Preparation and High Oxygen-Enriching Properties of Cross-Linking Polydimethylsiloxane/SiO_2 Nanocomposite Membranes for Air Purification

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Nanocomposite membrane based on polydimethylsiloxane (PDMS) and nanoscale SiO_2 particles were prepared by a convenient and mild sol–gel copolymerization of tetraethoxysilane as well as cross-linking reaction. The oxygen-enriching properties of cross-linking PDMS/SiO_2 nanocomposite membranes containing different silica conversion and SiO_2 contents were investigated. The results showed that the nanocomposite membranes exhibited good membrane-forming ability, superior mechanical properties, and high solvent resistance as well as excellent oxygen-enriching properties for air purification. The oxygen-enriching performance was regulated by the organic/inorganic ratio and silica conversion in the sol–gel synthesis process. Permeability and selectivity could increase simultaneously with the addition of nanoscale SiO_2. The oxygen permeation coefficient of the nanocomposite membrane increased to 680 Barrer and oxygen/nitrogen separation factor kept 3.0 or so, both higher than those of the corresponding pure PDMS membrane. The high oxygen-enriching properties of the nanocomposite membranes arose from the introduction of SiO_2 particles, the sol–gel copolymerization, and cross-linking method. © 2012 American Institute of Chemical Engineers *AIChE J*, 59: 650–655, 2013
Keywords: oxygen-enriching properties, nanocomposite membrane, sol–gel copolymerization, cross-linking, polydimethylsiloxane

Introduction

Recently, nanocomposite membranes have received considerable attention in the past decade as a special membrane material for gas separation and selective separation because they have the potential to combine the desired properties of organic and inorganic systems, for example, improving the thermal properties of inorganic ones with the flexibility and selectivity of organic ones.[1–10] The nanocomposite membranes show much higher gas permeabilities but similar or even improved gas selectivities compared to the typical polymeric membranes and have potential to provide a solution to the trade-off between gas permeability and selectivity as suggested by Robeson.[1,11–13] The preparation technology of the nanocomposite membranes includes the following three types, solution blending, *in situ* polymerization, and sol–gel copolymerization.[2,14–16] The previous two methods are difficult to avoid the aggregation of inorganic nanoparticles in the formed membranes. The sol–gel method is the most widely used preparation technology for nanocomposite membranes because of its moderate reaction conditions and easy controllability for the concentrations of organic and inorganic components.[4,17,18]

Polydimethylsiloxane (PDMS) membranes have an excellent oxygen permeability coefficient for air purification, which is attributed to its large free volume due to the flexibility of the siloxane linkages.[19–21] However, its oxygen/nitrogen ideal separation factor is very low, and its membrane-forming ability is so poor that direct applications are limited. PDMS membrane is a rubber polymeric membrane. However, for nanocomposite membranes based on rubber polymers by sol–gel process in a polymer matrix, an increase in selectivity but a decrease in permeability and vice versa were observed.[22,23] The gas separation performance of nanocomposite membranes can be further enhanced by chemical modification.[4] For example, cross-linking including covalent bonds and metal ion bonds is very effective in reinforcing polymeric membrane materials and improving gas selectivity.[24–26] In our previous researcher, cross-linking method could obviously enhance oxygen-enriching properties of PDMS membranes. Therefore, in the article, we first prepared a cross-linked PDMS solution based on PDMS containing vinyl groups and a cross-linking agent as matrix materials to increase gas separation performance. Then nanocomposite membranes based on the cross-linked PDMS, tetraethyl orthosilicate (TEOS), and nanoscale SiO_2 were synthesized by sol–gel copolymerization to improve simultaneously gas permeability and gas selectivity of PDMS membranes. The effect of nanoscale SiO_2 content and silica conversion on oxygen-enriching properties of PDMS nanocomposite membranes was investigated and discussed in the article.

