Influence of Surface-Treated SiO₂ on the Transport Behavior of O₂ and N₂ through Polydimethylsiloxane Nanocomposite Membrane

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Abstract

Mixed matrix membranes were prepared with polydimethylsiloxane (PDMS) and different weight percent surface-treated fumed silica (SiO_2) to investigate the influence of SiO_2 on transport behaviour of O_2 and N_2 gases in the nanocomposite membranes. Fourier transform infrared spectroscopy (FTIR) showed that OH functional group on the surface of SiO_2 was consumed upon incorporation of the silica into the polymer matrix. Thermogravimetric analysis (TGA) results revealed that SiO_2 -PDMS has improved thermal property over neat PDMS, supporting the argument that there is good interaction between the polymer and the fumed silica. Scanning electron microscopy (SEM) images of SiO_2 -PDMS membranes showed uniform dispersion of SiO_2 nanoparticles in PDMS matrix. SiO_2 nanoparticles disrupted and altered the PDMS polymer chains packing arrangement resulting in different membrane transport behaviour of both O_2 and N_2 gases in SiO_2 -PDMS compared to the neat PDMS membrane. While the O_2 flux through SiO_2 -PDMS membranes was observed to increase with time, N_2 flux decreased with time before attaining steady state. The 10wt% SiO_2 -PDMS membrane exhibited improved performance compared to neat PDMS membranes with O_2/N_2 selectivity and O_2 permeability increased from 2.43 to 3.46 and 590 Barrer to 640 Barrer, respectively, at 30 psig. This improvement is attributed to the influence of the well dispersed SiO_2 nanoparticles in the PDMS matrix.

Keywords: Oxygen separation, Neat PDMS membrane, Fumed silica, permeability.

1. Introduction

Membrane-based gas separation has become an important unit operation in the chemical industry for the past three decades [1]. Even though cryogenic distillation of air is still used today when high purity and tonnage quantities of oxygen is required, this technology is noted to be complex, expensive and energy intensive [2]. For small and intermediate scale air separation operations (like O₂-enriched air for medical, furnace applications, etc.), polymer membranes offer a number of benefits over other conventional gas separation technologies, such as operation flexibility, low capital and operating costs, lower energy requirement and, generally ease of operation and fabrication, etc.[3, 4]. The energy efficiency and simplicity of membrane separation mechanism makes it attractive for solving various fluid-phase separation problems. The performance of this relatively new technology strongly depends on the selection of membrane materials, their physicochemical properties, and the mechanism through which permeation occurs. The optimal choice of materials for ultrathin and dense gas separation membranes is much more complex than that of other membrane processes, where pore size and pore size distribution are the key factors [1, 5].

By far, one of the most challenging polymer membrane-based gas separation is the one involving O₂ and N₂ [4]. This is mainly due to their relatively similar sizes and shapes (and hence diffusivity), and also their solubility in most membranes. Considerable research efforts have focused on the selection and modification of polymeric materials that would enhance the separability of O₂ from N₂ by the incorporation of inorganic filler particles into polymers; giving rise to the concept of mixed matrix membranes (MMMs) [6, 7]. **Figure 1** illustrates this concept, where the solid (dispersed) phase is the inorganic filler particles and the continuous phase is the polymer matrix [8].

Figure 1. Schematic of: (a) neat polymer membrane and (b) mixed matrix membrane (MMM)

The development of a defect-free MMM with enhanced separation performance and the desired thermal and mechanical properties, depends on the proper selection of compatible polymer and filler materials, with their optimal wt% loading [9]. The choice of PDMS as one of the common polymers used for developing MMMs for gas separation [10], is based on its unusual combination of an inorganic chain similar to silicates that is associated with high surface energy, and organic methyl side groups with low surface energy. PDMS offers one of the highest permeability coefficients for a wide range of gas species, however with lower selectivity [11]. Due to its low cost, biocompatibility, nontoxicity, and ease of fabrication, PDMS provides the opportunity to utilize nano fumed (silica) fillers to fabricate nanocomposite membranes with enhanced gas separation performance and material integrity.

Many studies have shown that the use of non-porous nanosized fumed silica (SiO_2) (with properties contrary to porous inorganic fillers) in polymer matrix has potential to alter the molecular packing of the polymer chains. This consequently results in modifications in the gas separation properties of the resultant membrane [12, 13]. However, enhanced membrane gas separation performance can only be achieved where there are good matrix-filler interactions and when fillers are uniformly dispersed in the polymer matrix [14, 15].

