

Separation of CO₂/CH₄ by blended Polysulfone/ABS-Silica Nanocomposite Membranes

Leili Shams Salari^a, Mahmoud Salimi^{b,1}

^aDepartment of Chemical Engineering, Arak University, Arak, Iran ^bDepartment of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran

Article	Abstract (row height 0.8 cm)		
Article history: Received: 2021/03/10 Received in revised form: 2021/06/14 Accepted: 2021/06/19	In the present study, Polysulfone/ABS-10% composite and Polysulfone/ABS- 10%-silica nanocomposite membranes prepared for CO ₂ separation from CH ₄ . A dense blend polymeric membrane with two partially miscible polymers was made and nano-silica was added into it to improve gas transport properties. The membranes were prepared by solution casting method and characterized by		
Keywords: Gas Separation, Nanocomposite Membrane, Blended polymer matrix, Silica, polysulfone	Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM). Transport characteristics of single gas for CO_2 and CH_4 were investigated by the single gas test. Feed pressure altered from 2 to 6 bars and temperature kept at 25 °C. The gas permeability of methane and carbon dioxide were evaluated as a function of silica concentration. Permeability results show that by adding silica nanoparticles into the PSF/ABS matrix, permeability of both CO_2 and CH_4 increased and loading up to 3 wt.% increased the selectivity of CO_2/CH_4 from 9.13 to 24.48 Barrer at 2 bars.		

1. Introduction (head 1)

Methane is the main compound of natural gas and carbon dioxide is a major greenhouse gas and impurity in natural gas, that its needs to be removed from this gas streams. Low manufacturing cost and processing ability are the most important characteristics of polymeric membranes that make them conqueror in the industry [1-5]. The measurement performance of gas separation membranes is characterized by permeability (P) and selectivity (α), and membrane performance affected by material and structure [6-7]. Using new manufacturing process, formulate, and material were some of the researchers proceeding to overcome the problem with a polymeric membrane, achieving higher selectivity with similar processing ability and more persistent in the presence of harsh and aggressive feed is the most important issues [5,8]. Adding inorganic fillers in an organic polymer matrix is one of the good manners that improve both permeability and selectivity of gasses. Some of the inorganic

¹Corresponding author at: Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran Email address: m-salimi@iau-arak.ac.ir

Fax: +98- 912-7246004

particles may improve physical, thermal, and mechanical properties of the membrane. The permeability throughput of membranes can be enhanced by adding inorganic materials like silica particles into the polymeric matrix [5, 9-10]. Glassy polymers because of high gas selectivity and good mechanical features are the most domain membrane in industry. Polysulfone is a useful polymer for gas separations and because its high selectivity, it was the high consumption polymeric membrane for many years [8, 11]. Gas separation membranes follow solution-diffusion transport and this kind of membranes have many problems to overcome the limitation of 'upper bound' mixed matrix membranes (MMMs) that can enhance transport characteristic of the membrane [12]. Generally, inorganic particle phase are dispersed in the polymer matrix and their properties will affect by nanoparticles type, nanoparticle size, particle agglomeration, polymer/nanoparticles interface morphology [13-14]. Good mechanical strength, thermal stability, and chemical inertia are the most important characteristic of nanoparticles. Nano silica has most of this characteristic [15]. Poor distribution of particles and compatibility of nanoparticles and polymer is the first challenge facing MMMs [1]. Some mixed matrix membranes have the potential to achieve higher selectivity, permeability, or both relative compatibility of filler and polymer lead to aggressing this goal [16]. Polymer blending is a good manner to having good properties of two polymers in one matrix. Two polymers may are miscible, partially miscible or immiscible [17]. The ABS material has rubbery and glassy matrix (styrene-co-acrylonitrile) segments. Because of its rubbery region and glassy matrix, it has high permeability and selectivity [18]. Ahn et al. [19] characterized PSF/silica MMMs and they found CH₄ permeability is over five times greater than for the pure PSf membrane. Rafiq et al. [10] developed the membranes by Polysulfone/polyimide (PSF/PI) with inorganic silica nanoparticles. The highest permselectivity of $(CO_2/CH_4) = 61$ observed for treated membrane at 2–10 bars. Ismail et al. [20] investigated Blend of PES/PI incorporating zeolite 4A particles. Dorosti et al. [21] studied on dense PSF/PI membranes with zeolite. Xing [22] worked on PVA/PEG blend membranes with zeolite 5A filled for CO_2/CH_4 separation. In this research, the performance of PSF/ABS 10%-silica nanocomposite membranes in the permeation properties of CO_2/CH_4 has been studied. All nanocomposite membranes were prepared using solution casting method.

