properties of the hybrid membranes with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation were measured with a Shimadzu AG-I (Japan). The samples prepared were 20 mm (length) $\times$ 100 μm (thickness) $\times$ 16 mm (width), and the elongation rate was 30 mm/min. Every sample was tested three times at room temperature.

Permeation Measurements. According to the constant pressure/variable-volume method of Stern,[26] the oxygen and nitrogen permeability coefficients of the hybrid membranes were measured. The apparatus and experimental procedure used for the gas permeability measurements were described in the literature.[27–30] The oxygen permeability coefficient, nitrogen permeability coefficient, and ideal separation factor were calculated according to our previous reports and other literature.[9,28–30]

RESULTS AND DISCUSSION

Characterization

Chemical Structure Analysis. The chemical structure changes under the $scCO_2$ treatment conditions were monitored by FTIR spectroscopy and are shown in Figure 1. The structural characteristics of the membrane samples with no treatment [Figure 1(a)], membrane formation after $scCO_2$ treatment [Figure 1(b)], and $scCO_2$ treatment after membrane formation [Figure 1(c)] were characterized with FTIR analysis. As shown in Figure 1, the characteristic peaks of the O—Si—O groups at 1408 and 787 cm^{-1} were in the FTIR spectra, and the characteristic peaks of C—F groups at 1258 and 1009 cm^{-1} were also in the spectra. These

suggested that the chemical structure of the hybrid membrane showed no change after and before $scCO_2$ treatment.

Morphological Analysis of the Hybrid Membrane. The morphology of the hybrid membrane samples was further studied by SEM imaging. The characteristics of SFS and FS for the hybrid membrane under $scCO_2$ conditions were examined, as shown in Figure 2. As indicated in Figure 2, the membranes showed a completely amorphous morphology, either SFS or FS. The hybrid membrane had better membrane-forming properties, which were attributed to the occurrence of covalent bonds and the mutual network between the organic phase and the inorganic phase. The high transparency of the hybrid membrane implied that there should have been no macrophase separation and that there was good compatibility between the polymeric component and inorganic component.

Swelling Properties of the Membranes. Because the crosslinked polymers only swelled but did not dissolve in the organic solvents, the swelling degrees of the crosslinked membranes reflected their crosslinking degree chemically. Hence, the swelling degrees of the membranes for some typical solvents, such as xylene, THF, and chloroform were measured at room temperature to estimate their crosslinking behavior. The swelling test was carried out to make a membrane sample immersed in a solvent at 30°C for 4 h. The SIs of the membranes for different solvents, calculated according to the testing results, are listed in Table II. It can be seen that the SIs of the hybrid membrane under $scCO_2$ conditions were smaller than those of the pure PDMS membrane for the same solvents.

Mechanical Properties of the Hybrid Membrane. In general, the mechanical properties can show membrane-forming ability, segmental flexibility, structure–property relationships, and permselectivity of polymeric membranes. So, we investigated the mechanical properties of the hybrid membranes under $scCO_2$ conditions. The results are summarized in Table III. The mechanical properties of the hybrid membranes were related to the $scCO_2$ treatment conditions. The strain, stress, and elongation values of the hybrid membranes under $scCO_2$ conditions decreased significantly because of the swelling properties of the hybrid membranes under $scCO_2$ conditions. The results for the mechanical properties of the hybrid membranes under $scCO_2$ conditions were in accordance with the swelling properties. Therefore, we speculated that the $scCO_2$ treatment conditions had an effect on the gas separation properties of the hybrid membrane.