Several research efforts have focused on improving PDMS-silica interaction by applying various strategies of SiO₂ surface functionalization to remove Si-OH groups prior to blending with PDMS or by using different types of surface-modified silica; with the aim of developing MMM with improved gas permeabilities and selectivities. Beltran et al. [16] reported that by incorporation of two types of surface-treated silica (with chlorodimethylphenyl silane and chlorodimethyloctyl silane) into PDMS, C₃H₆/N₂ selectivities were increased by 35–44%. However, a reduction in O₂ and N₂ permeabilities was observed in silica-PDMS membranes compared to pure PDMS membrane [16]. The addition of unmodified silica nanoparticles of 12–400 nm size into PDMS matrix enhanced the separation factor of propylene from 5.2 to 7.3 and permeance from 31 to 36 GPU. However, when they used modified silica (treated with 3-mercaptopropyl-trimethoxysilane (MrPS)) in PDMS, the separation factor and permeance of propylene increased to 8.5 and 42 GPU, respectively [12]. Nisola et al. reported that, while the addition of 15wt% chlorodimethyl silane functionalized silica in PDMS matrix enhanced thermal properties, and O₂ and N₂ permeabilities, the O₂/N₂ selectivity decreased from 2.70 to 2.50 compared to the neat PDMS [13]. Recently, Hassanajili et al. used the commercial surface-modified silica (treated with polydimethylsiloxane) as fillers to investigate the dispersed particles influence on permeation of properties of polyesterurethane (PU)-silica nanocomposite membrane for separation of CO₂ from CH₄ [17]. However, to the best of our knowledge, no studies have been reported using polydimethylsiloxane surface-modified silica as fillers for PDMS mixed matrix membranes and their application for O₂/N₂ separation.

In this study, nanosized fumed silica (pretreated with polydimethylsiloxane) was used to synthesize SiO₂-PDMS matrix membrane to investigate the influence of dispersed fillers on the transport behavior of O₂ and N₂. Characterization techniques were used to: (i) determine if the

functionalized SiO₂ were uniformly dispersed with the PDMS matrix; (ii) identify the functional groups present in the surface-treated silica and in neat PDMS and SiO₂-PDMS membranes and; (iii) examine the influence of the filler on the thermal property of the mixed matrix membrane.

2. Experimental

2.1 Materials

PDMS (Sylgard 184 silicone elastomer) was generously provided by Dow Corning Corporation, (Greensboro, NC). Aerosil R202, hydrophobic fumed silica pre-treated with PDMS (polydimethylsiloxane) was generously provided by Evonik Industries (Greensboro, NC). Other chemical agents of analytical grade were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. **Table 1** shows the characteristics of the SiO₂ fumed silica with surfaces pre-treated with PDMS polymer.

Table 1. Specification of Aerosil R202 Fumed Silica[18].

Parameters	Specification Limits	Actual Values
BET surface area	80 - 120	88 m ² /g
pH	4.0 - 6.0	5.2
Moisture	< 0.50 %	0.30 %
Carbon content	3.5 - 5.0 %	4.8 %
Particle size	5.0 - 50.0 nm	~13 nm

2.2 Preparation of PDMS and PDMS MMM

The SiO₂-PDMS (MMMs) were prepared through solution casting. Required quantity of fumed silica (for 0, 10, and 15 wt% loading) was dispersed in measured quantity of toluene and stirred for 30 min followed by sonification for 30 min to ensure complete mixing at molecular level. Toluene was used to enhance the dispersion of silica particles and to control the viscosity

of the polymer solution. Ultrasonic bath from Branson Ultrasonics (CT, USA) was used for the sonication. The PDMS elastomer part A was added into the dispersion, stirred for 30 min and sonicated for 30 min. Part B of the elastomer was added (with a weight ratio A:B = 10:1) into the mixture followed by stirring for 30 min and 60 min of sonication. The SiO₂-PDMS solution was then poured into disposable aluminium weighing dishes to form a thin film which underwent 12 h drying at ambient condition. Then the film samples were vacuum-dried for 24 h at room temperature and annealed under vacuum at 80 °C for another 24 h. The membrane films were peeled off from aluminium dishes and stored for characterization and testing.

