



Preparation and Characterization of Amine-functional SAPO-34 Mixed Matrix Membranes for CO₂/CH₄ Separation

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PAPER INFO

Paper history:

Received 18 February 2022

Accepted in revised form 07 May 2022

Keywords:

Amine
SAPO-34
Polyethersulfone
CO₂ Separation

A B S T R A C T

Removal of CO₂ in natural gas refining has currently been the only membrane based process practiced on a large scale operation. Despite the predominance of polymeric membranes in the CO₂/CH₄ separation, the tradeoff limitation in between membrane selectivity and permeability hinders a good separation performance of these membranes. Mixed matrix membranes can offer dramatic improvement to overcome this shortcoming. In this study, polyethersulfone mixed matrix membranes incorporated with small pore amine modified SAPO-34 were proposed for CO₂ separation. SAPO-34 zeolite was used as inorganic fillers to enhance gas selectivity. The asymmetric membrane structure was prepared using the phase inversion method in order to improve permeance. SEM images and FTIR analysis were used to characterize the filler particles and the synthesized membranes. SEM images also indicated that, there were appropriate distribution particles in the polymer matrix. The effects of filler loading (0-10 wt%), feed temperature (303-343 K) and feed pressure (0.5-4 bar) on CO₂/CH₄ selectivity of the MMMs were investigated. The results indicated that addition of amine-functional SAPO-34 in the casting solution enhanced the membrane gas permeance and CO₂/CH₄ ideal selectivity. For the membrane with 10 wt% of amine loading, selectivity was 17% higher than the membrane without functionalizing with amine. Increasing the temperature from 303 to 343 K reduced selectivity around 25-30.5 %.

doi: 10.5829/ijee.2022.13.03.04

INTRODUCTION

Nowadays, energy and greenhouse gas emission have become a critical issue and have been chosen by many researchers to investigate their advantages and disadvantages. All ongoing activities in society relatively and directly depend on energy, which makes them vulnerable against this vital source and shows the importance of energy in the world. Unfortunately, today the main source of energy is fossil fuels, such as coal, natural gas products, and petroleum, which produce lots of hazardous carbon dioxide (CO₂) [1, 2]. Besides, atmospheric concentrations of greenhouse gases (GHGs) have increased considerably, especially over the past five decades. The current atmospheric concentration of carbon

dioxide, which is an important trace gas available on earth's surface and regarded as the major GHG, is 411 ppm. According to various research findings, the main reason for climate change between 1750-2005 came from CO₂ emitted from different sources [3, 4]. Therefore, it is necessary to make some firm decisions to control CO₂ emission and diminish the amount of CO₂ emission in the world by using new technologies.

Nowadays, the membranes-based technology has been considered in various types of gas and liquid-based separation processes, in which low cost, compact structures, environmental friendliness, low energy consumption, and user convenience are among the most important reasons for consideration [3]. Over the last few decades, different polymeric membranes such as

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polyimides (PI), polyamides (PA), polysulfone (PSU), polyurethane (PU), and polyetherimide (PEI) were chosen by many researchers to use in different processes such as gas separation, natural gas purification, hydrogen recovery in petrochemical industries, biogas separation, and food packaging [4]. It should be mentioned for many membranes separations; when the membranes are highly permeable, there is a lack of sufficient and efficient selectivity (trade-off) [5-7]. Substantial research efforts have been carried out to enhance the polymeric membranes performance for use in gas separation and overcome the trade-off limitation. One of the methods that can facilitate this issue (trade-off) is using the composite membranes (mixed matrix membranes that contain an inorganic phase in a polymer matrix), which can exhibit higher permeability along with the selectivity of organic-inorganic mixed phases [8].

Polysulfone (PS) is a polymer with exceptionally considerable flexibility in structure and properties. The properties of PSs are simply fitted, enabling restrained changes in the length of the Polyol chain, and also changing the proportions and chemical characteristics of the components which create the flexible and rigid segments of the polymer chain [9]. Inorganic fillers are porous or nonporous. The idea of adding inorganic fillers to polymer matrix in order to enhance separation and mechanical properties has been explored [10, 11]. It should be noted that the effect of interaction between the particles and the polymer chain and functional groups on the surface of the inorganic phase must be considered [12-15]. Addition of particles can improve the separation properties of MMMs by raising matrix tortuous surfaces and declining diffusion of larger gas molecules. To improve permeation performance, the notion of introducing inorganic filler to the matrix of the polymer was proposed. Addition of various particles like zeolites, carbon molecular sieves and activated carbons, mesoporous materials, non-porous silica, metallic organic- frameworks (MOFs), and graphite [16] into the matrix of polymer was investigated. The results of cited literatures show that the small sizes of particles with high specific area disperse appropriately in polymer matrices. Small pore zeolites especially SAPO-34 appeared as interesting fillers due to its high adsorption affinity to CO₂. SAPO-34 zeolite is a chabazite (CHA) structure zeolite that has a 0.38 nm framework pore size; which is nearly similar to molecule sizes of the various gasses in a natural gas mixture.

