

Preparation and Characterization of a Novel Polysulfone (PS) Mixed Matrix Membrane Modified with a SAPO-34 Nanofiller for CO₂/CH₄ Gaseous Mixture Separation

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ABSTRACT: *Blended matrix polymer membranes have attracted attention today due to their high efficiency in gas separation. In this study, PS / SAPO 34 polymer membranes were synthesized and evaluated by the phase separation method. Synthesized PS/SAPO-34 mixed matrix membranes (MMMs) were characterized via FESEM, TGA, and DSC analyses. Various parameters such as air gap distance, dope extrusion rate, and jet stretch were examined. After that, the process of separation of CO₂ and CH₄ gases was investigated. The results showed that the addition of SAPO nanoparticles improved membrane performance. The highest selectivity was obtained at a temperature 28 and a pressure 0.5 bar. Permeation results manifested that the PS/SAPO-34 fabricated at optimum conditions has incredible worth from the perspective of industrial separations of CO₂ from the flue and natural gas.*

KEYWORDS: *Hollow fiber; Membrane; SAPO 34; Polysulfone; CO₂ Separation.*

INTRODUCTION

Current developments in chemical and similar industries have focused on increasing process speeds and reducing energy consumption during the process. One of the most important and widely used processes in such industries is the separation of different materials. In order to perform industrial processes, the components of the raw material often have to be separated and the product obtained from these processes must also be separated and purified. On the other hand, in most industries, considering the laws of the environment, the need for separation

processes become more apparent[1-2]. In fact, the importance of separation processes and related devices and equipment is such that in many industries, most of the cost of a product is related to the cost of separation and purification of that product. Therefore, finding a simpler and less costly separation method can be considered[3-4]. In selecting a suitable separation method, the efficiency of that study on the membrane processes of the methods, access to equipment, separation costs, construction costs, and energy costs, should be fully evaluated, taking into

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account of environmental and political issues. Separation goals must also be specified in the process; In a separation process, different goals such as concentration, purification, separation, and displacement of the reaction equilibrium can be considered [5-8].

In this regard, membranes have been developed to separate different types of materials into solid, liquid, and gas states. Although the separation method with membranes is newer than other methods such as distillation, adsorption, crystallization, and liquid-liquid extraction, due to the efficiency and ease of use during the last two decades, a significant expansion in its use has been observed. A membrane is defined as the phase through which feed components selectively pass. In other words, the membrane operates as a phase through which the detachable components of the feed pass at different speeds. In this method, there is usually no phase change and the products can be mixed together [8].

In membrane processes, the part of the feed that passes through the membrane is called the exudate and the part that cannot pass through the membrane is called the retained part, each of which can be considered as a product based on the purpose of separation. In general, membrane methods are very effective when the concentration of substances is low. The driving force required in membrane processes can be in the form of differences in concentration, pressure, temperature, and electrical potential [9]. The simplest type of membrane is based on the difference in particle size, which is similar to filters in this respect, but membranes differ from filters in terms of pore size and size distribution, as well as flow. Membrane performance is determined by two parameters, which include discharge through the membrane and membrane selectivity [10].

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 [11]. 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 [12, 13]. 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 [14-17]. The addition of particles can improve the separation properties of MMMs by raising matrix tortuous surfaces and declining the diffusion of larger gas molecules. To improve permeation performance, the notion of introducing inorganic filler to the matrix of the polymer was proposed. The addition of various particles like zeolites, carbon molecular sieves, activated carbons, mesoporous materials, non-porous silica, Organic-Frameworks (MOFs), and graphite [18-21] into the matrix of the polymer was investigated. The results of cited literature show that the small sizes of particles with high specific areas disperse appropriately in polymer matrices. Small pore zeolites especially SAPO-34 appeared as interesting fillers due to their high adsorption affinity to CO₂. SAPO-34 zeolite is 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 [22-26].