2.3 Instruments

Shimadzu IR Prestige-21 Fourier transform infrared (FTIR) 8300 spectrometer equipped with mercury-cadmium-telluride (MCT) detector was used to identify the functional groups present in the nanocomposite membranes. Thermal property of the membrane samples was analyzed with thermal gravimetric analyzer (TA SDT Q600). This was performed in an argon gas flow of 100mL/min at a heating rate 5⁰C/min, from room temperature to 750⁰C and was held at constant temperature of 750⁰C for 30 min.

Hitachi S-4800 field emission-scanning electron microscope was used to investigate the nature of the dispersion of the surface-treated nano fumed silica in the polymer (PDMS) matrix.

2.4. Gas permeation test

Pure gas permeation tests through neat (PDMS) and composite (SiO₂-PDMS) membranes were performed at different feed pressures (10 - 35 psig, or 52 - 181 cmHg), through membranes with active area of 13.8 cm² at room temperature. Gas flow rates at the permeate stream were measured using bubble flow meter; pure gas (O₂ and N₂) flow rates measurements were

obtained/recorded in 20-minute intervals. The following equations were used to calculate gas flux and permeability:

$$Q = VA/t \quad (1)$$

$$P = Ql/\Delta p = DS \quad (2)$$

Where Q is the gas flux through membrane ($\text{cm}^3/\text{cm}^2/\text{s}$), V is the volume of the permeation gas (cm^3) in the time interval of t (s), A is the active membrane area (cm^2), P is the permeability coefficient of the gas in the polymer in Barrer ($10^{-10} \text{ cm}^3\text{-cm (STP)/cm}^2 \text{ s cmHg}$) and it is the product of diffusivity D and solubility S of the gas in the polymer, l is the thickness of the membrane (cm), and Δp is the pressure difference across the membrane (psig). The schematic laboratory set-up for single gas permeation test is shown in **Figure 2**.

Figure 2. Schematic laboratory set-up for single gas permeation test

3. Results and Discussion

3.1. FTIR Investigation

Fourier transform infrared was employed to identify the functional groups that make up the nanocomposite membranes and to confirm the extent of fumed silica surface modification (absence of silanol group - OH bond). **Figures 3a** and **3b** show the FTIR spectra of fumed silica and 0-15%wtSiO₂-PDMS membranes, respectively. All the samples in **Figures 3a** and **3b** exhibit a moderate intensity peak at 2960 cm⁻¹. These bands correspond to the symmetric C-H bond stretching vibrations of the (CH₃) alkyl chains of the PDMS molecule. The absorption bands around 1257 cm⁻¹ and 1012 cm⁻¹ are attributed to the asymmetric stretching vibrations of Si-O-Si bonds. The intense peak between 788 cm⁻¹ and 790 cm⁻¹ are attributed to the symmetric Si-O-Si bond vibrations [16, 19, 20].

The absence of hydroxyl bond vibrations (peaks) between 3200 cm⁻¹ and 4000 cm⁻¹ signifies that the surface OH groups of the fumed silica were successfully consumed through bonding with the silicon atom of the siloxane moiety of the PDMS during surface treatment. The hydrophobic behavior is brought about by reacting hydrophilic silanol groups on the surface of the untreated silica with organic group (siloxane). The organic group is anchored so firmly to the surface (via Si-O-Si-(CH₃)₂ covalent bonds) that it can only be removed by a process such as thermal decomposition [21]. OH groups on the surface of SiO₂ favors strong SiO₂-SiO₂ interaction (i.e. SiO₂ particle agglomeration) [22]. Therefore, the absence of the surface hydroxyl groups as shown by the FTIR spectra of the samples further explains why good particle

dispersion (absence of SiO_2 agglomeration) in PDMS matrix was achieved, which is confirmed by the SEM images shown later in **Figure 5**.

Figure 3. FTIR Spectra of (a) SiO_2 (b) 0-15% SiO_2 -PDMS matrix

3.2. Fumed Silica and SiO_2 -PDMS MMM Thermal Analysis

The thermal stability and degradation of the surface treated fumed silica (SiO_2), neat PDMS and SiO_2 -PDMS were examined using TGA as shown in **Figure 4**.