Gas permeation characteristics of PS-SAPO-34-HMA were investigated by Elif et al. [17]. The results showed that the permeability of all the gases through PS-SAPO-34-HMA membranes was significantly more than those through PS/HMA membranes. New MMMs based on polymerizable room-temperature ionic liquids and SAPO-34 as filler were studied [18]. It was shown that by increasing the ionic liquids in the MMMs, increases the CO₂ permeability. The effect of the addition of SAPO-34

as filler on the gas permeation properties of other polymers such as polyetherimide [19], polyether block amide (PEBAX) [20], polyethersulfone [21], and polysulfone [22] has been researched. So far, few studies have been conducted in the field of adding SAPO-34 particles into the polyurethane matrix. The effect of silica particles on the permeation properties of polyurethane membranes was investigated [23]. The obtained results indicated the reduction in permeability of CO₂, CH₄, O₂ and N₂ gases. But enhancement of CO₂/CH₄, CO₂/N₂ and O₂/N₂ selectivity by increasing silica content was observed. Recently, the defects in polyethersulfone (PES)/ zeolite MMA. was prepared by dry-wet spinning technique for the separation of CO₂/CH₄ mixtures [24]. Interfacial incompatibility between polymer matrices and nanoparticle fillers has largely restricted the implementation of MMMs into practical membranes [25-27]. Improving interfacial compatibility between polymer matrix and a polymeric nanoparticle filler would be an advantage, particularly if the filler simultaneously introduced tailored high-speed CO₂ transport channels. Some success for this approach in terms of greatly improved performance has already been achieved, whereby CO₂ transport channels in fillers were introduced, while improving the interfacial compatibility between nanofillers and polymer matrix.

PES membranes exhibit resistance to high temperature with low manufacturing cost and high efficiency in the separation process. As membrane types are currently becoming in demand for CO₂/CH₄ segregation, PES will be an advantageous alternative to have in further studies. Dense PES membrane exhibits lower gas permeability as well as high selectivity as compared to other glassy polymers. Therefore, it is highly desirable to produce membrane having high permeate by reducing the thickness. The considerations within the literature lead to the combination of two strategies in this study; incorporation of low molecular weight organic additives to the MMM formulation and surface coated with (3-aminopropyl)-diethoxymethyl silane (APDEMS) to improve the gas permeation properties for carbon dioxide separation. To our best knowledge, not much research work focuses on the silane modification of SAPO zeolites to prepare MMMs for CO₂ separation. APDEMS was selected as silane coupling agent because methoxy silanes are more readily in hydrolysis reaction compared to ethoxy groups. Preparation and operation parameters including SAPO-34 loading, feed temperature and feed pressure were investigated and CO₂/CH₄ ideal selectivity of the prepared membranes were measured.

MATERIALS AND METHODS

MMMs were prepared using PS (ULTRASON E6020P; BASF, Germany) as polymer matrix due to its excellent thermal and mechanical characteristics. CH₄ gas

(99.995% purity) was acquired from Air Products Co. (Tehran, Iran). Other chemicals were taken from Sigma Alderich (USA).

Membrane preparation

SAPO-34 zeolite was prepared via hydrothermal synthesis according to previous work [25]. For amine-functionalization of SAPO-34, one 50 ml volumetric flask was charged with 2 g SAPO-34, 2 g sodium hydride and 20 ml tetra hydro furan. After 5 min 5 ml epichlorohydrin was added to the mixture at 0 °C, it was stirred for 30 min at this temperature and for 24 h at room temperature. Finally, SAPO-34 was separated via centrifugation and washed several times with water and dried at room temperature. Another 50 ml volumetric flask was charged with 2 g of the resulting SAPO-34, 10 ml tetrahydrofuran and 5 ml PDMS. The mixture was stirred for 24 h and amino SAPO-34 was separated via centrifugation and was washed several times with water. Finally, the resulting amino SAPO-34 was dried at room temperature.

MMMs were prepared via phase inversion method. Amino SAPO-34 was suspended in prescribed amounts of 60ml dimethylacetamide (DMAC), and the mixture was stirred at room temperature. To adequately disperse the filler particles within the solvent; the solution was sonicated for 1 h. Then 10g. polymer was added and stirred at room temperature. Following the ultrasonication of the final mixture for 60 min, it was blade cast on a glass plate at room temperature in air using a stainless steel film applicator with a casting knife of 500 μm, and placed in an oven preheated to 40 °C. Temperature was then increased to 80 °C, and the film was dried at 0.2 bar for 8 h under nitrogen. After that, the film was peeled off from the glass plate and annealed for 24 h at 100 °C in N₂ at 1 bar to remove the residual solvent. To seal the membrane defects and improve its selectivity, the top surface of the prepared MMMs were coated by a solution of PVA 5 wt.%. The dip coating method was carried out for the coating process, and then the coated MMMs were left in the air for 48 h for PVA to dry.

Membrane characterization

Geometrical characteristics and morphology of AMINE SAPO-34 and MMMs were studied using a KYKY-EM3200 SEM. The membrane samples were prepared by fracturing in liquid N₂ then coated with Au. The measurements of the FT-IR spectra of the samples were performed using Bruker spectrometer (SENSOR 27). Tensile testing to study tensile strength, tensile modulus and elongation at break (mm) were performed using SANTAM 20KN (Iran) testing machine at ambient temperature. All tests were done according to ASTM D638 standard.