Membrane processes with advantages such as reduced energy consumption due to no phase change, low volume and no need for large space, variety in shape and size, low-pressure drop and high mass transfer, high separation efficiency for dilute solutions, low need for Additives and solvents, the simplicity of membrane design and their ease of use on industrial scales, and also because they are environmentally friendly, distinguish them from other separation methods. However, this method has disadvantages such as polarization 3 concentration and clogging of membranes, short membrane life, selectability, low flow through membranes, and high manufacturing costs.

In this research, the gas separation properties of PS-SAPO 34 hollow fiber MMMs were explored. Spinning process parameters such as air gap distance, dope extrusion rate, and jet stretch have been systematically studied in order to identify the optimum fabrication conditions. The fabricated hollow fiber membranes were characterized using FESEM, DSC, and TGA. Operation parameters including feed temperature and feed pressure were investigated and CO₂/CH₄ ideal selectivity of the prepared membranes was measured.

EXPERIMENTAL SECTION

MMMs were prepared using PS (ULTRASON E6020P; BASF, Germany) as polymer matrix due to their excellent thermal and mechanical characteristics. CO₂ gas (99.99% purity) was purchased from Farafan Gas Co. (Tehran, Iran) and CH₄ gas (99.995% purity) was acquired

from Air Products Co. (Tehran, Iran). Other chemicals were taken from Sigma-Aldrich (USA).

Membrane preparation

SAPO-34 nanostructured zeolite (SAPO-34) was synthesized by hydrothermal method and using an optimal combination of molds according to the research of Najafi et al. [1]. The molar ratio of the primary gel used in their research was 1.0 Al₂O₃: 1.0 P₂O₅: 0.6 SiO₂: 2 (Template combination): 70 H₂O. The composition ratio used for the TEOH: Morpholine: DEA: TEA synthesis mold was 1.0: 0.4: 0.4: 0.2. The synthesis of this zeolite involved the preparation of a pioneer solution and the hydrothermal synthesis. First, according to the mentioned molar ratios, aluminum isopropoxide was deionized with water and the solution obtained from the combination of molds was stirred at room temperature under a magnetic stirrer for 90 minutes to obtain a homogeneous solution. Then, TEOS silica source was added to the resulting solution under a magnetic stirrer. Finally, phosphoric acid was added dropwise to the resulting solution and stirred for another hour to obtain a homogeneous initial gel. The crystallization step was performed using the hydrothermal method. The gel was poured into an autoclave and then, the autoclave was placed in an oven at 200 °C for 14 h. After this step, the autoclave was removed and placed at room temperature to cool. The synthesized zeolite was then washed several times with deionized water and then filtered and placed overnight in an oven at 115 °C. After drying the zeolite, in order for the mold (a combination of the four molds mentioned) to be removed from the zeolite structure, the sample was placed in a stream of air at 560 °C for 5 h and the calcination process was performed [1].

Method of preparation of polymer solution / SAPO-34 zeolite

In general, if the particles and the polymer are dissolved separately in the solvent and then the particle suspension is added to the polymer solution, it creates better distribution for the inorganic particles in the membrane structure because the solvent and the inorganic particles are separated from each other. Prevents particles from sticking together by applying high rates of shear forces [2]. SAPO-34 zeolite particles were placed in an oven for 8 hours to remove vapors or adsorbed gases

before using them. To prepare the polymer/zeolite solution,

first, dispense an appropriate amount of SAPO-34 zeolite (10-30% by weight of the polymer weight) in 100 mL of NMP solvent and place it in the ultrasonic apparatus for one hour. Zeolite particles are well dispersed in the solvent. Then, 20 g of sulfone polyether was added to the solution in two steps. In the first step, 10 g was added and stirred on a magnetic stirrer for one hour. Then, the rest of the polymer was gradually added to the solution. It is important to note that the bubbling of the polymer solution was then performed with an ultrasonic system and then gently stirred for 24 h to obtain a homogeneous PS/SAPO-34 solution for the preparation of hollow fibers.

