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Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation $\stackrel{\text{\tiny{\%}}}{\xrightarrow{}}$

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Abstract

Mixed-matrix membranes (MMMs) are based on polymeric membranes filled with inorganic particles as a means to improve their gas separation performance. In this study, MMMs were prepared from polysulfone (PSf) containing embedded nonporous fumed silica nanoparticles and the gas permeation properties of the resulting membranes were investigated. Physical properties such as film density, thermal degradation and glass transition temperature of PSf/silica MMMs were characterized. The distribution of the silica nanoparticles in PSf was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Furthermore, the interface between the polymer and silica agglomerates was studied in relation with the gas transport properties. The gas permeabilities of hydrogen, helium, oxygen, nitrogen, methane, and carbon dioxide were measured as a function of silica volume fraction and diffusion and solubility coefficients were determined by the time-lag method. The effect of silica nanoparticles in PSf membranes on gas permeability is in contrast with predictions based on the Maxwell model. The O₂ permeability is approximately four times higher and CH₄ permeability is over five times greater than in a pure PSf membrane. However, the performance comprising permeability versus selectivity of PSf/silica MMMs for O₂/N₂ and CO₂/CH₄ follows a similar slope to that of the trade-off upper bound with increasing silica content.

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Keywords: Mixed-matrix membranes; Silica nanoparticle; Polysulfone; Gas permeation

1. Introduction

While polymeric materials have been extensively studied for gas separation [1,2], there is a performance trade-off between permeability and selectivity, which is evident for O_2/N_2 and CO_2/CH_4 separation [3–5]. For nearly a decade, incorporation of inorganic particles such as porous zeolites, carbon molecular sieves and nonporous silica into a polymer matrix has been conducted to advance the performance of gas separation membranes [6]. The goal in the development of ideal polymer/inorganic mixed-matrix membranes (MMMs) is to improve both the permeability and selectivity, and overcome the limitation of the established 'upper bound' that exists for solution-diffusion type transport in purely polymeric membranes. However, the gas transport behavior of polymer/inorganic MMMs is considerably influenced by a variety of factors such as: (1) polymer and inorganic materials properties and (2) their compatibility and absence of interfacial defects, (3) morphology, and (4) membrane formation process.

Polysulfone (PSf) is one of the most widely used glassy polymer membrane materials, and its pure- and mixed-gas permeation properties have been extensively explored for gas separation. Hence, PSf is a fairly attractive material for incorporating porous inorganic fillers to enhance the transport properties [7]. Previous research examined the use of zeolite and carbon molecular sieves in PSf-based MMMs [8–10]. For example, Wang et al. [9] fabricated about 100-nm-sized porous zeolite nanocrystals, which had improved interfacial compatibility and fewer defects at the polymer–zeolite interface. The addition of

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this type of nanosized zeolite in PSf enhanced the O_2 gas permeability from 1.3 to 1.8 barrer and the O_2/N_2 selectivity increased from 5.9 to 7.7 at 25 weight% (wt.%) zeolite loading. In contrast with porous zeolites, Kim et al. [10] prepared PSf membranes embedded with modified 10 Å nanoporous carbon nanotubes. At 10 wt.% loading, the O_2 permeability was slightly enhanced from 0.84 to 1.23 barrer and the O_2/N_2 selectivity increased from 5.07 to 5.35. For CO₂, the permeability was enhanced from 3.9 to 5.2 barrer, whereas the CO₂/CH₄ selectivity decreased from 24 to 18. In this case, incorporation of nanosized carbon did not significantly change the gas permeation performance.

Recently, Pinnau and He reported that the addition of nonporous nanosized-fumed silica, which has opposing properties with porous inorganic fillers, can alter polymer chain packing in glassy, high-free-volume polymers [11]. This resulted in an increase in free volume leading to a significant enhancement in permeability. Merkel et al. [12–14] extended this approach and demonstrated enhancement in permeabilities of a variety of high-free-volume polymers such as poly (4-methyl-2-pentyne) (PMP) and poly (1-trimethylsilyl-1-propyne) (PTMSP), as well as poly (2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-cotetrafluoroethylene) (Teflon AF2400). Moreover, He et al. [15] have shown a remarkable enhancement in mixture vapor/gas selectivity of PMP by introducing nanosized silica in the matrix of high-free-volume glassy polymers. This attractive result is in complete contradiction to the Maxwell model prediction of a reduction in permeability and little effect on selectivity by the addition of nonporous fillers to a polymer matrix [16]. In another study, the interface between polymer and silica agglomerates was investigated by observation of the morphology of fumed silica in amorphous, low-free-volume glassy poly(ether imide) [17,18]. It was shown that void formation occurs during film fabrication, which has a significant effect on the gas transport properties of the hybrid membrane.