Figure 4. TGA scans of (a) fumed silica, (b) 15wt%SiO₂-PDMS, (c) 10wt%SiO₂-PDMS, (d) 5wt%SiO₂-PDMS, and (e) neat PDMS.

The surface treated fumed silica had a total weight loss of 8.09% which can be attributed to the attached PDMS on the SiO₂ surface and the trace ambient contamination [13]. Neat PDMS exhibited a significant weight loss of 94.20% with almost no char residue after the TGA test. This was due to the loss of methyl groups on the Si-O backbone [23]. The SiO₂-PDMS MMMs with 5wt%, 10wt%, and 15wt% silica loadings showed weight loss of 67.97%, 62.65, and 50.18%, respectively, as depicted in **Figure 4**.

All the SiO₂-PDMS samples exhibited a similar degradation pattern as shown by neat PDMS in the temperature range with degradation onset from between 200-325 °C and most abrupt degradation at 400 °C. It should be noted that, when there is less or no material interaction the organic parts of the SiO₂-PDMS should be completely lost during the heating, leaving behind silica residue equal to silica weight percent added to PDMS matrix. However, all the SiO₂-PDMS samples had residues much higher than their respective silica contents (amount of silica incorporated into the polymer matrix). This shows that the PDMS did not degrade completely during the heating period because the silica had altered the thermal property of the polymer matrix. SiO₂ has superior heat insulation property and as filler in PDMS, it can act as mass transport barriers by retarding the release of volatile organic components during thermal decomposition [24]. The higher residue weight (than the actual silica weight added to PDMS

matrix), thus indicates a level of interaction between the polymer and silica chains and hence the improved thermal property (stability) of the PDMS MMM [25].

3.3. Membrane Morphology Investigation

Figure 5. SEM images of neat PDMS (a1 and a2); 5%SiO₂-PDMS (b1 and b2); 10%SiO₂-PDMS (c1 and c2); 15% SiO₂ PDMS (d1 and d2), and 5%SiO₂-PDMS (e1) at different magnifications.

The dispersion of the surface-treated fumed silica in PDMS matrix was investigated at different SEM magnifications. **Figure 5 (a1 and a2)** show the SEM image of the surface at x35 magnification and the cross-section image at x30, 000 magnifications of neat PDMS respectively. The cross-section SEM images of the nanocomposite membranes, as in **Figure 5 (a2, b2, c2, d2 and e1)** show uniform distribution of the surface-treated fumed silica; confirming good material compatibility between SiO₂-PDMS. The enhanced material interaction can be attributed to the surface pre-treatment of fumed silica (by the manufacturer) which weakened particle-particle (SiO₂-SiO₂) interaction and enhanced particle-polymer interaction [22]. The laboratory procedure used in the synthesis of the membranes achieved uniform dispersion of particles in the PDMS matrix. However, the surface images of the neat PDMS and the SiO₂-PDMS MMMs at x35 and x45 on **Figure 5 (a1, b1, c1, and d1)** show the presence of foreign particles on the surface of membrane. The foreign particles may have settled on the membrane surface during drying or material handling (of membrane film). Foreign particles on the surface of the membrane may affect the performance of the membrane depending on its nature.

3.4. Pure Gas Permeation Tests

The transport behavior of gases in polymers and nanocomposite membranes varies depending upon the type of gas. To examine the effect of surface treated SiO₂ incorporation into PDMS matrix on the transport pattern of O₂ and N₂, single gas flux for O₂ and N₂ through membranes with different SiO₂ loadings (0wt%, 10wt%, and 15wt%) were determined at room temperature and a constant pressure of 30 psig for 180 min. The fluxes of O₂ and N₂ through the neat PDMS (0wt%SiO₂-PDMS) exhibited similar transport trend for both gases as shown in **Figure 6**. Both O₂ and N₂ permeabilities through 0wt%SiO₂-PDMS membrane maintained near steady state for the entire duration of the tests. The effect of the dispersed fillers on the molecular packing of the

polymer chains significantly altered O₂ and N₂ transport (flux) pattern through the membrane as illustrated by the plots of 10wt%SiO₂-PDMS and 15wt% SiO₂-PDMS in **Figure 6**. Unlike the N₂