Effects of the $scCO_2$ Treatment Conditions on the Permeation Properties

On the basis of a convenient and mild sol–gel process and a crosslinking reaction, the hybrid membrane containing fluorinated side chains was also prepared with 13-fluorinated triethoxysilane and PDMS containing vinyl groups as matrix materials. According to the previous characterization, the chemical structure and morphology of the hybrid membrane showed little or no change after and before $scCO_2$ treatment. Previous research demonstrated that crosslinking can be a powerful approach for improving the performance of rubbery polymers.[9,30] Crosslinking can provide enhanced plasticization
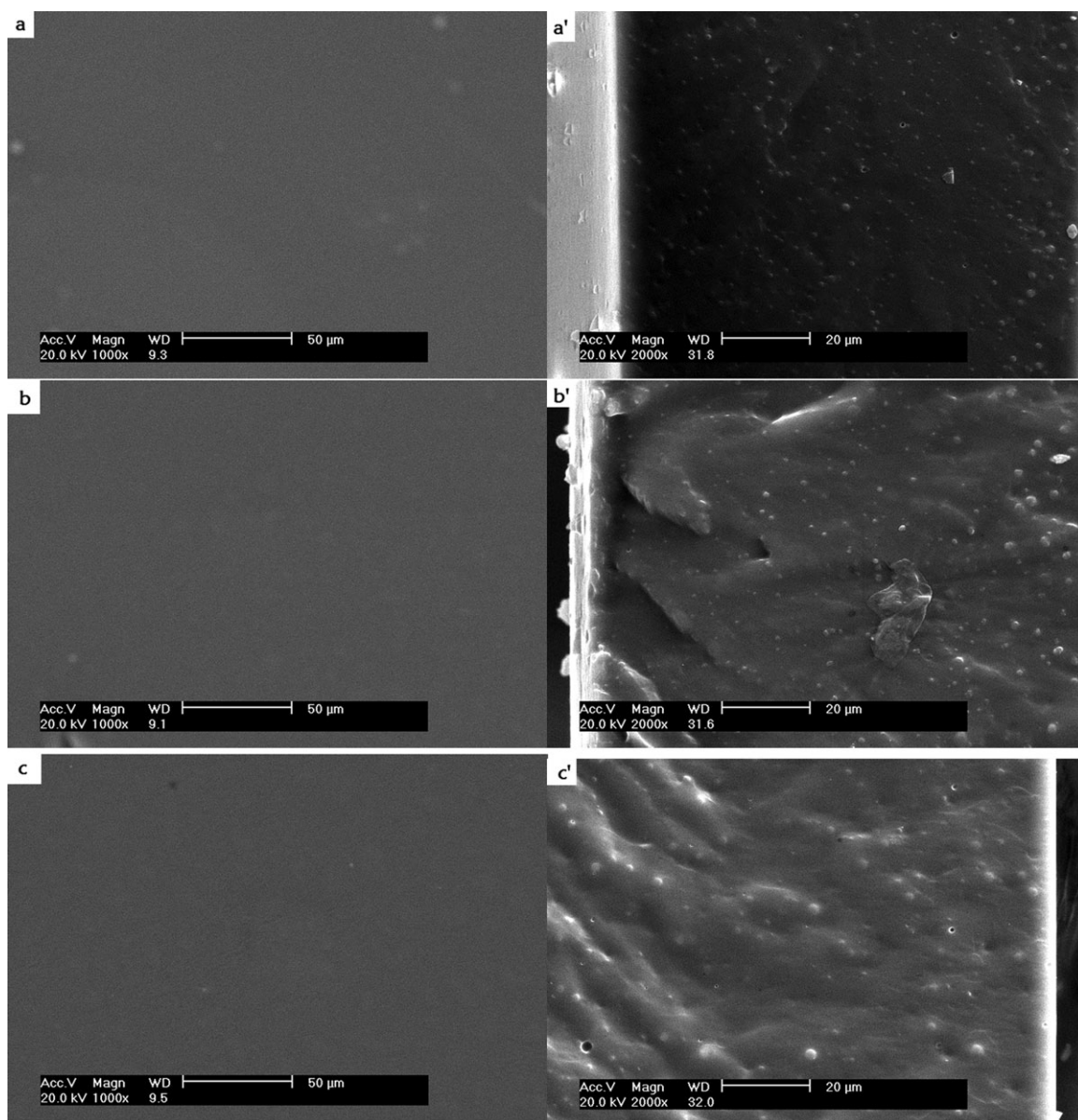
Figure 2. SEM photographs of the hybrid membranes with (a) no treatment, (b) membrane formation after $scCO_2$ treatment, and (c) $scCO_2$ treatment after membrane formation. The figure shows the SFS and the FS.

resistance and can also provide intrinsic selectivity increases in some cases.[23,31,32] In addition, the mechanical properties of $scCO_2$ are highly dependent on the pressure and temperature; this makes it possible to fine-tune the reaction environment. Therefore, we investigated the effects of the $scCO_2$ conditions on the permeation properties of the fluorinated PDMS hybrid membrane. The effects of different treatment temperatures, treatment times, and treatment pressures on the oxygen permeability coefficient, nitrogen permeability coefficient, and oxygen/nitrogen separation factor are listed in Table IV (testing temperature = 30°C and pressure difference = 0.1 MPa).