In the present study, the effects of silica nanoparticles in conventional, low-free-volume glassy PSf was examined. The gas transport and separation properties of PSf/silica MMMs are strongly related to the morphology of the membranes. The objective of this work is not an attempt to overcome the Robeson upper bound line, but rather to investigate the mode of gas transport and general trends in nonporous nanosized silica/low-free-volume glassy polymers, for which there is little prior reported work.

2. Background

2.1. Gas transport in polymeric membranes

Gas transport of nonporous dense polymeric membranes is based on the 'solution-diffusion' mechanism [19]:

$$P = DS \tag{1}$$

$$P = \frac{Nl}{p_2 - p_1} \tag{2}$$

where *P* is the gas permeability, *D* and *S* are the diffusion and solubility coefficients, respectively, *N* is the permeation flux, *l* is the membrane thickness, p_2 is the upstream pressure and

 p_1 is the downstream pressure. The gas permeability is commonly expressed by the barrer unit (1 barrer = 10^{-10} cm³(STP) cm/(cm² s cmHg)). To evaluate the gas transport properties, we used the 'time-lag method' [20,21], which has been widely applied to determine the diffusion coefficient, and hence, provides an estimate of the solubility coefficient from Eq. (1), as S = P/D. The diffusion coefficient is obtained from the initial transient regime, which determines the *x*-intercept defined as time-lag (θ):

$$\theta = \frac{l^2}{6D} \tag{3}$$

The selectivity of a dense gas separation membrane is defined as

$$\alpha_{\rm AB} = \frac{P_{\rm A}}{P_{\rm B}} = \left(\frac{S_{\rm A}}{S_{\rm B}}\right) \left(\frac{D_{\rm A}}{D_{\rm B}}\right) \tag{4}$$

where P_A and P_B are the permeability coefficients of gas A and B, and (S_A/S_B) and (D_A/D_B) are the solubility and diffusion selectivity, respectively.

2.2. Gas transport of conventional mixed-matrix membranes

In general, the predicted gas permeation properties of nonporous inorganic filled mixed-matrix membranes can be predicted by the Maxwell equation [16]:

$$P_{\rm f} = P_0 \left(\frac{1 - \phi_{\rm f}}{1 + (\phi_{\rm f}/2)} \right) \tag{5}$$

$$D_{\rm f} = \frac{D}{\tau} \tag{6}$$

$$S_{\rm f} = S_0(1 - \phi_{\rm f}) \tag{7}$$

where P_f and P_0 are the permeability coefficients of the inorganic-filled polymer matrix and of the pure polymer, respectively. ϕ_f is the volume fraction of the inorganic component, and τ is the tortuousity derived from $(1 + \phi_f/2)$ in the case of spherical particles. D_f and S_f are the diffusion and solubility coefficients of the inorganic-filled polymer matrix, respectively.

3. Materials and methods

3.1. Materials

Polysulfone (Udel P-1700 grade) was obtained from Solvay Advanced Polymers (Alpharetta, GA). The fractional-free-volume of PSf is 0.16 as calculated by the Bondi group contribution method [22]. The reported (Solvay) and in-house measured density of PSf is 1.24 g/cm³.

Fumed silica (Cabosil TS 530) used as filler in this study was kindly supplied by Cabot Corporation (Tuscola, IL). The fumed silica is hydrophobic because the surface hydroxyl groups are modified with trimethylsilyl groups. The density and the B.E.T. surface area is 2.20 g/cm^3 and $205-245 \text{ m}^2/\text{g}$, respectively [23]. The average equivalent spherical particle diameter

Table 1		
Polysulfone/silica	mixed-matrix	membranes properties

Silica volume fraction, $\phi_{\rm f}$	Weight percent (wt.%)	$\rho_{\rm M}~({\rm g/cm^3})$	$T_{\rm g}$ (°C)
0.00	0.0	1.24	182
0.05	8.5	1.28	182
0.10	16.5	1.31	182
0.15	23.8	1.35	188
0.20	30.7	1.39	187

The accuracy of measured density ($\rho_{\rm M}$) is within $\pm 0.002\,{\rm g/cm^3}$ and $T_{\rm g}$ is $\pm 0.3~{\rm ^\circ C}$.

(d) is 11.1–13.3 nm, which was calculated by $d=6/(\text{surface area} \times \text{density})$ for spherical particles.