Preparation of PS / SAPO-34 hollow fiber membrane

In the phase separation method, in fact, the liquid polymer solution is used after contact with a strong non-solvent in this case (water is converted to the solid state of the membrane). In order to make suitable membranes, controlling the manufacturing conditions such as the air distance of the spinner from the phase change container and the speed of the collecting drum is important parameters. To prepare the hollow fiber membrane in this study, first, the phase change and detergent containers were filled with water, in which case water plays the role of phase change from polymer liquid to the solid membrane. The bubble-free polymer solution was poured into a special tank and injected into the spinner with a gear pump. Then, using a syringe pump, the cavity fluid, which is usually water or a combination of solvent and water was squeezed into the spinning machine. The polymer solution leaving the spinner was immediately immersed in water to phase change and the membrane was made of the hollow fiber.

Detergents removed the solvent and non-solvent additive from the membrane and finally, the young membrane was collected on rollers. Then, to remove all solvents and non-solvent additives from the membrane were kept in distilled water for 3 days. The membranes were immersed in pure ethanol for 15 minutes to prevent shrinkage and destruction of cavities while drying in ambient air. Then, the hollow fiber membranes are suspended in ambient air for three days to dry completely. After this, the membranes are ready to be characterized and tested. Table 1 summarizes the process parameters and spinning conditions controlled in this study. The Jet–Stretch (JS) ratios of the spin line were

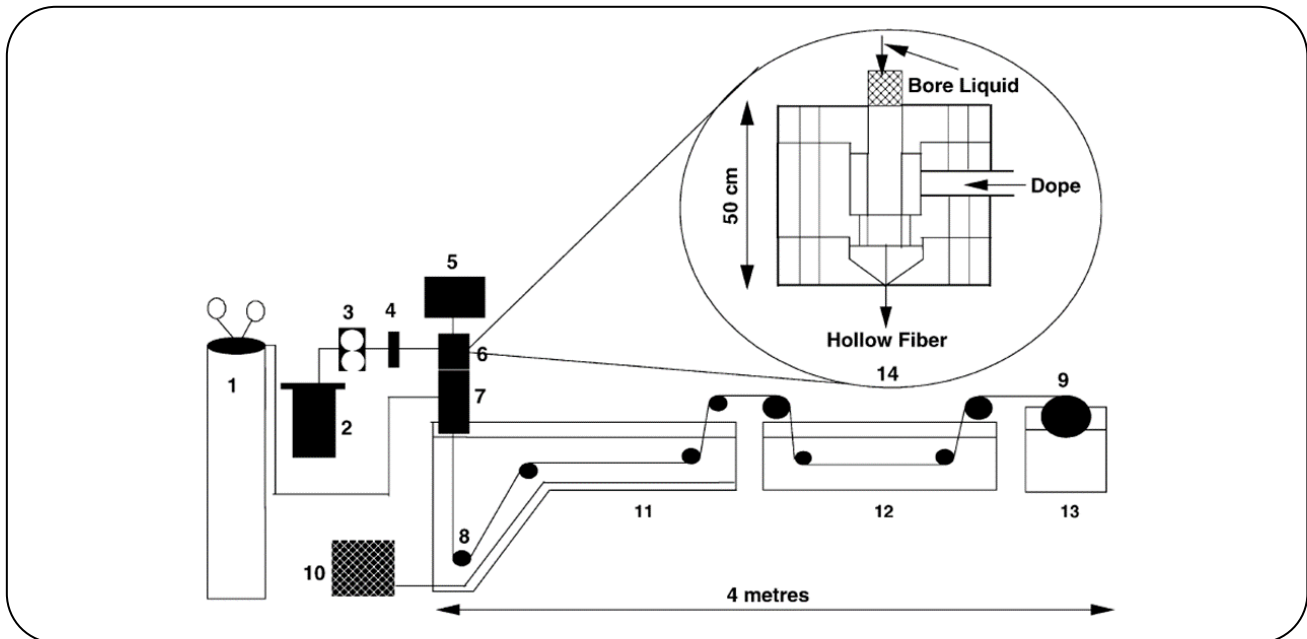


Fig. 1: Hollow fiber membrane spinning system: (1) nitrogen cylinder; (2) dope reservoir; (3) gear pump; (4) on-line filter, 7 mm; (5) syringe pump; (6) spinneret; (7) forced convective tube; (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath; (13) wind-up bath; and (14) schematic spinneret.

manipulated by adjusting the take-up rate. The JS ratio is defined as the following equations.

$$JS = \frac{V_2}{V_1} \quad (1)$$

V_1 is the linear extrusion rate of the extruded fiber (cm/s), while V_2 is the rate at which the fiber is collected at the end of the spin line i.e. take-up rate (cm/s). Fig.1 shows the schematic of the experimental setup. Spinning parameters are listed in Table 1.