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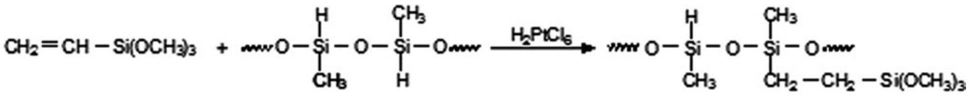


Scheme 1. Synthesis of the cross-linking agent.

Experimental

Materials

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

Synthesis of the cross-linking agent

According to molar ratio of 1:1, polymethylhydrosiloxane and VTMO were mixed in ice-bath under vigorous mechanical stirring. Chloroplatinic acid solutions (0.01 g) were added slowly into the mixed solution under 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 and transparent cross-linking agent was obtained. The synthesis of the cross-linking agent was shown in Scheme 1.

Nanocomposite membrane preparation

PDMS (1.0 g) was dissolved in 25 mL tetrahydrofuran (THF) under continuous mechanical agitation to form a PDMS solution. The above cross-linking agent (0.24 g) and chloroplatinic acid solutions (0.01 g) were dropped slowly into the PDMS solution and stirred for 1 h at room-temperature. Nanoscale SiO_2 (2.5 wt %, 0.025 g) and nanoscale SiO_2 (5.0 wt %, 0.05 g) were added into the PDMS solution, respectively. The solution was stirred to form a uniform mixture solution. Then, predetermined amounts, 5–40 wt % (based on polymer content) of TEOS were added to the PDMS mixture solutions. A 0.5 M HCl aqueous solution was then dropped. The sol was obtained by the hydrolysis of TEOS in THF with the H_2O/TEOS mol ratio of 4, the TEOS/THF volume ratio of 3, and a pH value of 4 at room-temperature after stirring vigorously for 2 h at 60°C.

The nanocomposite membranes were prepared by casting the sol onto a polyethylene terephthalate (PET) sheet at room-temperature. The resulting membranes were easily removed after 12 h and then dried in a vacuum for 24 h at 60°C to remove any residual solvent. The flexible and transparent nanocomposite membranes were approximately 40–60-μm thick, roughly calculated by determining the thickness of more than five locations on any membranes. The preparation process of the nanocomposite membranes was shown in Scheme 2.

Permeation measurements

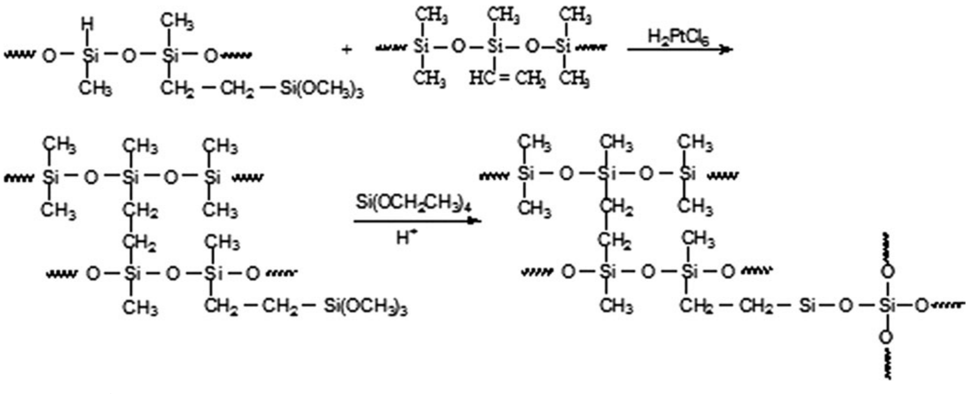
The oxygen and nitrogen permeability coefficients (1 Barrer = 10^{-10} cm^3 standard temperature and pressure (STP) cm/(cm^2 s cm Hg)) of the membranes were measured according to the variable-volume method of Stern et al.[27] The operation process is described elsewhere.[26,28] The oxygen permeability coefficient, nitrogen permeability coefficient, and ideal separation factor were calculated according to the previous report.[29] The apparatus and experimental procedure used for the gas permeability measurements had been described in the previous literature.[26,30]

Characterizations

Fourier Transform Infrared Spectroscopy Measurement. Fourier transform infrared spectroscopy (FTIR) spectra of the nanocomposite membranes prepared by 2.5 wt % g nanoscale SiO_2 and 5.0 wt % g nanoscale SiO_2 were obtained with Bruker EQUINX 55 of German, respectively. Each sample was vacuum dried at 60°C for 24 h to remove the absorbed water in the membranes.