3.2. Polysulfone/silica mixed-matrix membrane preparation

The PSf and silica-filled PSf mixed-matrix membranes were prepared by solution-casting. PSf was degassed and dried in a vacuum oven, dissolved (2 wt.%) in chloroform under stirring for 1 day and then filtered through a 0.45- m pore size PTFE syringe filter. Measured amounts of silica were added to the solution. The silica content was calculated as volume fraction (ϕ_f) by the following equation and is shown in Table 1:

$$\phi_{\rm f} = \frac{w_{\rm f}/\rho_{\rm f}}{(w_{\rm p}/\rho_{\rm p}) + (w_{\rm f}/\rho_{\rm f})} \tag{8}$$

where $w_{\rm f}$ and $w_{\rm p}$ refer to the weight of filler and polymer, respectively, and $\rho_{\rm f}$ and $\rho_{\rm p}$ are the density of filler and polymer, respectively. The polymer/silica particle mixture was then sonicated to ensure the silica nanoparticle dispersed homogeneously in the polymer solution. Typically, the polymer and silica mixture was sonicated initially for 2 h and then left standing for 1 day. This procedure was repeated once for low silica loadings, and was increased up to three times for high silica loadings in the polymer solution. Thirty minutes before casting, the mixture was sonicated again. The solution was cast on a flat, leveled glass plate and was slowly evaporated at ambient conditions for 1 day; then the film was removed by soaking in water. Finally, the membrane films were further dried at 60 °C for 3 days in a vacuum oven to remove residual solvent and moisture. The membrane thickness was measured by a micrometer and it was typically in the range of 60–80 m.

3.3. Membrane characterization

3.3.1. Thermal properties

Residual solvent was removed from the test films by drying overnight in a vacuum oven at 180 °C. The thermal degradation was conducted by thermal gravimetric analysis (TGA) (TA instrument 2950, TA instruments, New Castle, DE). Ten to 20 mg of sample was loaded in a pre-tarred platinum pan and pre-heated above 120 °C to remove moisture. After cooling, the sample was reheated from 25 to 1000 °C at a rate of 10 °C/min.

The glass transition temperature (T_g) was obtained by differential scanning calorimetry (TA Instruments 2920, TA instruments, New Castle, DE) calibrated from the melting point of indium at 156.6 °C and tin at 231.9 °C. Then, 10–20 mg of

sample was encapsulated in hermetically sealed aluminum pans with lids. Samples were first heated from room temperature up to 230 °C at a rate of 10 °C/min, and then maintained isothermally for 1 min before being quenched in liquid nitrogen to remove any thermal history. The sample was reheated up to 250 °C at a rate of 10 °C/min under a N₂ flow. The glass transition temperature was determined in the second heat cycle and calculated from the T_g onset point using an Universal Analysis 2000 program.

3.3.2. Morphology

The distribution of 13-nm-sized fumed silica particles, embedded in PSf was observed by transmission electron microscopy (TEM) (Philips CM 20 with a Gatan UltraScan 1000 CCD camera). The four different silica-filled membranes (i.e., silica volume fraction (ϕ_f) of 0, 0.05, 0.10, and 0.20) were layered together to compare the difference in particle distribution under the same conditions and then the samples were hardened in epoxy. The cross-section of the membranes was then cut to a thickness of 20–30 nm using an ultra glass knife controlled by an ultracut E microtome (Reichert-Jung, Germany). The thin sample was then laid on a 400 mesh copper grid and dried for 1 day in a desiccation chamber under vacuum. The silica nanoparticle image was examined using an accelerating voltage of 120 kV.

The morphology of nonporous silica nanoparticles in PSf was observed by scanning electron microscopy (SEM) of freezefractured specimens. The samples were sputter-coated with gold. The samples were then examined using a JEOL 840A scanning electron microscope equipped with an Oxford instruments 6560 INCA x-sight light element energy dispersive X-ray (EDX) spectrometer and image capturing software. All photos were taken using an accelerating voltage of 30 kV.

3.4. Gas permeation tests

The pure-gas (H₂, He, O₂, N₂, CH₄, and CO₂, see Table 2) permeation properties of PSf and PSf/silica MMMs were carried out using a constant volume/variable pressure method [24,25]. The gas permeability apparatus allows permeability and diffusion coefficients to be determined simultaneously by recording the increase of downstream pressure with time. Except for light gases such as H₂ and He, the time-lag of other gases was adequate to determine their diffusion coefficient. The downstream and upstream parts of the membrane cell were evacuated by an oil-free vacuum pump before exposure of the gases to

Table 2	
Molecular gas properties [36]	