2. Materials and methods

2.1. Materials

Polysulfone (Ultrason S6010, T_g189 ^oC)) with reported density of 1.23 g/cm³ was supplied by BASF Company, ABS-SD-0150 supplied by (T.P.C). The organic solvent Dichloromethane (DCM, 99%) was supplied by Merk. The nanoparticle of Silica was supplied from US Research Company. Silica nanoparticles have size about 5-10 nm. The CO₂ (purity 99.99%) that used for gas permeation test was purchased from Iran Azote Charger gas Company and CH₄ was purchased from Iran Arian Gas company. The chemical structures of PSF and ABS are shown in Fig. 1.

2.2. Polysulfone/ABS membrane preparation

Samples with different blends of PSF/ABS containing 10, 15, 20, 25, and 30 wt% ABS were prepared by solution casting method, in order to compare their permeability results and choose the best membrane. For this purpose, a known weight of PSF powder was dissolved into the dichloromethane solvent and mixed using a magnetic stirrer for about 1hours. In the next step, the needed weight amount of ABS was dissolved in the solution and dispersed by stirring. The polymers were dissolved and continue stirring at 27 °C for 2-3 hours then the solution placedin ultrasonic for 20 minutes to have the homogenous solution. The solution filtered with a $0.2\mu m$ filter to separate undissolved materials and impurities. The nanocomposite membrane films were cast on the clean glass plate. Finally, then the nocomposite membranes were dried in a vacuum oven at $65^{\circ}C$ for 10 hours to evaporate the solvent completely. The mentioned technique was used for the preparation of five samples with various compositions.



Figure 1. Chemical Structure of (a) PSF and (b) ABS

2.3. Polysulfone/ABS silica nanocomposite membrane preparation

After comparison of the gas permeability results of prepared mixed matrix membrane, the suitable blend was chosen for nanocomposite preparation. In preparation of nanocomposite membrane at 10 %wt. ABS in PSF is selected because of the best performance result respect to the other blend composition. Then, the silica nanoparticles with different weight percentage added to the polymer solution (PSF/ABS-10%) and mixed well at 27 °C for 2-3 h then the solution placed in the ultrasonic bath for 20 minutes to remove the bubbles and homogenous solution completely. Then a nocomposite membrane films were cast on the clean glass plate. Finally, the membranes were dried in a vacuum oven at 65 °C for 10 hours to evaporate the solvent completely.

2.4. Membrane characterization

The morphological characteristic of prepared membranes was analyzed by VEGA//TESCAN-LMU. The film was ruptured in the liquid nitrogenand then coated with gold. The distribution of silica nanoparticles in the prepared membranes was investigated too by scanning electron microscope. The FT-IR spectrum of the developed membranes was evaluated using Unicom galaxy series FT-IR 5000 spectrophotometer in the range of 400–4000 cm⁻¹.