Scanning Electron Microphotography Observation. The substrate-facing surface (SFS) and the fracture surface (FS) of the nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 (20 wt % and 40 wt % silica conversion) and 5.0 wt % nanoscale SiO_2 (20 wt % and 40 wt % silica conversion) were coated with gold and observed using a German Scanning Electro Microscope of JEOL JSM-T300, respectively.

Swelling Testing. To attain the physical performance and the degree of chemical cross-linking, the swelling behavior of the cross-linking nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 (20 wt % and 35 wt % silica



Scheme 2. Preparation process of the nanocomposite membrane.

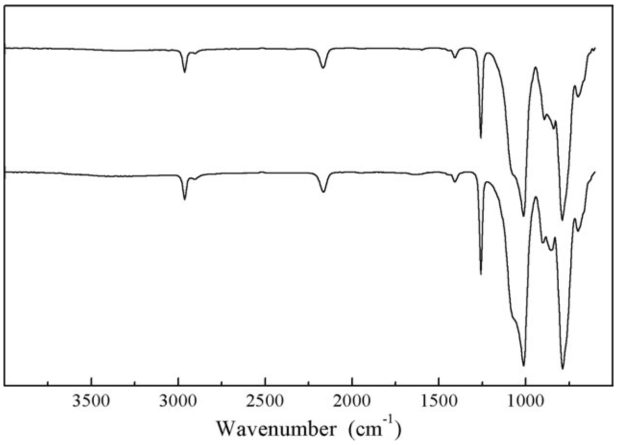


Figure 1. FTIR spectra of the nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 (a) and 5.0 wt % nanoscale SiO_2 (b).

conversion) and 5.0 wt % nanoscale SiO_2 (20 wt % and 35 wt % silica conversion) were studied. The swell coefficients were measured according to the literature.[31] The membranes were dipped in THF, xylene, and chloroform for 4 h at room-temperature, respectively.

Mechanical Properties. Mechanical properties of the cross-linking nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 (20 wt % and 35 wt % silica conversion) and 5.0 wt % nanoscale SiO_2 (20 wt % and 35 wt % silica conversion) were measured using Shimadzu AG-I of Japan. The samples were prepared for 20 mm (length) ×100 μm (thick) ×16 mm (width) and elongation rate was 30 mm/min. Every sample was tested three times under room-temperature.

Results and Discussion

Characterization

Chemical Structure Analysis. The chemical structure changes of the nanocomposite membranes were shown in Scheme 2 and monitored by FTIR. Based on VTMO and polymethylhydrosiloxane as matrix materials, the cross-linking agent containing silicon–hydrogen bonds and trimethoxylsilicon groups was synthesized by silicon–hydrogen addition reaction. In theory, each cross-linking agent molecular containing two hydrogen bonds could cross-linked further with silicone rubber containing vinyl groups. By controlling molar ratio among of the matrix materials, the silicon–hydrogen bonds of the cross-linking agent could react with both the vinyl group of PDMS and TEOS, leading to form the cross-linking hybrid network and to reduce the cross-linking density.

The characteristic absorption band of vinyl groups at 1600 and 3000 cm^{-1} for PDMS completely disappeared in the FTIR spectra of the nanocomposite membrane, which suggested that vinyl groups of PDMS reacted with silicon–hydrogen groups of the cross-linking agent. Typically, the most intensive peaks at 1025 cm^{-1} representing Si—O—Si asymmetric stretching were presented in the spectra of the nanocomposite membrane. In addition, as shown in Figure 1, the spectra of the nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 and 5.0 wt % nanoscale SiO_2 were similar. These results suggested that the introduction of nanoscale SiO_2 had no effect on the chemical structure of the nanocomposite membranes.