Gas	Critical temperature, T _c (K)	Critical volume, V _c (cm ³ /mol)	ennard–Jones diameter, d _{LJ} (Å)
Не	5.2	57.5	2.55
H_2	33.2	64.9	2.83
O ₂	154.6	73.5	3.47
N ₂	126.2	89.3	3.80
CO_2	304.2	91.9	3.94
CH ₄	190.6	98.6	3.76

the feed side of the membrane. The downstream pressure was recorded up to 10 Torr, which was displayed by a pressure transducer (MKS Company, Andover, MA) and the upstream pressure was monitored using a pressure indicator (Ashcroft Co., Shelron, CT). The whole system was contained in a temperaturecontrolled cabinet and the experiments were performed at 35 °C. The upstream pressure was 50 psig and the initial downstream pressure was maintained at less than 10 mTorr. The leak ratio, that is, the downstream pressure increase occurring without gas flow, was within 10^{-5} to 10^{-6} Torr/s, indicating a negligible effect (1% of the gas permeation rate). The effective membrane area was 10 cm^2 . The gas tests were performed from the fastest to the slowest gases, except for CO₂, which is prone to cause plasticization. Consequently, gas permeability was measured in the following order: H2, He, O2, N2, CH4 and CO_2 .

4. Results and discussion

4.1. Thermal properties of polysulfone/silica mixed-matrix membranes

The thermal properties of unfilled PSf and silica-filled PSf MMMs were characterized by TGA and DSC analysis. The onset decomposition temperature of the samples was observed at about 520 °C, as shown in Fig. 1. The glass transition temperature (T_g) is strongly dependent on thermal, mechanical or processing history of the sample. The T_g of PSf is typically



Fig. 1. Thermal degradation of unfilled and a variety of silica-filled polysulfone matrix membranes.

reported as 188 °C; TGA analysis suggests that no residual solvent was present in the films. The T_g of silica-filled PSf is slightly higher relative to that of pure PSf as presented in Table 1. Increased T_g reflects the change in long-range segmental mobility of polymer chains [26]. It also indicates that a rigidified polymer region occurs due to the stresses arising during membrane formation that may form at the polymer–silica interface [27,28].



Fig. 2. TEM images of cross-sections of polysulfone containing silica nanoparticles: (1) 5 vol.%, (2) 10 vol.%, (3) 15 vol.%, and (4) 20 vol.% taken at a magnification of 50,000.



Fig. 3. SEM images of cross-sections of polysulfone containing silica nanoparticles: (1) 5 vol.%, (2) 10 vol.%, (3) 15 vol.%, and (4) 20 vol.% taken at a magnification of 50,000.

4.2. Morphology of polysulfone/silica mixed-matrix membranes

The morphology strongly affects the transport properties in silica-filled PSf MMMs [28]. Therefore, the distribution of fumed silica was observed by TEM taken at high magnification. As shown in Fig. 2, the silica nanoparticles are dispersed, but appear to form agglomerates in the polymer matrix and the agglomerate size increases at higher silica content [29,30]. The agglomerate size is as high as a few 100 nm. However, the dispersion of the nanoparticles in these materials may be somewhat better than that apparently indicated by the transmission electron microscopy results. If one considers that the distance between the particles could be less than the thickness of the cross-section of the films that were cut for the TEM study, the particles could appear to be overlapping by juxtaposition through the depth of the film, even if reasonable particle dispersion was achieved. The aggregated form is more evident in the SEM image presented in Fig. 3, which shows that the spherical fumed silica particle cluster is embedded in the polymer matrix. However, it was impossible to detect the molecular interface between the polymer and silica network, at which the presence of voids is considered.

4.3. Gas permeability of polysulfone/silica mixed-matrix membranes

The permeability, diffusion and solubility coefficients to O_2 and N_2 of PSf in this study are very similar to those reported

in the literature [31–33], as shown in Table 3. Table 4 shows the permeability, diffusion and solubility coefficients to CO₂ and CH₄ and pure-gas selectivities of PSf at 35 °C. McHattie et al. [31] reported CO₂ and CH₄ permeabilities of 6.3 and 0.27 barrer, respectively, at 35 °C and Δp of 4.4 atm. The CO₂ value reported in this study is consistent with previous literature data; however the CH₄ permeability is slightly lower. As a result, the CO₂/CH₄ selectivity in the present study is higher than that previously reported in the literature. Furthermore, the comparatively higher solubility of CO₂ than that reported in the literature might be due to the dual mode sorption effect [33,34]. The pressure for measuring of CO₂ transport in this study was 4.4 atm, which is significantly lower than that typically reported in the literature (10 atm). Therefore, the solubility coefficients are somewhat higher at lower CO₂ pressure.