Table II. Swelling Indices of the PDMS Hybrid Membranes under $scCO_2$ Conditions for Several Different Solvents

Membrane	Xylene	THF	Chloroform
Untreated	1.08 ± 0.01	1.00	0.97 ± 0.02
Membrane formation after $scCO_2$ treatment	1.05 ± 0.01	1.00	0.91 ± 0.02
$scCO_2$ treatment after membrane formation	1.03 ± 0.02	1.00	0.94 ± 0.01

Treatment Pressure. The properties of $scCO_2$ are very sensitive to small changes in the pressure and temperature and may have influenced the permselectivity of the hybrid membrane. As shown in Table IV, the oxygen permeability coefficient and nitrogen permeability coefficient of the hybrid membranes with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation exhibited little or no change

Table III. Mechanical Performances of the Hybrid Membrane under $scCO_2$ Conditions

Membrane	Strain at break (%)	Stress at break (MPa)	Elastic (MPa)
Untreated membrane	1.965 ± 0.003	1.611 ± 0.004	0.820 ± 0.005
Membrane formation after $scCO_2$ treatment	1.814 ± 0.002	1.512 ± 0.004	0.781 ± 0.003
$scCO_2$ treatment after membrane formation	1.823 ± 0.003	1.595 ± 0.002	0.802 ± 0.002

with increasing treatment pressure. For the hybrid membrane under $scCO_2$ treatment after membrane formation, the oxygen/nitrogen separation factor increased with increasing treatment pressure and was up to 3.32 under a treatment temperature of 60°C, a treatment time of 2 h, and a treatment pressure of 25 MPa. However, for the hybrid membrane with membrane formation after $scCO_2$ treatment, the oxygen/nitrogen separation factor decreased with increasing treatment pressure.

Treatment Temperature. For the hybrid membrane with membrane formation after $scCO_2$ treatment, the oxygen permeability coefficient and nitrogen permeability coefficient decreased, and the oxygen/nitrogen separation factor increased with increasing treatment temperature. For the hybrid membrane with $scCO_2$ treatment after membrane formation, the oxygen permeability coefficient and nitrogen permeability coefficient increased with increasing treatment temperature, and the oxygen/nitrogen separation factor remained between 3.1 and 3.3.

Treatment Time. The oxygen permeability coefficient and nitrogen permeability coefficient of the hybrid membranes with membrane formation after $scCO_2$ treatment and $scCO_2$ treatment after membrane formation exhibited little or no change with increasing treatment time. For the hybrid membrane with membrane formation after $scCO_2$ treatment, the oxygen/nitrogen separation factor increased with increasing treatment time. However, for the hybrid membrane under $scCO_2$ treatment after membrane formation, the oxygen/nitrogen separation factor increased first and then decreased with increasing treatment time.

Treatment Method. The oxygen/nitrogen separation factors of the hybrid membrane with membrane formation after $scCO_2$ treatment and for $scCO_2$ treatment after membrane formation were smaller than those of the untreated hybrid membrane. However, the oxygen permeability coefficients and nitrogen permeability coefficients of the hybrid membrane with $scCO_2$ treatment after membrane formation were larger than those of the untreated hybrid membrane and the hybrid membrane with membrane formation after $scCO_2$ treatment.