2.5. Gas permeation experiments

The permeation performance of synthesized membranes was evaluated by two parameters. One of those is the permeability and the other is selectivity. The permeability of all the fabricated polymeric blends and mixed matrix membranes for CO₂ and CH₄ were determined constant volume/variable pressure technique. Polysulfone/ABS-silica flat sheet nanocomposite membranes with an effective area of 22.4cm² were used for gas separation experiments. The feed pressure was varied from 2 to 10 bars and the temperature was kept at 25°C. The permeate side was kept at atmospheric pressure. The gas permeability of prepared membranes was calculated using the following equation [19, 23]:

$$P = \frac{273.15LV}{76p_0 AT} \frac{dp(t)}{dt}$$
(1)

The permeability are reported in Barrer where 1 Barrer is 10^{-10} cm³ (STP) cm/cm² s cm Hg, V is the volume of the downstream chamber(cm³), A is the effective area of prepared membrane (cm), L is the membrane thickness (cm), T is the temperature (K), dp(t)/dt the steady state rate of pressure in the downstream chamber and p0 is the feed pressure with the same unit of p (t). The selectivity of membrane for gases can be calculated as:

$$\alpha_{AB} = \frac{P_A}{P_B} \tag{2}$$

Where, PA and PB are pure gas permeability of gas A and gas B, respectively.

3. Results and discussion

3.1. Membrane Characterization

3.1.1. FTIR Spectroscopy

The FTIR spectra of the prepared membranes were showed in Fig. 2. The peak of 3396 cm⁻¹ in curves A and B that relate to pure silica and PSF/ABS-silica respectively conform to the presence of Si-OH, so this peak describes the existence silica nanoparticle in the membrane matrix. The peaks related to Si–O-Si symmetry stretching occurred at 810 cm⁻¹ and 1118 cm⁻¹. The presence of silica particles had shifted the peak 1903 cm⁻¹ describes the existence of an interaction between polymer and silica. After adding silica particles in the membrane, the peak of 1585 cm⁻¹ disappeared. There is no obvious changes in the intensity and weakness of peaks in curve relate to pure polysulfone in comparison to PSF-ABS blend (curves D and C). So the interaction between two polymers is enough to cause good distribution ABS in polysulfone matrix.



Figure 2. FTIR spectra of: (A) npure silica (B) PSF/ABS 3 wt% silica (C) PSF/ABS (D) pure PSF

3.1.2. Scanning Electron Microscope

As above mentioned, the membrane structures were investigated by scanning electron microscopy (SEM). Images of the flat sheet nanocomposite membranes with various contents of nanosilica particles are shown in Fig.3. From the membrane's structure can be observed that polysulfone and ABS are partially miscible. The micro ABS phase is dispersed in the continuous polysulfone phase.



Figure 3. SEM images of: PSF/ABS (90/10), (a) cross section images of membrane without silica (b) cross section images of membrane with 1 wt% silica (c) cross section images of membrane with 3 wt % silica (d) cross section images of membrane with 5 wt% silica (e) surface image of membrane without silica (f) surface image of membrane with 3 wt% (g)) surface image of membrane with 5 wt% silica (h) high magnification of membrane with 5 wt% silica

According to the description of MMM, this blend matrix can be considered as MMM [16]. SEM images show that the obtained membrane without nanoparticle is dense and uniform in cross-section. As images with high magnification show compatibility between nanoparticles and polymers are acceptable and there is not rupture between the polymer and nanoparticles. Morphology diversity depended on the silica concentration. In the nanocomposite membrane with 3%wt. silica particles loading, SEM imagesrevealed good adhesion between polymer and silica particles. As 5 wt% silica particles loading SEM results of MMMs exhibited more irregular with non-uniform structure in surface furthermore MMMs with 5%wt. silica loading showed more agglomeration in cross section. The particles in micron size appeared after adding 5%wt. nanoparticle that results from the agglomeration of nano silica particles. Due to the formation of aggregates, the membrane did not show homogeneity in comparison to other surfaces. The gas permeability of the membrane is not only dependent on the membrane structure andthe gas properties but also, poor adhesion between inorganic particles and polymer chain could influence the permeability [13].