Gas separation performance

The variable-pressure/constant-volume apparatus (Model NM1395, Iran) was used to determine the permeabilities

of membranes. The gas permeation test rig contains four sections including; feeding of the gases, heating (oven), separation of the gases (permeation cell) and product collection. Pressure sensors (2.600 G BD pressure sensors, accuracy of 0.25 FSO and DMP 343 BD pressure sensor, accuracy of 0.175% FSO, 1 mbar) and a temperature sensor (PT-100 sensors, accuracy of 0.1 K) were used. After evacuating both sides of the membrane inside the module for several hours, the upstream side of the membrane was pressurized with a gas and permeation rates were measured. The cell exposed an effective membrane area of 11.95 cm² to permeation.

The membrane module was sealed with gasket in a stainless steel cell which was fixed inside an oven. The pressure-normalized flux or permeance, (P_i/l) was calculated by the following equation:

$$\frac{P_i}{l} = \frac{N}{\Delta P} = \frac{Q}{A \times \Delta P} \left(\frac{273.15 \times 10^6}{T} \right) \quad (1)$$

$$\alpha_{ij} = \frac{\frac{P_i}{l_i}}{\frac{P_j}{l_j}} \quad (2)$$

where (P_i/l) is the gas permeance of a membrane in GPU (1 GPU = 1 × 10⁻⁶ cm³(STP)/cm² s cmHg), i represents the penetrating gas i , Q_i is the volumetric flow rate of gas permeated through the membrane (cm³/s, STP), A the effective membrane area (cm²), ΔP is the trans-membrane pressure (cmHg), and T is the temperature at which the permeation experiment being performed. Chromatograph (Perkin Elmer) was used to investigate the composition of gases side. α_{ij} represents ideal selectivity of gas i to j . The experimental setup as testing rig is shown in Figure 1.

RESULTS AND DISCUSSION

Characterization

The typical FTIR spectra of pure PES membrane, SAPO-34 crystal and all the PES/SAPO-34 MMMs samples used

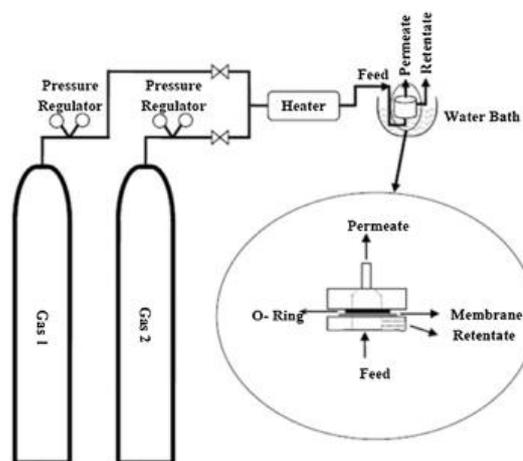


Figure 1. Schematic of the experimental setup

in this work were shown in Figure 2 a and b. The FTIR (Figure 2(a)) spectrum of the PES sample displayed bands at 1290 cm^{-1} and 1325 cm^{-1} , signifying the symmetric stretch vibration of $\text{O}=\text{S}=\text{O}$ bonding. The asymmetric $-\text{CH}_3$ stretching vibration consequenced in the occurrence of bands at 2960 cm^{-1} and 1380 cm^{-1} , while $\text{C}=\text{C}$ conjugation of benzene ring was distinguished at 1565 cm^{-1} [28]. Moreover, the demonstrated peak exactly at 1080 cm^{-1} and 1013 cm^{-1} in neat PES showed the vibration of $\text{C}-\text{C}$ bonding in PES structure [29]. The FTIR spectrum for SAPO-34 powder showed great vibration in the range $850\text{--}1200\text{ cm}^{-1}$, signified the internal tetrahedral asymmetric of $\text{Al}-\text{O}$ or $\text{Si}-\text{O}$ group in the zeolite [24]. In addition, a weak band was seen at range $650\text{--}700\text{ cm}^{-1}$ in SAPO-34 powder spectra, which corresponded as CHA structure [24]. The FTIR spectra of the Amine-functionalized SAPO-34 shows the presence of the NH band in 3439 cm^{-1} while the characteristic bands due to an NH_2 group are absent. As shown in Figure 2(b), the fabricated membrane showed comparable FTIR patterns to the pure PES membrane. However, higher shoulder band was observed in the range of $900\text{--}1200\text{ cm}^{-1}$. The strong adsorption shoulder band in $800\text{ to }1200\text{ cm}^{-1}$ range corresponds to the frequencies for the naturally occurring aluminosilicate-CHA structure (tetrahedral asymmetric of $\text{Al}-\text{O}/\text{Si}-\text{O}$ group) [24].