According to previous reports, only fluoropolymers and silicon-containing polymers can be dissolved in $scCO_2$; other polymers

Table IV. Permeability Coefficient and Ideal Separation Factor of the Hybrid Membrane under Different $scCO_2$ Conditions

Membrane	$ScCO_2$ treatment conditions	O_2 permeability coefficient (Barrer)	N_2 permeability coefficient (Barrer)	O_2/N_2 separation factor
Untreated		649.1 ± 0.5	190.8 ± 0.2	3.40
Membrane formation after $scCO_2$ treatment	30°C, 10 MPa, 2–3 h	665.8 ± 0.8	214.8 ± 0.1	3.10
	40°C, 10 MPa, 2–3 h	571.6 ± 0.7	180.9 ± 0.2	3.16
	50°C, 10 MPa, 2–3 h	564.2 ± 1.2	176.9 ± 0.4	3.19
	60°C, 10 MPa,2–3 h	551.3 ± 0.6	171.7 ± 0.1	3.32
	60°C, 15 MPa, 2–3 h	548.1 ± 0.5	171.3 ± 0.3	3.20
	60°C, 20 MPa, 2–3 h	544.3 ± 0.8	171.2 ± 0.2	3.18
	60°C, 25 MPa, 2–3 h	536.4 ± 1.3	170.3 ± 0.3	3.15
	60°C, 15 MPa, 1–2 h	545.1 ± 0.3	170.3 ± 0.2	3.20
	60°C, 15 MPa, 4–5 h	547.3 ± 0.2	169.4 ± 0.4	3.23
$scCO_2$ treatment after membrane formation	30°C, 10 MPa, 2–3 h	673.5 ± 0.4	215.2 ± 0.5	3.13
	40°C, 10 MPa, 2–3 h	693.4 ± 0.1	216.0 ± 0.1	3.21
	50°C, 10 MPa, 2–3 h	711.6 ± 0.2	217.6 ± 0.2	3.27
	60°C, 10 MPa, 2–3 h	724.8 ± 0.5	219.6 ± 0.2	3.20
	60°C, 15 MPa, 2–3 h	720.1 ± 0.6	219.5 ± 0.1	3.28
	60°C, 20 MPa, 2–3 h	728.5 ± 0.3	221.4 ± 0.1	3.29
	60°C, 25 MPa, 2–3 h	735.2 ± 0.2	221.4 ± 0.2	3.32
	60°C, 15 MPa, 1–2 h	718.4 ± 0.8	222.4 ± 0.2	3.23
	60°C, 15 MPa, 4–5 h	722.8 ± 0.1	221.7 ± 0.4	3.26

Testing temperature = 30°C and pressure difference = 0.1 MPa.

are indissoluble but can be swollen and plasticized. On the basis of the previous experimental characterization, the chemical structure and morphology of the hybrid membrane before and after $scCO_2$ treatment showed no change. So, the $scCO_2$ conditions had no obvious effect on the permeation properties of the hybrid membrane.

Early researchers recognized that fluorinated polymers possess many unique and useful properties, such as chemical and thermal stability. In this study, hybrid membranes under $scCO_2$ treatment conditions still possessed better oxygen permeabilities and oxygen/nitrogen selectivities. These attributes stemmed from their strong covalent carbon–carbon and carbon–fluorine bonds and the protective sheath of fluorine atoms around the carbon backbone.[33]

CONCLUSIONS

$scCO_2$ is commonly used for the synthesis and modification of polymers because of its accessible critical conditions, low cost, and low toxicity. In this study, novel PDMS hybrid membranes containing fluorinated side chains were first prepared by a mild sol–gel process and a crosslinking reaction. The effects of the $scCO_2$ treatment conditions, such as treatment temperature, treatment time, and treatment pressure, on the permeation properties of the containing fluorinated membrane were investigated. Surprisingly, the $scCO_2$ conditions had no obvious effect on the permselectivity of the membrane, and the membrane still possessed better permeabilities and selectivities. Before and after $scCO_2$ treatment, the separation factors for the hybrid membranes remained relatively unchanged, and the permeability coefficient of the membrane with $scCO_2$ treatment after membrane formation increased slightly. These results may have been due to the enhancements of additional free volume under $scCO_2$ conditions.