Morphologic Analysis. Scanning electron microphotography (SEM) measure is a convenient method to judge the dispersing status of inorganic phase in polymer matrix for hybrid materials. The morphology of the nanocomposite membrane samples was further studied by SEM images. The characteristics of SFS and FS for the nanocomposite membranes prepared by different SiO_2 contents and silica conversion were examined as shown in Figure 2. As indicated in Figures 2a, a′, b, b′, c, c′, the membranes showed a completely amorphous morphology either SFS or FS. The nanocomposite membranes possessed better membrane-forming properties that were attributed to the occurrence of covalent bonds and mutual network between the organic phase and the inorganic phase. The membranes are highly transparent, suggesting that there should be no macrophase separation, and had a good compatibility between polymeric component and inorganic component. Additionally, much denser cross-linked morphology in their inside could be also observed. However, from Figures 2d, d′, when the nanocomposite membranes were prepared by 5.0 wt % nanoscale SiO_2 and 40 wt % silica conversion, there are some blocky-shaped domains and scraggly chases as well as ridges that are mainly attributed to the occurrence of rigid inorganic framework network phase formed from TEOS and nanoscale SiO_2 in the membrane.

Swelling Properties. As the cross-linked polymers can only swell but not be dissolved in the organic solvents, the swelling degrees of the cross-linking membranes reflect chemical cross-linking degree. Hence, the swelling degrees of the nanocomposite membranes for some typical solvents such as xylene, THF, and chloroform were measured at room-temperature to estimate their cross-linking behaviors. The swelling test was performed to make a membrane immerging into a solvent at 30°C for 4 h. The swelling indices (SIs) of the membranes for different solvents calculated according to the testing results are listed in Table 1. It can be seen that SIs of the nanocomposite membranes containing nanoscale SiO_2 were smaller than those of the cross-linking PDMS membrane for the same solvents, suggesting that the introduction of the nanoscale SiO_2 could decrease slightly the cross-linking degree of the nanocomposite membrane. Consequently, the swelling behavior may change the free volume and permeation properties of the nanocomposite membranes.

Mechanical Property. In general, mechanical properties can show membrane-forming, segmental flexibility, structure–property relationships, and permselectivity of polymeric membranes. We had investigated the mechanical performance of the nanocomposite membranes containing different nanoscale SiO_2 contents and silica conversion. The results are summarized in Table 2. The strain, stress, and elongation values of the nanocomposite membranes decreased significantly with an increase of nanoscale SiO_2 contents and silica conversion. The nanocomposite membranes exhibited better membrane-forming ability, superior mechanical properties, and high solvent resistance.

Oxygen-Enriching Properties. We investigated the oxygen-enriching properties of the nanocomposite membrane containing different silica conversion and SiO_2 contents under testing temperature of 25°C and pressure difference of 0.1 MPa. The permeability coefficient and ideal separation factor of the nanocomposite membrane are listed in Table 3. The results suggested that the high oxygen-enriching performance was regulated by the organic/inorganic ratio and silica conversion in the sol–gel synthesis process.