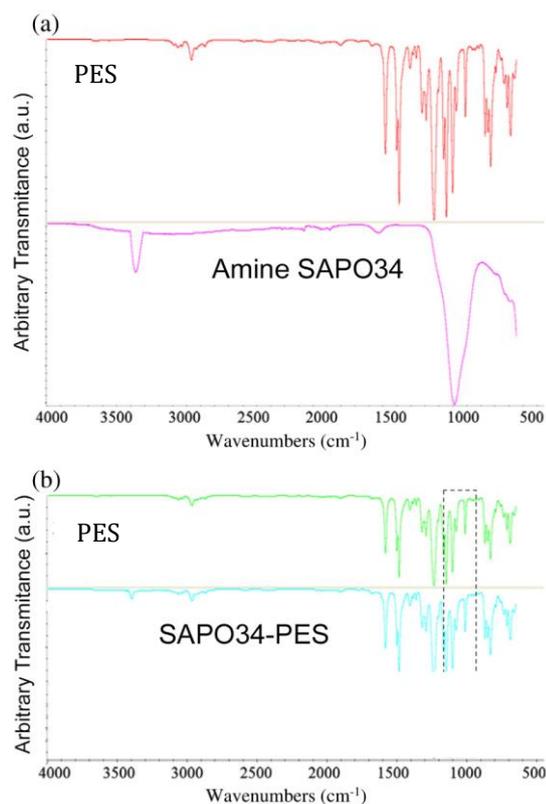


Figure 2. FTIR of the (a) PES-00 with SAPO-34 and (b) produced membrane

The thermal behavior and thermal decomposition were investigated to sketch the influence of adding the SAPO-34 on the key properties of the PES membranes. The thermal behavior of the pure PES and PES/SAPO-34 MMMs was evaluated by the thermal gravimetric analysis (TGA). The TGA thermograms of nanocomposites are displayed in Figure 3 as compared to the neat PES membrane. The results show that both the neat PES and PES/SAPO-34 MMMs have two weight loss stages in the temperature range of $150\text{--}292$ and $423\text{--}757\text{ }^{\circ}\text{C}$ for the neat PES and range of $148\text{--}270$ and $433\text{--}770\text{ }^{\circ}\text{C}$ for the nanocomposite. These stages are due to the loss of residual solvent and the decomposition of the main polymer chain, respectively. These results show that weight loss in the neat PES membrane was quite rapid but the decomposition of nanocomposite was slow. It was also observed that by adding SAPO-34 particles, the start point of decomposition shifted from $423\text{ }^{\circ}\text{C}$ to a higher temperature of about $433\text{ }^{\circ}\text{C}$. Therefore, it can be concluded that the heat resistance of membranes was improved by the addition of SAPO-34. To understand the inorganic constituent effect on the polymer membrane thermal properties, the DSC thermal analysis also was performed for both the PES and PES/SAPO-34 MMMs. Figure 3b displays the differential scanning calorimetry (DSC) diagram for the PES and PES/SAPO-34, in which the glass transition temperature (T_g) of the neat PES and PES/SAPO-34 MMMs is indicated. It can be seen that

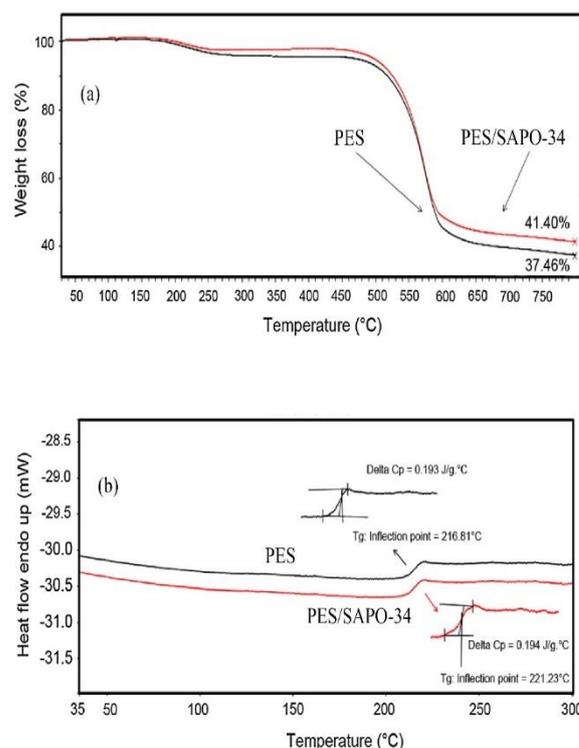


Figure 3. a: TGA, b: DSC thermograms of nanocomposite membranes as compared to neat PES membrane

the T_g of the MMMs is about 221.23 °C, and that of the neat PES is 216.18 °C. A higher T_g value can be engineered by altering the degree of branching or cross linking in PES through the addition of SAPO-34 particles and polymer–filler interaction (Figure 3) and, therefore, this provides necessary evidence for the improvement in thermal characteristics being rendered by the SAPO-34.

Cross-section and top surface SEM images of the prepared MMMs are also presented. Figure 3a shows top surface SEM image of the neat PES membrane. As observed the surface is relatively smooth. Figure 4b, c, e and f shows cross-section SEM images of neat and MMM with 5% loading at different magnifications. As observed all membranes show typical characteristic of asymmetric porous structure with a dense skin top-layer followed by a finger-like porous sub-layer. The finger-like pores for the MMM are slightly wider than that of the neat PES membrane. The nature of SAPO-34 increases the mass transfer rate between the solvent and the non-solvent during phase inversion and lead to the formation of larger pore channels. It is obvious that the relative diffusion rate and driving force between non-solvent and solvent are the characteristic parameters for structure of the membranes. Consequently, it is assumed that the SAPO-34 have a better affinity to non-solvent, establishing elongated macrovoids and finger-like structures because of the superior exchange rate of the solvent/non-solvent.