Based on these reasonable base-line gas permeation data for PSf, we evaluated the effects of silica nanoparticles in the PSf matrix on the gas permeation properties. Table 5 presents the pure-gas permeabilities of unfilled PSf and silica-filled PSf nanocomposite membranes with varying silica volume fraction (ϕ_f) at 35 °C and Δp of 4.4 atm. As typically observed in glassy polymers [35,36], the gas permeability in both unfilled and silica-filled PSf generally decreases with penetrant molecular size in the following order:

$$H_2 > He > CO_2 > O_2 > N_2 > CH_4$$

In addition, the gas permeabilities of silica-filled PSf are higher than those of unfilled PSf and increase as the ϕ_f increases. This trend is more clearly shown in Fig. 4, which presents the

Table 3

$\overline{P(\times 10)}$ cm/(cm	D^{-10} cm ³ (STP) n ² s cmHg), barrer)	$D(\times)$	$10^{-8} \text{cm}^2/\text{s}$	$S (\text{cm}^3)$	(STP)/cm ³ atm)	P_{O_2/N_2}	D_{O_2/N_2}	S_{O_2/N_2}	$\Delta p (\text{atm})$	Reference
O ₂	N ₂	O2	N ₂	O ₂	N ₂	-				
1.29	0.22	3.4	0.85	0.29 ^a	0.19 ^a	5.7	4.0	1.5	10	[33]
1.4	0.25	4.4 ^b	1.22	0.24	0.15 ^a	5.6	3.6	1.6	5	[31]
1.4	0.24	4.5 ^b	1.24	0.23	0.15	5.6	3.4	1.7	4.4	This study

Dormonhility	diffusion and	olubility	agafficiants t	<u>.</u>	and M.	and cala	ativition	of nol	uculfona	ot 25	°C
renneadinty,	unitusion and	soluointy	coefficients u	$0 O_2$	and m ₂	and sele	cuvines	or por	ysunone	at 55	C

^a S (sorption coefficient) was measured using a transducer barometric device.

^b D (diffusion coefficient) was estimated from permeation time-lag.

Table 4

Permeability, dif	ffusion and solubility	coefficients to CO	2 and CH4 and	l selectivities of polysulfone at 3	35°C
				1 7	

$\overline{P(\times 10^{-10} \text{ cm}^3 \text{ (STP)})}$ cm/(cm ² s cmHg), barrer)		$D (\times 10^{-8} \text{ cm}^2/\text{s})$ $S (\text{cm}^3 (\text{STP})/\text{cm}^3 \text{ atm})$		$P_{\rm CO_2/CH_4}$	$D_{\rm CO_2/CH_4}$	$S_{\rm CO_2/CH_4}$	$\Delta p (\text{atm})$	Reference		
CO ₂	CH ₄	$\overline{\text{CO}_2}$	CH ₄	CO ₂	CH ₄	_				
5.5	0.24	2.0	0.35	2.08 ^a	0.67 ^a	23	7.4	3.1	10	[33]
5.6	0.25	2.0	0.34	2.1 ^a	0.56 ^a	22	5.9	3.7	10	[31]
6.3	0.22	1.2 ^b	0.27	4.0	0.6	29	4.5	6.5	4.4	This study

^a S (sorption coefficient) was measured using a transducer barometric device.

^b D (diffusion coefficient) was estimated from permeation time-lag.

relative permeability of PSf/silica MMMs to H₂, He, O₂, N₂, CH₄, and CO₂ as a function of the ϕ_f . For all penetrant gases, the permeability of silica-filled PSf is higher than that of unfilled PSf and also increases with increasing silica content. This result is in contradiction to the Maxwell model, which predicts that the gas permeability of a mixed-matrix membrane containing non-porous filler is lower than that of the unfilled polymer and also decreases with increasing filler content due to the decrease in diffusivity by increasing the tortuousity in the polymer matrix.

The gas transport properties of PSf/silica MMMs are strongly associated with a substantial change of free volume (i.e., quantity of nanospace) caused by introduction of silica nanoparticles. Previously, it was reported that the addition of nonporous silica nanoparticles to rigid, glassy high-free-volume polymers (e.g., PMP and PTMSP) increases the total free volume of the membrane by disrupting the polymer chain packing [11–13,15]. The increase in free volume was proved by positron annihilation lifetime spectroscopy (PALS) [37]. Ultimately, more spacious pathways lead to an increase in diffusivity, thereby resulting in increased permeability of PSf/silica MMMs.