3.2. Gas permeation properties of prepared membranes

3.2.1. Evaluation the effects of ABS the concentration on the gas permeability

Membranes with a various weight percent of PSF and ABS content were investigated by CO_2 and CH_4 permeation test to delineate effect of ABS content on the transport properties of the membranes. Table1 shows that the blend membranewith a composition of 90/10 (PFS /ABS) hasmaximum selectivity and as ABS amount increases in blend membrane, the selectivity of gases decreases and on the other hand permeability of both CO_2 and CH_4 increased. As the results showed that mixed matrix membraneis able to offer higher permeability and acceptable selectivity in comparison to the pure membranes. So this blend (PFS /ABS-10%) was chosen to investigate the effect of adding silica nanoparticles on characteristics and transport properties of the blend of PSF/ABS membranes.

Membrane	P _{CO2}	P _{CH4}	α _{CO2/CH4}
PSF	1.52	0.18	8.44
PSF/ABS(90/10)	1.89	0.21	9
PSF/ABS(80/20)	2.6	0.3	8.66
PSF/ABS(70/30)	2.9	0.36	8.05
ABS	3.78	0.378	7.14

 Table 1: Gas permeability (in Barrer) and ideal selectivity at 5 bars through the pure and blend membranes.

3.2.2. The effect of adding silica nanoparticles on the gas permeability

Mixed matrix membranes with blends of Polysulfone–ABS 10% filled with the different content of silica nanoparticles were fabricated (Table 2). The blend membranes with 10 %wt. ABS showed a CO_2 permeability of 1.89 Barrer and a CO_2/CH_4 selectivity of 9 at 5 bar (Fig. 4). With the addition of 1 %wt. silica contents in membranes composition, the CO_2 permeability increased from 1.9 to 4.0 Barrer at 4 bars feed pressure, compared to unfilled membranes.



Figure 4. Permeability of pure CO₂ gas for PSF/ABS 10% membraneat with different silica compositions against feed pressures



Figure 5. Permeability of pure CH4 gases for PSF/ABS-20% membraneat different silica compositions against feed pressures

Because of the solution-diffusion mechanism of permeation in polymeric membrane OH groups of silica increase the CO_2 dissolving in the membrane. Furthermore adding silica nanoparticles increase molecular sieve property of membranes so smaller molecules can permeate more than larger one [24]. After adding silica nanoparticles permeability of two gases increase but an enhancement in the permeability of CO_2 was more than CH_4 (Fig. 6) because of molecular sieve property of composite membranes and larger molecular size of CH_4 in comparison to CO_2 . So according to this fact and results obtained from permeability test, it's obvious that the permeability of CO_2 is more than CH_4 because of its condensability and polar properties.

The permeability of CO_2 increases by adding more silica content until 30Barrer for a membrane with 5 %wt. nano-silica. As silica contents increase CH_4 permeability (Fig. 5) enhanced similar to CO_2 . It was noticed that this is due to the fact that the silica particles caused disrupting in the polymer chain packing and increase the permeability of the membrane. So the structure will be disordered and free volume growth which caused increasing the gas permeability [22].

			Permeability(Barrer)		Selectivity
Run	SilicaPercentage	Feed	P _{CH4}	P _{CO2}	aco2/CH4
	(wt.%)	Pressure(bar)	-		
1	0	2	0.23	2.1	9.1304
2		3	0.22	2.01	9.1363
3		4	0.2201	1.9	8.63
4		5	0.21	1.89	9
5		6	0.199	1.79	9.04
6	1	2	0.4	4.1	10.25
7		3	0.399	4	10.02
8		4	0.36	4	10.25
9		5	0.35	3.58	10.022
10		6	0.31	3.13	10.02
11	2	2	0.3	3.00	10.00
12		3	0.8	9.5	11.87
13		4	0.78	9.01	11.55
14		5	0.75	9	12
15		6	0.69	8.6	12.46
16		2	0.68	8.2	12.05
17		3	0.67	8.1	12.08
18	3	2	0.98	24	24.48
19		3	0.97	23.6	24.32
20		4	0.96	24.27	23.3
21		5	0.95	23.00	24.21
22		6	0.94	22.6	24.04
23	4	2	1.37	27	19.70
24		3	1.36	26.5	19.48
25		4	1.35	26.4	19.55
26		5	1.34	26.3	19.625
27		6	1.33	26.1	19.626
28	5	2	2.4	30	12.5
29		3	2.39	29.6	12.38
30		4	2.38	29.1	12.22
31		5	2.36	27.6	11.94
32		6	2.32	27.1	11.68