The images also indicated that the filler particles were distributed appropriately in the membrane. It must be mentioned that these results were obtained when surface

modifying agent was used and the contact between “filler particles – polymer chains” was acceptable and it was also confirmed by permeation measurements. In Figure 5 the upper uniform thin PVA layer can also be observed. The thickness of PVA layer that coated by dip coating method is homogeneous. As observed the thickness of this uniform layer and individual SAPO-34/PES MMM are 5.61 and 234.76 μm respectively.

Gas permeation

Effect of SAPO-34 loading on separation performance of MMMs

CO_2 and CH_4 permeabilities and CO_2/CH_4 ideal selectivity through the PES/SAPO-34 and PES/amine SAPO-34 MMMs at 5 bar are presented in Figure 6 and Table 1. As observed, both permeabilities and selectivities increase with increasing the filler content and these increments for AMINE SAPO-34 loaded MMMs are higher than SAPO-34 loaded MMMs. This characteristic can be attributed to the presence of SAPO-34 domains in PES matrix that significantly alters diffusivity by creating more cavities for the diffusing molecules. More importantly, facilitated transport of CO_2 is due to the presence of amine groups on SAPO-34. In facilitated transport mechanism, CO_2 reacts with active sites present within the matrix, producing a chemical enhancement of the CO_2 permeance through the membrane. In this work, amine reacts with CO_2 . The reaction can be described by means of the zwitterion mechanism.

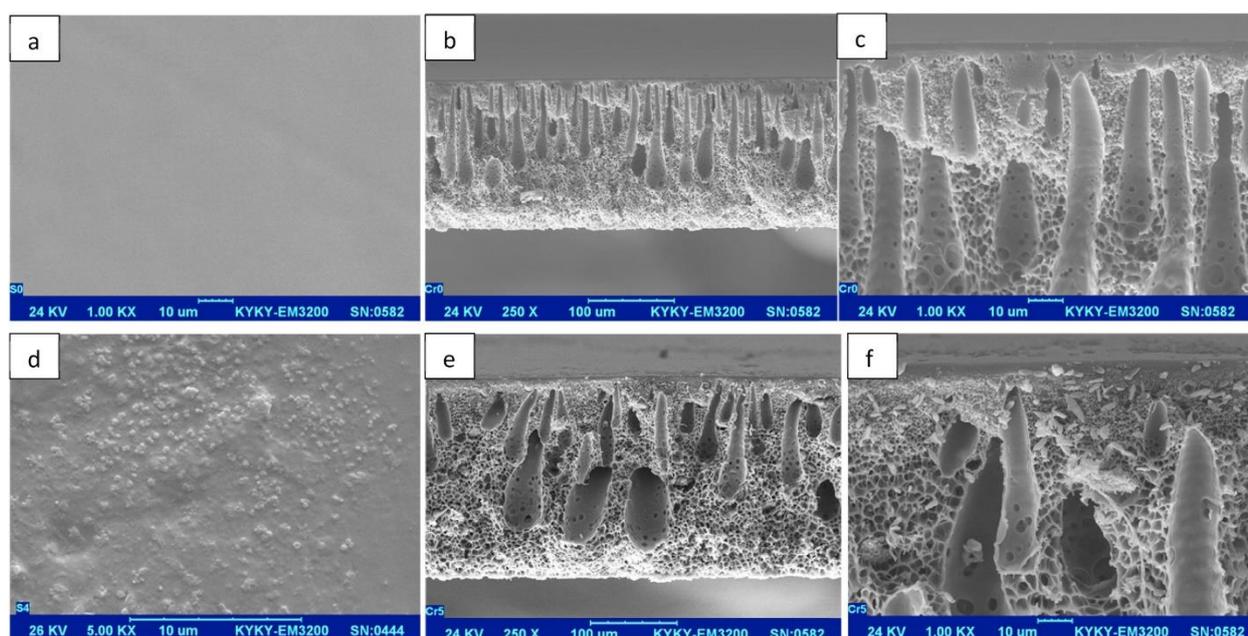


Figure 4. SEM images of the (a) neat PES membrane surface, (b) and (c) cross section of neat PES membrane at different magnifications, (d) surface of MMM with 5% filler loading, (e) and (f) cross section MMM with 5% filler loading at different magnifications