Generally, the fractional-free-volume (*FFV*) can be calculated from group contribution methods as the ratio of the difference between the polymer bulk specific volume (v_{sp}) and

Table 5

Gas permeabilities of polysulfone and polysulfone/silica mixed-matrix membranes as a function of silica content at 35 $^\circ C$ and Δp of 4.4 atm

$\phi_{ m f}$	Permeability, P (barrer)									
	H ₂	He	O ₂	CO ₂	N_2	CH ₄				
0.00	11.8	11.8	1.4	6.3	0.24	0.22				
0.05	13.8	13.1	1.8	7.7	0.31	0.29				
0.10	15.9	14.9	2.0	9.3	0.40	0.38				
0.15	22.7	20.1	3.4	12.9	0.67	0.62				
0.20	32.3	27.7	5.0	19.7	1.12	1.10				

volume occupied by polymer chains (v_0) to v_{sp} by the following equation [38]:

$$FFV = \frac{v_{\rm sp} - v_{\rm o}}{v_{\rm sp}} \tag{9}$$

In glassy polymers, the *FFV* is comprised of the excess free volume elements frozen into the polymer matrix as well as the normal free volume arising from incomplete polymer chain packing.

Besides the inefficient chain packing that decreases the overall density, it is considered that another important element exists that increases the excess free volume. It is believed that this over-



Fig. 4. Enhancement of permeability (i.e., ratio of permeability of silica-filled polymer to that of unfilled polymer) of polysulfone–silica mixed-matrix membranes to a variety of penetrants as a function of silica volume fraction at 35 °C and Δp of 4.4 atm.



Fig. 5. Void vol.% derived by (e.g. Eq. (11)) the difference between theoretical and measured density in polysulfone/silica mixed-matrix membranes as a function of silica volume fraction.

riding factor might be related to voids at the interface between the polymer and silica nanoparticles or by agglomeration of silica nanoparticles. Previous literature [17,18] indicates that in impermeable silica-filled conventional rigid, glassy polymers, substantial voids exists around the silica nanoparticles. The presence of void volume certainly affects the gas permeation behavior in MMMs. This is unlike an ideal composite [6], whereby the introduction of filler into the polymer matrix may occur without voids and be evenly dispersed without aggregates, consistent with the Maxwell prediction.

In this study, the presence of excess void volume can be explained as a result of a lower measured density (shown in Table 1) than the theoretically calculated density [39] of PSf/silica MMMs. The theoretical density ($\rho_{\rm T}$) can be calculated as Eq. (10), if the polymer volume fraction ($\phi_{\rm p}$) is $1 - \phi_{\rm f}$.

$$\rho_{\rm T} = \rho_{\rm p} \phi_{\rm p} + \rho_{\rm f} \phi_{\rm f} \tag{10}$$

The excess specific volume fraction (ϕ_{ex}) can be estimated as follows [17]:

$$\phi_{\rm ex} = 1 - \frac{\rho_{\rm M}}{\rho_{\rm T}} \tag{11}$$

where $\rho_{\rm M}$ is the measured density (gravimetric analysis, i.e., samples of known area and thickness weighed on an analytical balance). Fig. 5 shows the existence of excess void volume, which increases with increasing the silica volume fraction. Although this excess free volume is extremely small, less than 3% in PSf containing 0–20 volume% (vol.%) of silica, the existence of this small excess free volume supports the observation of an increase in sorption coefficient in PSf/silica MMMs due to sorption on the PSf–silica interface, which will be discussed later.

An increase in total free volume from both inefficient chain packing and the presence of void volume, results in increases in diffusion and solubility coefficients and thus leading to the increase in permeability. This is clearly seen in Fig. 6, which presents permeability, diffusion and solubility coefficients of PSf/silica MMMs relative to unfilled PSf for each penetrant (e.g., O_2 , N_2 , CO_2 , and CH_4) as a function of ϕ_f . The relative permeability is strongly affected by the diffusion coefficient and less affected by the solubility coefficient, and it is a result of the increase in packing density [40]. In comparison with gradually increased diffusion coefficient, it is observed that the solubility coefficient of a low-content silica-filled PSf matrix is lower than that of unfilled PSf, whereas it is higher in the high-content silicafilled PSf matrix. As mentioned earlier, the excess free volume affecting the sorption capacity is extremely small, particularly in a low-content silica-filled PSf matrix. For low silica volume contents ranging from 5 to 10 vol.%, the filler may reduce the solubility coefficient by reducing sorption volume of polymer in the filled membrane, consistent with Eq. (7). However, in the higher silica volume fraction content range of 15-20 vol.%, the greater amount of excess free volume overcomes the previous effect to enhance the solubility.