Figure 6. Transport pattern of O₂ and N₂ through (a) neat PDMS,

(b) 10wt%SiO₂-PDMS, and (c) 15wt%SiO₂-PDMS membranes at 30 psig

Goh et al. [26] suggested that the addition of filler (nano fumed silica) into the polymer matrix does not directly contribute to the change of transport property, but it alters the molecular

packing of the polymer chains, which may result in an improvement of the permeation as well as the selectivity. They reported that the addition of fumed silica with active OH group sites to polymer matrix resulted in an increase in solubility and a corresponding decrease in the diffusivity of the gases through the MMMs [26]. It led to an enhanced permeability of more condensable gas (such as CO₂) in the polymer matrix and reduction in the permeability of the non-condensable (like N₂) gas, thereby changing the dominant gas permeation mechanism from diffusion to solution diffusion. However, the fumed silica used in this study was factory treated with PDMS and has no residual OH group on its surface as confirmed by the FTIR analysis in **Figure 3**. Further studies are underway to investigate the reasons for the altered transport behavior of the penetrant gases. This would help in synthesizing novel membranes that will continuously and progressively slowdown (decrease) N₂ flux; while at the same time having the ability to progressively increasing O₂ flux for a long runtime before attaining steady state.

3.5. Membrane performance for separation of O₂/N₂

Figure 7: (a). Neat PDMS; (b) 10% SiO₂ PDMS Performance for O₂/N₂ Separation

The selectivity of 0wt%SiO₂-PDMS and 10wt%SiO₂-PDMS were calculated from the ratio of the two slopes for O₂ permeability and N₂ permeability in **Figure 7 (a)** and **(b)** using steady state permeability values. It should be noted that while 0wt%SiO₂-PDMS has the selectivity (O₂ over N₂) of 2.43 and O₂ permeability of about 590 Barrer, 10wt%SiO₂-PDMS has an improved selectivity (O₂ over N₂) of 3.46 and a O₂ permeability of about 640 Barrer at 30 psig. The improved performance of the composite membrane is attributed to the influence of the well dispersed silica nanoparticles in the PDMS matrix.

Table 2. Performance of Neat PDMS and PDMS MMM

Membrane	Crosslinking	PO ₂ (Barrer)	Selectivity (O ₂ /N ₂)
Neat PDMS	10:1	590	2.43
5% SiO ₂ -PDMS	10:1	529	3.28
10% SiO ₂ -PDMS	10:1	640	3.46
15% SiO ₂ -PDMS	10:1	585	2.76

The performance of different membranes is summarized in **Table 2**. Among all the membranes synthesized, 10wt%SiO₂-PDMS exhibited the best performance, while others showed improvement over the neat PDMS.

4. Conclusions

Neat polydimethylsiloxane (PDMS) and surface-treated fumed silica filled PDMS (SiO₂-PDMS) membranes were prepared to investigate the influence of the dispersed surface-modified SiO₂ on the transport behavior of O₂ and N₂. FTIR analysis confirmed the absence of silanol (OH) group (the culprit for SiO₂ particle agglomeration) on the surface-treated fumed silica and

SiO₂-PDMS. Thermogravimetric analysis showed that the incorporation of SiO₂ into PDMS improved the thermal property (stability) of the nanocomposite membrane, which was attributed to the good interaction between polymer and silica. SEM images of the nanocomposite membranes showed uniformly dispersed surface treated fumed silica in PDMS matrix. Good filler dispersion is attributed to the influence of the (industrial) surface modification of the fumed silica which weakened particle-particle (SiO₂-SiO₂) interactions and enhanced filler-polymer interaction. The laboratory procedure used in the synthesis of the membranes also helped in achieving uniform dispersion of silica particles in the PDMS matrix. The dispersed silica altered the molecular packing of the polymer chains, consequently modifying the gas separation properties of the resultant membrane (SiO₂-PDMS). The O₂ flux through SiO₂-PDMS increased with time while N₂ flux decreased with time before attaining steady state. The 10wt%SiO₂-PDMS membrane exhibited improved selectivity from 2.43 to 3.46 compared to neat PDMS membrane. The O₂ permeability also increased in 10wt%SiO₂-PDMS from 590 to 640 Barrer at 30 psig. This improvement could be attributed to optimal filler loading and the influence of the well dispersed filler in PDMS matrix. Further studies are ongoing to understand the reasons for the altered transport behaviour of the penetrant gases. This would help in synthesizing membranes with better selectivity and permeability.

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