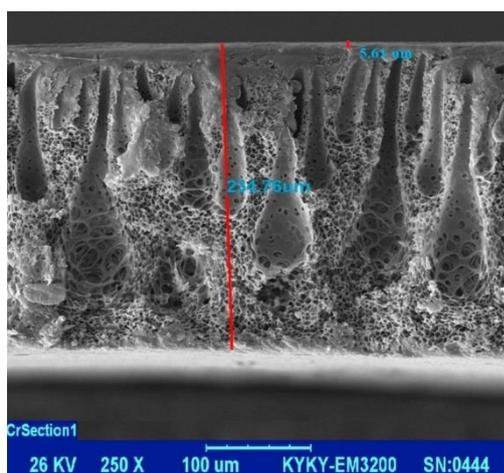


Figure 5. SEM image of PVA layer on the top of membrane

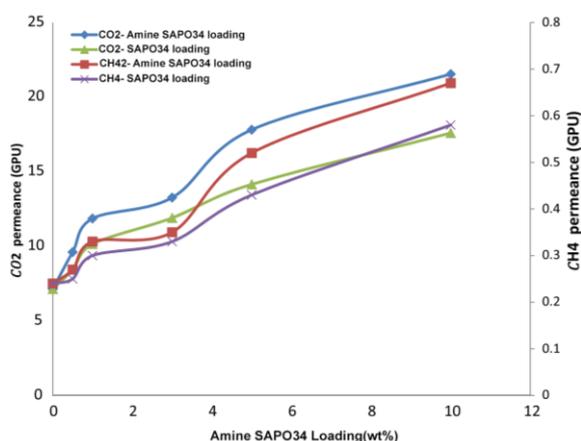


Figure 6. Effect of AMINE SAPO-34 loading on CO₂ and CH₄ permeabilities and ideal selectivity for the PES/AMINE SAPO-34 MMMs at 5 bar

Table 1. Experimental CO₂/CH₄ permeations and selectivity of membranes

Volume fraction of filler particles (%)	Permeance (GPU)		Ideal selectivity (CO ₂ /CH ₄)
	CO ₂	CH ₄	
0(neat polymer)	7.13	0.24	29.7
0.5(AMINE SAPO-34)	9.61	0.27	35.59
0.5(SAPO-34)	8.43	0.25	33.72
1(AMINE SAPO-34)	11.86	0.33	35.93
1(SAPO-34)	10.15	0.3	33.83
3(AMINE SAPO-34)	13.26	0.35	37.88
3(SAPO-34)	11.9	0.33	36.06
5(AMINE SAPO-34)	17.81	0.52	34.25
5(SAPO-34)	14.15	0.43	32.9
10(AMINE SAPO-34)	21.54	0.67	32.14
10(SAPO-34)	15.59	0.58	26.87

As noted above, to enhance the performance of the membranes, the membranes were covered by 5% PVA solution. The hydrophilic Features of PVA causes absorption of the water required for the facilitated transport of CO₂ in the dense skin layer of the membrane. Thus as shown in Table 1, selectivity of AMINE SAPO-34 added MMMs increased.

Increasing permeabilities can be also due to interfacial voids that are much larger than the penetrating molecules. It must be mentioned that CO₂ is the smaller molecule and it is also polar and these can be responsible for the faster transport of CO₂ through the neat membrane.

The separation performance for CO₂/CH₄ mixture is shown in Figure 7 for all the MMMs prepared in this work including the membranes loaded with SAPO-34 and AMINE SAPO-34, on a permeability-selectivity diagram showing the CO₂/CH₄ Robeson upper bound limit. As observed with increase in filler loading, the membrane separation performance trend approaches the 2008 CO₂/CH₄ Robeson upper bound limit.

Effect of feed pressure on separation performance of MMMs

Figures 8 and 9 present CO₂ and CH₄ permeabilities of the PES/AMINE SAPO-34 MMMs as a function of upstream pressure. As observed, the both permeabilities reduce with increasing pressure. This reduction can be related to the dual-mode sorption model which predict the reduced permeability with increasing pressure.

Effect of temperature on separation performance of MMMs

Effect of operating temperature from 303 to 343 K on permeability and selectivity of the PES/AMINE SAPO-34 MMMs are presented in Figures 10-12, respectively. As operating temperature is increases, permeabilities increase, while selectivity decreases.

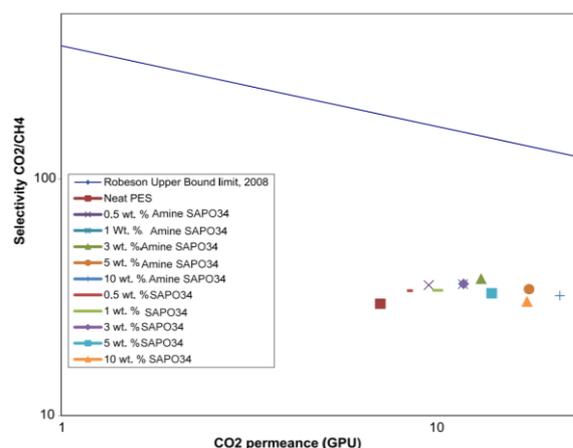


Figure 7. Robeson plot of PES MMMs for CO₂/CH₄ separation

Gas permeation through dense polymeric membranes is considered as an activated process which can be represented by an Arrhenius equation, expressing temperature dependency of permeation. The value E_p for the different of membrane showed in Figures 10 and 11, R is the universal gas constant [8.314×10^{-3} kJ/mol K], and T is the absolute feed temperature [K], and E_d and ΔH_s are activation energy for diffusion and heat of solution, respectively. Gases with larger kinetic diameter have higher diffusion activation energy. Therefore, increasing operating temperature can more elevate diffusivity of larger gas molecules CH_4 (3.8 Å) than smaller gas molecules, CO_2 (3.3 Å). For CO_2 molecules, two opposing effects exist such that heat of sorption is negative and solubility decreases with increasing temperature, while diffusivity increases with increasing temperature. Due to the fact that diffusivity is stronger function of temperature than solubility, permeability increases. However, due to the reduced solubility of CO_2 , permeability of CH_4 increases more significantly than CO_2 , and therefore selectivity of the MMMS decreases.