Membrane characterization

The thermal stability of polyurethane MMMs was investigated using thermogravimetric analysis (TGA) within the temperature range of 30–800 °C at 10 °C/min, under an atmosphere of nitrogen (Mettler TOLEDO model SDTA 851). The morphology of the obtained crystals and MMMs were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-900). Membrane samples were prepared by mechanically breaking the membranes into small pieces. All samples were coated with a layer of Pt–Pd by ion sputtering (E-1030, Hitachi) with a current of 15 mA for 15 s. Differential Scanning Calorimetry (DSC)

analysis was performed using a PerkinElmer DSC 8000 calorimeter.

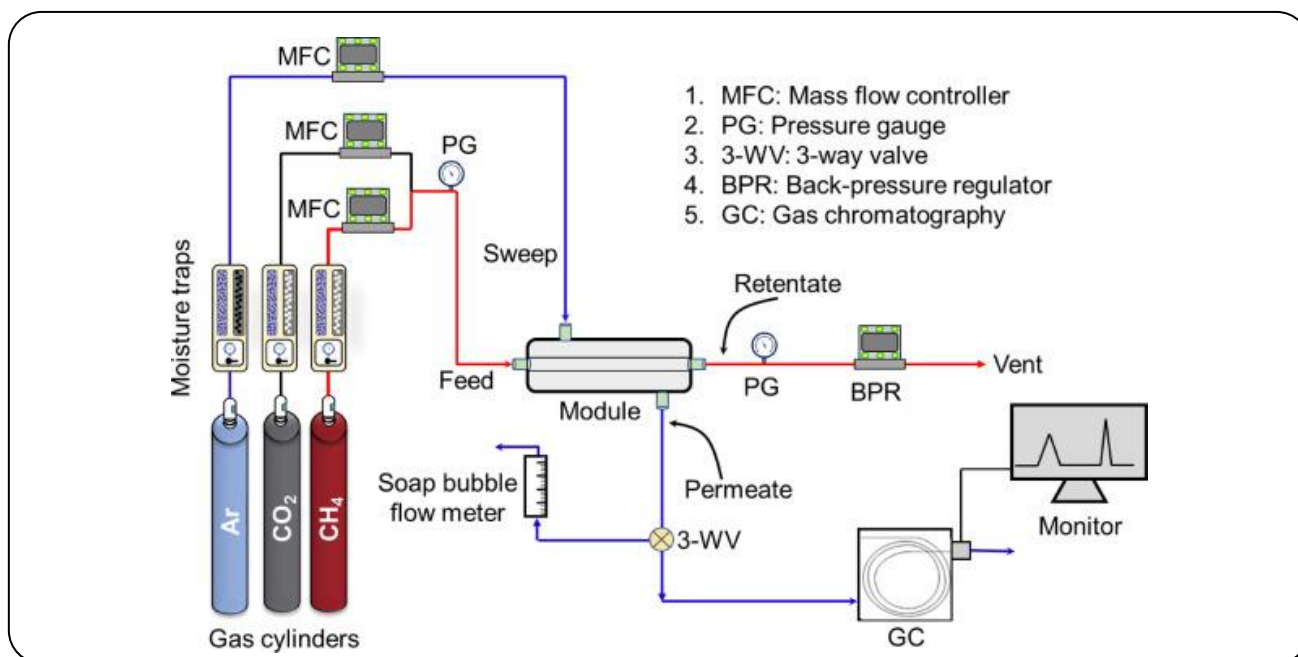
Gas Separation Performance

The permeability performance of the gases was performed using CO₂ and CH₄ gases with very high purity (99.999%) at ambient temperature and at different feed pressures. Optimal gases enter through the transverse portion of the categorized membrane. For permeability testing, 3 hollow fibers with an effective surface area of 9 cm² were placed next to each other, and then one side (beginning of the fiber bundle) was glued and sealed using epoxy glue. After 3 hours, the other side was glued and allowed to dry for 24 hours. The grouped fibers were then placed inside the module and re-insulated with epoxy adhesive so that the gas could pass only through the side walls of the fibers. Thus, the permeability cell module was prepared. Due to the need for permeability tests to be performed at a constant temperature, the permeability tube is placed in an oven.