ACKNOWLEDGMENTS

REFERENCES

1. Stern, S. A. *J. Membr. Sci.* **1994,** *94*, 1.

2. Aoki, T. *Prog. Polym. Sci.* **1999,** *24*, 951.

3. Zhong, S. H.; Sun, H. W.; Wang, X. T.; Shao, H. Q.; Guo, J. B. *J. Membr. Sci.* **2006,** *278*, 212.

4. Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. *J. Science* **2002,** *296*, 519.

5. Yeon, S. H.; Lee, K. S.; Sea, B.; Park, Y. I.; Lee, K. H. *J. Membr. Sci.* **2005,** *257*, 156.

6. Uragami, T.; Okazaki, K.; Matsugi, H.; Miyata, T. *Macromolecules* **2002,** *35*, 9156.

7. Liu, J. S.; Ma, Y.; Hu, K. Y.; He, H. M.; Shao, G. Q. *J. Appl. Polym. Sci.* **2010,** *117*, 2464.

8. Hibshman, C.; Cornelius, C. J.; Marand, E. *J. Membr. Sci.* **2003,** *211*, 25.

9. Rao, H. X.; Zhang, Z. Y.; Song, C.; Qiao, T.; Xu, S. B. *Sep. Purif. Technol.* **2011,** *78*, 132.

10. Sameer, P. N.; Francesco, P.; Janssen, L. P. *Prog. Polym. Sci.* **2006,** *31*, 19.

11. Rao, H. X.; Zhang, Z. Y. *Polym. Adv. Technol.* **2008,** *19*, 770.

12. Cansell, F.; Aymonier, C. *J Supercrit Fluid* **2009,** *47*, 508.

13. Ohde, H.; Ohde, M.; Wai, C. M. *Chem. Commun.* **2004,** *8*, 930.

14. Liu, H. C.; Shih, H. H.; Tsai, C. C.; Wu, C. T.; Liu, W. B. U.S. Pat. 2,003,057,197 (**2003).**

15. Xu, A. H.; Yuan, Z. W.; Zhao, J. H.; Li, H.; Zhang, H.; Zhang, Y. M. *J. Appl. Polym. Sci.* **2012,** *124*, 1785.

16. Zhang, Z. Y.; Huang, K. J.; Liu, Z. H. *Macromolecules* **2011,** *44*, 820.

17. Hyatt, J. A. *J. Org. Chem.* **1984,** *49*, 5097.

18. De Simone, J. M.; Guan, Z. *Science* **1992,** *257*, 945.

19. Yilgor, I.; McGrath, J. E.; Krukonis, V. *J. Polym. Bull.* **1984,** *12*, 499.

20. Guan, Z.; Combs, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993,** *26*, 2663.

21. Hoefling, T. A.; Newman, D. A.; Enick, R. M.; Beckman, E. J. *J. Supercrit. Fluid* **1993,** *6*, 165.

22. Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. *J. Macromolecules* **2003,** 36, 1882.

23. Kratochvil, A. M.; Koros, W. *J. Macromolecules* **2010,** *43*, 4679.

24. Kratochvil, A. M.; Damle-Mogri, S.; Koros, W. *J. Macromolecules* **2009,** *42*, 5670.

25. Mathew, L.; Joseph, K. U.; Joseph, R. *Bull. Mater. Sci.* **2006,** *29*, 91.

26. Stern, S. A.; Sinclair, T. F.; Gareis, P. A. *Mod. Plast.* **1964,** *42*, 154.

27. Hong, J. M.; Lee, S. W. *J. Ind. Eng. Chem.* **1997,** *3*, 165.

28. Zimmerman, C. M.; Koros, W. *J. Macromolecules* **1999,** *32*, 3341.

29. Benny, D. F. *Macromolecules* **1999,** *32*, 375.

30. Rao, H. X.; Zhang, Z. Y. *J. Appl. Polym. Sci.* **2012,** *123*, 191.

31. Hillock, A. M. W.; Koros, W. *J. Macromolecules* **2007,** *40*, 583.

32. Wallace, D. W.; Williams, J. P.; Staudt-Bickl, C.; Koros, W. *J. Polymer* **2006,** *47*, 1207.

33. Drobny, J. G. Technology of Fluoropolymers; CRC: Boca Raton, FL, **2001;** p 172.