 Table 2. The effect of the silica percentage on the gas permeability and selectivity of the nanocomposite membranes made of PSF/ABS-10% silica



Figure 6 Effect of feed pressure on CO_2/CH_4 selectivity for MMMs with different silica content at 27 $^{\circ}\mathrm{C}$



Figure 7 Effect of loading percentage of silica on CO2 permeability at 4 bars

Fig. 7 shows the permeability of CO_2 and CH_4 versus loading percentage of silica particles at 4 bars. Thehydroxyl and other functional groups on the surface of these nano-materials may also interact with polar gases and thusimprove the penetrant solubility in the resultant nanocomposite mixed matrix membranes [25].Permeability results illustrate that the selectivity decrease after adding more than 3 wt.% nanoparticle,membrane selectivity increase with increasing nanoparticle till 3 %wt. (24.48 at 2 bars)but after that decreasing in selectivity was observed. In relation with SEM images, it is seen that with the highest silica loading of 5 %wt., silica particles aggregates increase. As noticed at higher silica contents disorder and free space increase and chain packing decrease so these changes caused enhancement in the gas permeation [10]. Formation of voids and an interfacial defect is a result of poor adhesion of polymers matrix and nanoparticles [26]. The predominant problem facing glassy polymers are used in the preparation of MMMs is adhesion between the polymer phase and particles, weak compatibility of polymer-filler caused the formation of voids and free space without selectivity [11]. The free volume that created by silica aggregations is disadvantages of incorporating nanoparticles in glassy polymers. More condensable gases show higher permeation in nonporous glassy polymer membrane [27]. Considering the SEM images with different magnification reveals the presence and distribution of silica particles in micron and nanometer as shown in Fig. 3, there are particles in micron size in the polymer matrix with 5 %wt. silica because of nano-silica particles agglomeration. As illustrated in FTIR spectra there is good interaction between polymer and silica particle but with adding more silica content and appearing more aggregation permeability will not be controllable. Increasing the feed pressure is the cause of decreasing both selectivity and permeability. It is because of permselectivity properties of PSF that dominate in the polymer matrix. As increasing the feed pressure permeation site saturate and permeability decrease.

4. Conclusion

In this study, the transport of CO_2 and CH4 in PSF/ABS blend membranes with different ratio of polymers at 27°C and 2–6 bar feed pressure were investigated. Gas transport property was measured using pure CO2 and CH₄ gases and suitable content of ABS was used to investigating the effect of silica nanoparticles on transport properties of PSF/ABS blend.Adding silica nanoparticles into the PSF/ABS matrix increased both CO_2 and CH₄ permeation, and increasing of CO_2/CH_4 selectivity as the silica loading increased to 3wt.% (24.48 at 2 bar) and decreasing after adding more than this content was probably due to the formation of agglomerates and poor adhesion of silica nanoparticles with polymer.

FTIR spectra confirm the desirable mixing of the silica in polymer and a weak compatibility between the two polymers. A comparison between polymer blend membranes shows that membranes with 90/10wt% ABS and 3 wt.% nanoparticles have higher selectivity, since that this result is highly dependent on manufacturing condition as a general conclusion it can say that blending of PSF/ABS polymers is effective in improving the permeation properties and economical point of view.

Disclosure of potential conflicts of interest

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