Using MFC, the inlet flow rate of each gas into the permeability cell is controlled. Two MFCs are installed at the entrance to the permeation cell. Through the two FCs in the feed path, the amount and composition

Table 1: Hollow fiber membrane Table 2. Hollow fiber spinning conditions.

Spinning parameters	Condition A	Condition B	Condition C
Air gap distance	10, 15, 20, 25	20	20
Dope extrusion rate (cm ³ /min)	2.5	1.5, 2.0, 2.5, 3.0	2.5
Bore fluid flow rate (cm ³ /min)	0.83	0.50, 0.66, 0.83, 1.0	0.83
Jet–stretch ratio (V ₂ /V ₁)	1	1	1, 2, 3

**Fig.2: Schematic of the experimental setup.**

percentage of gas entering the permeability cell is regulated. During permeation tests, in order to keep the composition of the gas percentage constant, the input feed flow rate is 3 or 4 times higher than the membrane permeability value. In addition, the waste flow rate is automatically adjusted to keep the feed flow pressure constant. It should be noted that due to the evaporation of water in the membrane network as well as the low permeability of dry CO₂ gas, the feed stream is humidified before entering the tube by using a spark plug. In order to increase the contact surface of water and gas flow, porous metals in the humidification column and also in order to fine-tune the flow rate of water transferred to the humidification column, an injection pump has been used. Due to the fact that the gas flow through the membrane must be free of moisture during analysis by the GC device, a water trap in the gas flow path entering the GC is used to remove the gas moisture.

RESULTS AND DISCUSSION

Spinning factors

In order to find the most suitable spinning conditions for SAPO-34/PS mixed matrix dope, the effects of air gap distance were first studied. Referring to Fig. 3 (a and b), macro-voids are produced in resultant SAPO-34/PS at the air gap distance of 5 cm and 10 cm. Meanwhile, Fig. 4 shows the internal morphology of SAPO-34/PS at different air gap distances. Referring to Fig.4, the internal spongy structure of the membrane is non-uniform, loosely packed, and non-selective voids are presented in the internal structure of the membrane. Internal morphology of SAPO-34/PS was produced as shown in Fig. 4(b). On the other hand, based on Fig. 4, when the air gap distance of SAPO-34/PS was further increased from 15 cm to 20 cm, macro-voids were produced in the MMMs.

Table 2: Effect of various air gap distances on hollow fiber permeation properties.

Air gap Distance(cm)	Permeance, GPU ^a		Selectivity
	CH ₄	CO ₂	CO ₂ /CH ₄
5	5.60 ± 0.16	95.30 ± 13.08	17.02
10	4.11 ± 0.12	86.42 ± 10.06	21.02
15	2.87 ± 0.08	73.15 ± 1.08	25.48
20	3.32 ± 0.23	75.90 ± 3.85	22.86

^a 1 GPU = 1 × 10⁻⁶ cm³ (STP)/cm² s cmHg.