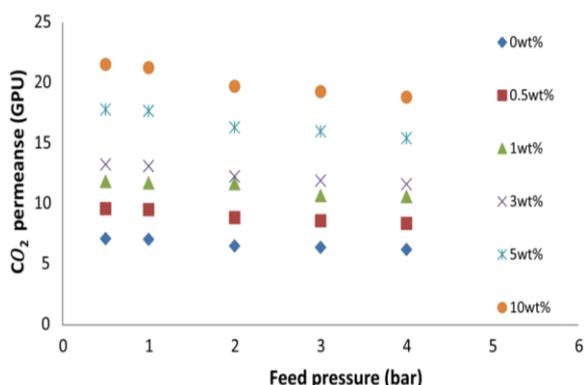


Figure 8. Effect of feed pressure on CO_2 permeance of the MMMS

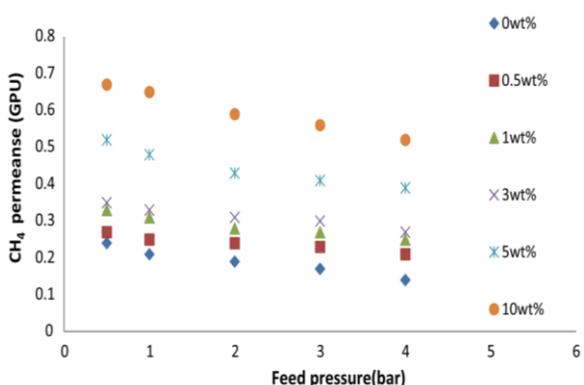


Figure 9. Effect of feed pressure on CH_4 permeance of the MMMS

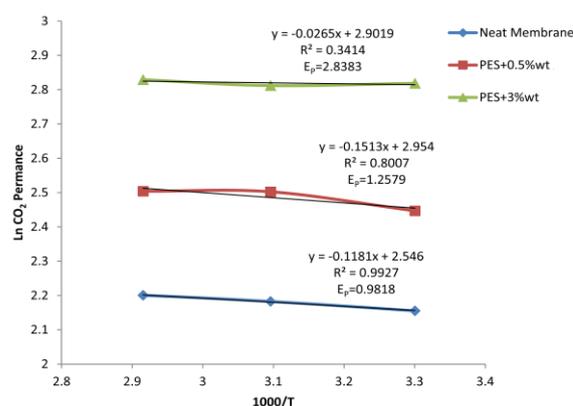


Figure 10. Effect of temperature on CO_2 permeance of the MMMS

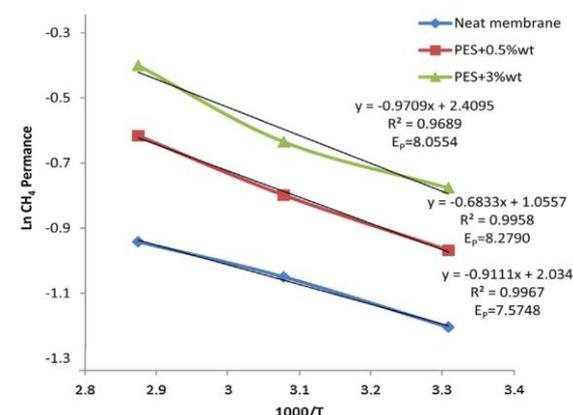


Figure 11. Effect of temperature on CH_4 permeance of the MMMS

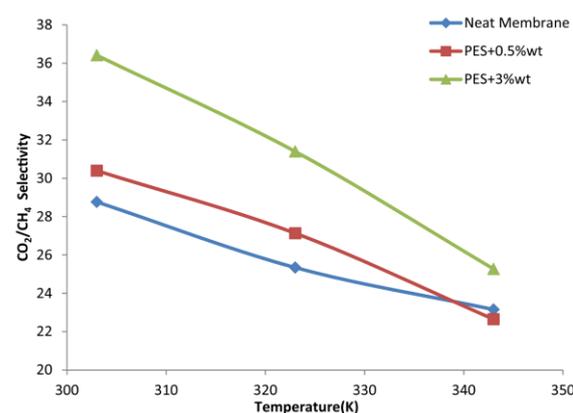


Figure 12. Effect of temperature on ideal Selectivity CO_2/CH_4 through the MMMS

Table 2 shows the effect of the modified SAPO-34 incorporation on the essential mechanical properties of the membranes. Generally, SAPO-34 is used in polymeric matrices to improve the thermal and mechanical