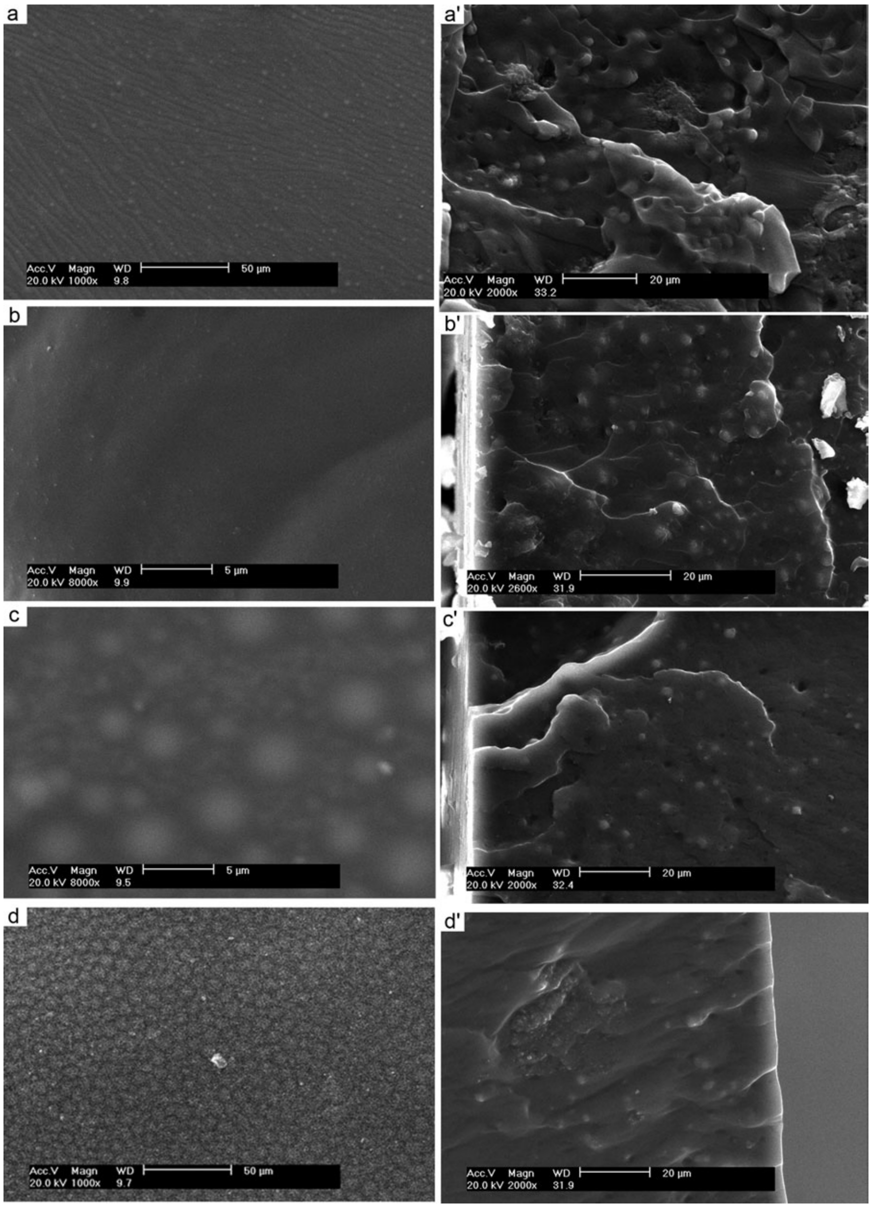


Figure 2. SEM photographs of the SFS and the FS for the nanocomposite membranes prepared by 2.5 wt % nanoscale SiO_2 (20 wt % (a) and 40 wt % (c) silica conversion) and 5.0 wt % nanoscale SiO_2 (20 wt % (b) and 40 wt % (d) silica conversion).

Effect of the nanoscale SiO_2 content on oxygen-enriching properties

As shown in Table 3, with increase in the nanoscale SiO_2 content, the oxygen permeability coefficient of the nanocomposite membrane decreased and the oxygen/nitrogen separation factor kept constant. The oxygen permeation properties increased to 680 Barrer and oxygen/nitrogen separation factor kept 3.0 or so with increasing the SiO_2 particles, both higher than those of the pure PDMS membrane and larger than those of Robeson's upper bound. Contrary to the conventional trade-off relationship between selectivity and gas permeability in polymers, that is, a decrease in selectivity is typically accompanied with an increase in gas permeability and vice versa, the nanocomposite membrane possessed higher oxygen permeability coefficient and oxygen/nitrogen separation factor. Consequently, the nanocomposite membrane clearly showed a significantly better oxygen-enriching property than the unfilled PDMS membrane. The presence of SiO_2 particles that were small enough to disrupt polymer-chain packing increased fraction free volume, enhanced gas diffusion, and, in turn, increased the gas separation properties of PDMS membrane. The enhancement of the oxygen-