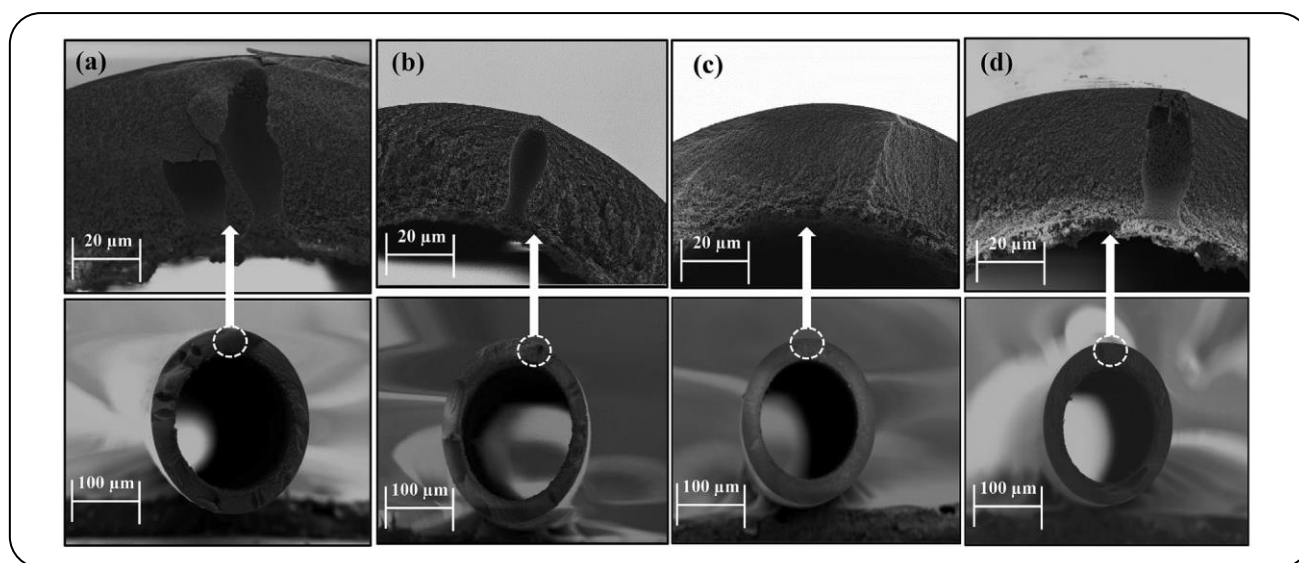


Fig. 3: FESEM images of the cross-sectional view of SAPO-34/PS with a different air gap distance of; (a) 5 cm, (b) 10 cm, (c) 15.0 cm, (d)20 cm.

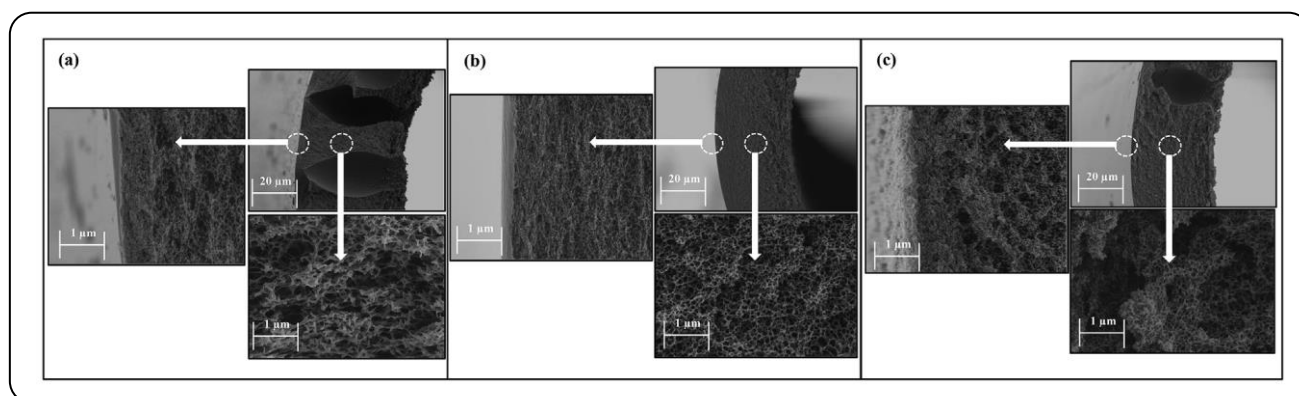


Fig. 4. Internal morphology of SAPO-34/PS with different air gap distance; (a) 5 cm, (b) 10 cm, (c) 15.0 cm.

The Dope Extrusion Rate (DER) varied from 1.5 to 3.0 cm³/min. The gas permeation results can be found in Table 3. The results clearly showed that with increasing DER, the permeance and selectivity obey an up-down pattern.