Furthermore, increasing free volume by increasing $\phi_{\rm f}$ is associated with the fumed silica nanoparticle distribution, as observed by TEM and SEM in Figs. 2 and 3. The fumed silica nanoparticles are generally aggregated over all $\phi_{\rm f}$ ranges, rather than being isolated in the polymer matrix [29] and the agglomerate size is increased with increasing $\phi_{\rm f}$. It is possible that the size of voids existing at the PSf-silica interface or within the agglomerates is dependant on the size of the agglomerates. That is, an increase in agglomerate size with silica content results in an increase in void size, eventually leading to permeability enhancement. Increasing aggregate size with silica content is likely to increase the interface space, thereby enhancing sorption. Thus, as silica content increases, because of enhancements in both diffusion and sorption, the relative permeability increases nonlinearly. Hence, the trend of increased relative free volume with silica content corresponds with that of the relative gas permeability [37]. Consequently, the nonlinear increase in gas permeability with silica content may arise from a tendency of free volume increase due to nanoparticle agglomeration [41]. As a result, the permeability of PSf is increased remarkably by the addition of silica nanoparticles. For example, in the case of CH₄, the permeability enhancement of PSf containing 20 vol.% of silica is approximately 500% greater than that of unfilled PSf, whereas a 73% reduction in permeability is predicted by the Maxwell model. This relative enhancement in permeability is higher than that in highfree-volume glassy polymers, such as PMP and PTMSP. This in accordance with the observations of a previous study [13]. Polymer chain packing is more hindered by the incorporation of silica in polymers with relatively low-permeability and lowfree-volume rather than in high-permeability, high-free-volume polymers.

Fig. 4 also shows that the relative enhancement in permeability depends significantly on the molecular size of the penetrant, the permeability enhancement is in the following order:

$$CH_4 > N_2 > O_2 > CO_2 > H_2 > He$$

The permeability enhancement of the larger penetrants is greater than that of smaller gases in PSf/silica MMMs because any increase in molecular spacing in a hybrid membrane will have a larger effect on the diffusion coefficient and permeability



Fig. 6. Enhancement of gas transport properties for (a) O_2 , (b) N_2 , (c) CO_2 , and (d) CH_4 as a function of silica volume fraction; enhancement in permeability coefficient (), diffusion coefficient ().

for large gases. This behavior is clearly shown in Fig. 7, which shows the relative gas permeability in a variety of silica-filled membranes having various ϕ_f as a function of the critical volume of penetrants (V_c), which is shown in Table 2. As can be seen, the permeability enhancement is dependant on the penetrants' molecular properties and it generally increases with V_c . Moreover, the increase in relative permeability with V_c increases with ϕ_f . Originally, the relative permeability was anticipated to be independent of the penetrants' molecular size, even taking into account the presence of the excess free volume, void interface space [18]. This unpredicted result may be related to the size of the free volume cavity due to an increase in void size. The increase in free volume indicates an increase in average free volume cavity size and this enhancement in nanospace size has been observed by PALS analysis in a previous study [42,43].

Table 6
Diffusion and solubility coefficients to O_2 and N_2 of silica-filled polysulfone with increasing volume fraction of silica at 35 °C and Δp of 4.4 atm

$\overline{\phi_{\mathrm{f}}}$	$D (\times 10^{-8} \mathrm{cm^2/s})$		S (cm ³ (STP)/cm ³ atm)		$D_{\mathrm{O}_2/\mathrm{N}_2}$	$S_{\rm O_2/N_2}$	P_{O_2/N_2}
	$\overline{O_2}$	N ₂	$\overline{O_2}$	N ₂	-		
0.00	4.2	1.2	0.25	0.15	3.4	1.7	5.6
0.05	6.4	1.7	0.21	0.14	3.8	1.5	5.6
0.10	7.0	2.3	0.22	0.13	3.0	1.7	5.3
0.15	9.4	2.7	0.28	0.19	3.5	1.4	5.1
0.20	11.9	4.4	0.32	0.19	2.7	1.7	4.5



Fig. 7. Relative permeability, diffusion and solubility coefficients of silica-filled polysulfone as a function of the critical volume (V_c) of penetrants at 35 °C and Δp of 4.4 atm.

For example, in a high-free-volume glassy polymer, PTMSP, the average diameter of the free volume cavity is approximately 0.42 nm for small cavities and 1.2-1.4 nm for large cavities. The incorporation of fumed silica in PTMSP increases the larger cavities more than smaller ones. On the other hand, in the case of low-free-volume PSf, the average free volume cavities are small compared with those in high-free-volume glassy polymers, approximately 0.436 nm [44]. Presumably, the effect of increasing free volume size is more directed towards small cavities, and thus larger penetrants such as methane, which have low permeability in PSf, have a larger relative permeability enhancement than smaller gases such as oxygen. Specifically, a larger penetrant CH₄ (d_{LI} : 0.376 nm) has a relatively higher permeability enhancement than a smaller penetrant O₂ (d_{LI} : 0.347 nm) resulting from increased nanospace size due to the introduction of the fumed silica. Unfortunately, this effect leads to a decrease in ideal selectivity for O2/N2 and CO2/CH4 with the silica loadings in PSf/silica MMMs.