Table 1. SIs of the Nanocomposite Membranes Containing Different Silica Conversion and SiO_2 Contents for Several Different Solvents

Film Sample	SiO_2 Contents	Silica Conversion (wt %)	SIs		
			Xylene	THF	Chloroform
1	2.5 wt %	5	1.16	0.92	1.01
2		20	1.19	0.87	0.85
3		35	0.94	0.96	0.92
4	5.0 wt %	5	1.04	0.91	0.98
5		20	1.17	0.97	0.92
6		35	1.08	0.92	0.96
7	0 wt %	0	1.27	1.02	0.97

Table 2. Mechanical Performances of the Nanocomposite Membranes Containing Different Silica Conversion and SiO_2 Contents

Film Sample	SiO_2 Contents	Silica Conversion (wt %)	SIs		
			Strain at Break (%)	Stress at Break (MPa)	Elastic (MPa)
1	2.5 wt %	5	2.214 ± 0.002	1.998 ± 0.005	0.681 ± 0.003
2		20	2.200 ± 0.005	1.901 ± 0.003	0.620 ± 0.002
3		35	1.985 ± 0.006	1.786 ± 0.004	0.501 ± 0.005
4	5.0 wt %	5	2.105 ± 0.003	1.875 ± 0.005	0.597 ± 0.002
5		20	2.054 ± 0.006	1.752 ± 0.007	0.642 ± 0.003
6		35	1.824 ± 0.005	1.543 ± 0.004	0.492 ± 0.006
7	0 wt %	0	2.342 ± 0.005	2.125 ± 0.003	0.807 ± 0.004

enriching properties was related to the increase in gas permeation to changes in the free volume distribution in the PDMS membrane and the enhanced chain segmental mobility resulted from the removal of sol–gel technique by introducing the SiO_2 nanoparticles. The results were consistent with many experimental observations.[1,32] In addition, it should be pointed out that the cross-linking structures of the PDMS nanocomposite membranes can not only restrict the nanoscale SiO_2 content (5 wt %) to some extent but also increase gas separation performance and enhance forming-membrane ability.

Effect of the silica conversion on oxygen-enriching properties

The effect of silica conversion on the oxygen-enriching properties of the nanocomposite membrane was determined at 30°C and 0.1 MPa. The silica conversion was varied between 5 and 45 wt %. The effects of increasing the silica conversion in the nanocomposite membrane containing 2.5 wt % nanoscale SiO_2 on the oxygen permeability coefficient and oxygen/nitrogen separation factor were shown in Figure 3.

With increasing silica conversion, oxygen permeability coefficient and oxygen/nitrogen separation factor of the nanocomposite membrane first increased and then decreased. For example, the oxygen permeability coefficient and oxygen/nitrogen separation factor increased significantly with increasing silica conversion up from 605 Barrer and 2.92 at 5 wt % silica conversion to 680 Barrer and 3.09 at 20 wt % silica conversion, then decreased obviously to 370 Barrer and 2.31 at 40 wt % silica conversion, respectively. The PDMS nanocomposite membranes based on rubbery polymer prepared by sol–gel process presented increased selectivity by decreasing swelling of the PDMS membrane according to the swelling degrees of the nanocomposite membranes. However, the conversion degree of the precursor has a significant impact on gas permeability and gas selectivity of PDMS membranes. For incomplete conversions, residual silica will be inside the membrane decreasing the oxygen permeation coefficient and oxygen/nitrogen separation factor. In addition, the permselectivity through blend and hybrid membranes strongly depends on their morphology: the volume fraction and the size and shape of the dispersed and continuous phases.[33] Therefore, when the silica conversion was up to 20 wt %, the nanocomposite membrane presented better oxygen-enriching properties. However, with increasing silica conversion, rigid TEOS framework hindered gradually the PDMS chain movements and influenced the oxygen-enriching properties of the membrane. These showed that the cross-linking method and proper TEOS content for polymer membrane were beneficial factors for increasing the gas permeability coefficient and permselectivities.