Table 2. Mechanical properties of the PES membranes modified with SAPO-34

Membrane	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (mm)
PES	2.75	53	0.5
PES SAPO-34	3.7	69	1.87

properties. Whereas it has high values of mechanical properties in polymeric matrices, this matter can be an increasing agent of matrix stiffness [28]. The uniform distribution of SAPO-34 in polymer matrix can be prompts the mechanical property of the membrane. As can be seen, the tensile modulus and strength sequentially enhanced with adding the SAPO-34. The free motion of polymeric chains is partly restricted by the intermolecular forces between the polymeric chains and the SAPO-34 dispersed uniformly in a polymer. The membrane containing SAPO-34 showed the higher moduli and tensile strength that were much higher than that of PES itself while showing strengths comparable to that of neat PES membrane. Also, the elongation at break was reasonably decreased with SAPO-34 addition due to the strong interaction between the SAPO-34 and the polymer, which restricts the movement of the polymer chains.

Comparison with other membranes

Fabrication of membranes have been extensively reported in the literature due to good mechanical and thermal stability, easy processability, and attractive gas permeability–selectivity combinations. But only a few studies on PES MMMs have been reported. Table 3 has

Table 3. A comparison of PES/SAPO-34 hollow fiber mixed matrix membranes for CO₂/CH₄ separation

Membrane	Permeance, GPU		Ref.
	CH ₄	CO ₂	
PSF	2.52	18.11	[26]
PES + 0.1% fumed silica	1.75	10.04	[26]
PSF + 2% carbon black	0.16	6.25	[27]
PES + 5% μ CX	1.45	25.40	[28]
PES	1.19	21.09	[29]
PES + 0.05% Cloisite® 15A	1.41	16.25	[29]
PES/Amine SAPO-34	0.7	22.34	Present Study

μ CX = microporous carbon xerogel

gathered the recently published CO₂/CH₄ separation performance of PES-based MMM hollow fiber. Our developed SAPO-34 MMM exhibited lower selectivity than that of other MMMs in the literature, but with a relatively high permeance. This comparison is made to emphasize the ability of SAPO-34 to impart strong influence in improving the matrix selectivity even when the amount of the filler incorporated was extremely low. In the near future, it would be definitely interesting to investigate the role of SAPO-34 in improving matrix selectivity on novel polymers such as PIMs (polymer with intrinsic microporosity) which intrinsically have high permeability but low selectivity.

CONCLUSION

In this study, PES MMM using Amine modified SAPO-34 was prepared. These membranes were used for CO₂/CH₄ separation. The effects of SAPO-34 zeolite loading on the membrane characteristic and gas transport properties for asymmetric PSf/SAPO-34 MMMs had been successfully studied. All of the membrane was prepared using the phase inversion method. The surface and cross-section SEM images of the MMMs provided evidence for good dispersion of the particles in the polymer. The effects of modified Amine modified SAPO-34 loading, feed temperature and feed pressure on permeation and CO₂/CH₄ selectivity of membranes were investigated. The MMMs showed better performance than the neat PES membrane.

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Persian Abstract

چکیده

حذف CO₂ در پالایش گاز طبیعی در حال حاضر تنها فرآیند مبتنی بر غشاء است که در یک عملیات در مقیاس بزرگ انجام شده است. علیرغم غلبه غشاهای پلیمری در جداسازی CO₂/CH₄، محدودیت مبادله بین گزینش پذیری غشا و نفوذپذیری مانع عملکرد جداسازی خوب این غشاها می شود. غشاهای ماتریس مخلوط می توانند بهبود چشمگیری برای غلبه بر این نقص ارائه دهند. در این مطالعه، غشاهای ماتریس مخلوط پلی اترسولفون با SAPO-34 اصلاح شده با منافذ کوچک برای جداسازی CO₂ پیشنهاد گردید. زئولیت SAPO-34 به عنوان پرکننده های معدنی برای افزایش گزینش پذیری گاز استفاده شد. ساختار غشایی نامتقارن با استفاده از روش وارونگی فاز به منظور بهبود نفوذ تهیه شد. تصاویر SEM و آنالیز FTIR برای توصیف ذرات پرکننده و غشاهای سنتز شده استفاده شد. تصاویر SEM همچنین نشان داد که توزیع مناسب ذرات در ماتریس پلیمری وجود دارد. اثرات بارگذاری پرکننده (۰-۱۰ درصد وزنی)، دمای خوراک (۳۰۳-۳۴۳ K) و فشار خوراک (۴ - ۰/۵ bar) بر گزینش پذیری CH₄/CO₂ از MMMها بررسی شد. نتایج نشان داد که افزودن SAPO-34 عامل آمین در محلول ریخته گری باعث افزایش نفوذ گاز غشا و گزینش پذیری ایده آل CO₂/CH₄ می شود. برای غشا با ۱۰ درصد وزنی بار آمین، گزینش پذیری ۱۷ درصد بیشتر بود. نسبت به غشاء بدون عملکرد با آمین افزایش دما از ۳۰۳ به ۳۴۳ کلوین باعث کاهش گزینش پذیری در حدود ۳۰/۵-۲۵ درصد شد.