4.4. Correlation of permeability, diffusion and solubility coefficients selectivity

Table 6 shows the O_2 and N_2 diffusion and solubility coefficients as well as the ideal selectivities of the membranes. The decreased selectivity is more affected by diffusion selectivity rather than solubility selectivity. Similar to O_2/N_2 gas transport behavior, the CO_2/CH_4 selectivity generally decreases with silica content resulting from the significant decrease in diffusion selectivity, as shown in Table 7. However the decrease in CO_2/CH_4 selectivity is greater than that of O_2/N_2 selectivity. A distinct reduction in CO_2/CH_4 selectivity was observed in PSf containing 20 vol.% of silica, which was caused by a significant increase in CH_4 permeability. This result is ascribed to strong effects on the diffusion coefficient and permeability with increasing free volume and inter-molecular spacing.



Fig. 8. Trade-off between O_2 permeability and O_2/N_2 selectivity of polysulfone and polysulfone–silica mixed-matrix membranes relative to the Robeson upper bound.

4.5. Evaluation of gas permeation performance

Based on the present results, the gas permeation properties of PSf/silica MMMs were evaluated by correlation of the gas permeability and selectivity for O_2/N_2 and CO_2/CH_4 as presented in Figs. 8 and 9, respectively. PSf is a membrane material which has comparatively low permeability and moderately high selectivity, which is typical of a number of glassy polymers for gas separation. The gas permeation properties of PSf are changed by the addition of nanosized-fumed silica. As the silica content in PSf is increased, the gas permeability is increased, whereas the selectivity is slightly decreased for both O_2/N_2 and CO_2/CH_4 . Specifically, in PSf containing 20 vol.% of silica, the relative permeability to O_2 gradually increases up to 380%, whereas the O_2/N_2 selectivity decreases by 80%. It is also observed that the relative permeability to CO_2 gradually increases up



Fig. 9. Trade-off between CO_2 permeability and CO_2/CH_4 selectivity of polysulfone and polysulfone–silica mixed-matrix membranes relative to the Robeson upper bound.

$\phi_{ m f}$	$D (\times 10^{-8} \text{ cm}^2/\text{s})$		$S (\text{cm}^3 (\text{ST}))$	$S (\text{cm}^3 (\text{STP})/\text{cm}^3 \text{atm})$		$S_{\rm CO_2/CH_4}$	P _{CO₂/CH₄}
	CO ₂	CH ₄	$\overline{\text{CO}_2}$	CH ₄	-		
0.00	1.19	0.27	4.02	0.62	4.5	6.5	29
0.05	1.47	0.37	3.97	0.59	4.0	6.7	27
0.10	1.82	0.52	3.87	0.55	3.5	7.0	25
0.15	2.38	0.66	4.14	0.72	3.6	5.7	21
0.20	3.79	1.25	3.96	0.66	3.0	6.0	18

Diffusion and solubility coefficient to CO_2 and CH_4 and selectivity of silica-filled polysulfone with increasing volume fraction of silica at 35 °C and Δp of 4.4 atm

to 310%, whereas the CO_2/CH_4 selectivity decreases by 62%. As a result, the gas permeation performance of silica-filled PSf reflects exactly the upper bound slope with increasing silica volume fraction on the trade-off of permeability and selectivity. Although this behavior does not overcome the upper bound, this work makes a significant contribution to the understanding of gas transport in silica-filled low-free-volume glassy polymers that enhance their gas permeability.

5. Conclusions

Glassy polysulfone mixed-matrix membranes were prepared by introducing nonporous nanosized silica particles to investigate the effect of filler on the gas transport properties. Similar to the case of high-free-volume glassy polymers, the addition of silica significantly enhances the gas permeability of polysulfone with increasing silica content. This behavior results from an increase in free volume because of the inefficient chain packing as well as the presence of extra void volume at the interface between polymer and silica clusters. Moreover, the permeability of large gases is more enhanced by the addition of silica resulting from the increase in free volume, which strongly increases the diffusion coefficient and permeability, and results in a reduction in pure-gas selectivity. Consequently, the incorporation of fumed silica did not result in an overall improvement in performance of permeability versus selectivity in relation to the upper bound. However, it is notable that nonporous nanosized silica disrupts polymer chain packing leading to an increase in free volume in low-free-volume glassy polymers. Furthermore, the relative enhancement in permeability is significantly greater than in high-free-volume glassy polymers.

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Table 7

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