Table 3. The Permeability Coefficient and Ideal Separation Factor of the Nanocomposite Membranes Containing Different Silica Conversion and SiO_2 Contents (Testing Temperature of 30°C and Pressure Difference of 0.1 MPa)

SiO_2 Content	Silica Conversion (wt %)	O_2 Permeability Coefficient (Barrer)	O_2/N_2 Separation Factor
0 wt %		500.0	2.10
2.5 wt %	5	605.6	2.92
	10	610.2	2.94
	15	634.5	3.01
	20	680.3	3.09
	25	677.2	3.04
	30	609.4	2.90
	35	540.1	2.81
	40	370.8	2.31
5.0 wt	5	592.7	2.90
	10	600.1	2.92
	15	620.3	2.95
	20	635.3	3.02
	25	621.1	3.03
	30	562.5	3.01
	35	349.9	2.98
	40	–	–

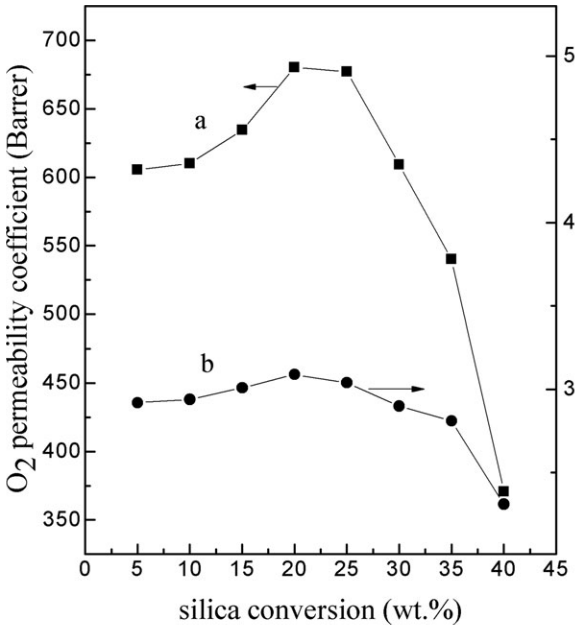


Figure 3. Effects of the silica conversion in the nanocomposite membrane containing 2.5 wt % nanoscale SiO_2 on the oxygen-enriching properties.

Conclusions

Our results demonstrate clearly that the cross-linking nanocomposite membranes prepared via *in situ* polymerization of TEOS using the sol–gel process possessed a significantly better oxygen-enriching than the unfilled PDMS membrane for air purification. The permeability and selectivity of the membranes increased simultaneously with the addition of nanoscale SiO_2. The oxygen permeation properties increased to 680 Barrer and oxygen/nitrogen separation factor kept 3.0 or so with increasing the SiO_2 particles in the nanocomposite membrane, both higher than those of the corresponding pure PDMS membrane. The transport properties of the membrane are significantly larger than those of Robeson's upper bound. The results were in contrast to the conventional trade-off relationship between selectivity and gas permeability in polymers. The nanocomposite membranes had better membrane-forming ability, superior mechanical properties, high solvent resistance as well as excellent oxygen-enriching properties, and are expected to be a high-performance gas separation membrane. The remarkable oxygen transportation capabilities of the nanocomposite membranes facilitated possible large-scale membrane applications for air purification. On the basis of experimental analysis, it was concluded that the increase in the oxygen-enriching properties of the cross-linking nanocomposite membrane arose from an increase of the free volume in the membrane by the presence of SiO_2 particles and the sol–gel copolymerization as well as an appropriate cross-linking method.

Acknowledgments

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