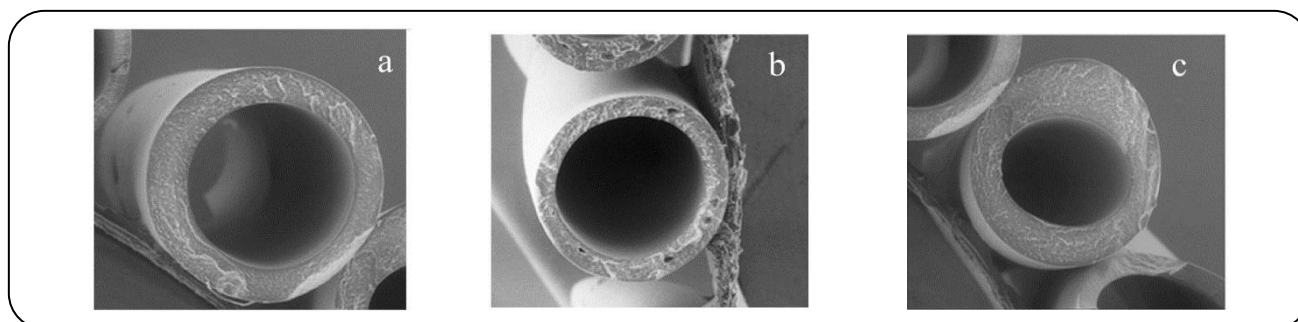
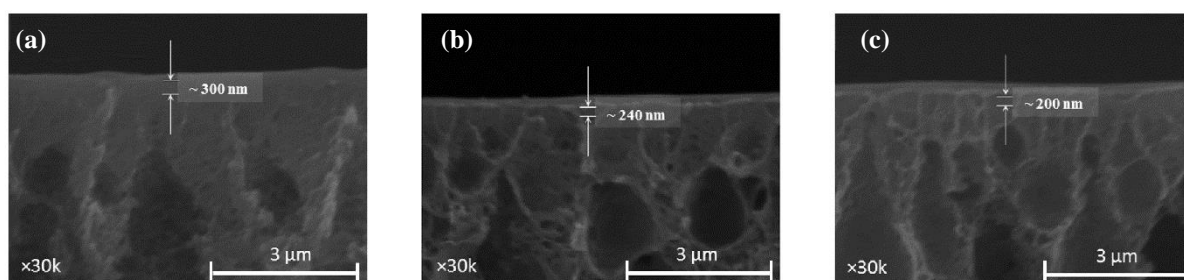
The Jet–Stretch (JS) ratio was systematically varied from 1:1 to 2:1 and 3:1 ratio and its effect on fibers geometry and permeability were studied. The cross-section images (Fig. 5) somehow do not show any significant changes in membrane morphology. Table 4 reports the gas permeation

Table 3: Effects of dope extrusion rates on hollow fiber properties.

DER (cm ³ /min)	Permeance, GPU		Selectivity
	CH ₄	CO ₂	CO ₂ /CH ₄
1.5	2.16 ± 0.01	51.39 ± 1.00	22.79
2.0	2.87 ± 0.08	73.15 ± 1.08	25.48
2.5	3.41 ± 0.15	96.25 ± 0.39	28.2
3.0	1.86 ± 0.06	42.42 ± 0.76	22.81

Table 4: Effect of various jet–stretch ratios on hollow fiber permeation properties.

Jet stretch ratio (V ₂ :V ₁)	Hollow fiber dimensions		Permeance, GPU		Selectivity
	OD (μm)	ID (μm)	CH ₄	CO ₂	CO ₂ /CH ₄
1:1	564	330	3.41	90.25	28.2
2:1	361	210	2.70	60.81	25.48
3:1	302	180	1.73	30.19	21.49

**Fig. 5: SEM images showing the effect of spinning under different jet–stretch ratios on hollow fiber geometry (a- 1:1, b-2:1, and c-3:1).****Fig. 6: SEM morphologies in the cross-section near the active skin layer of hollow fibers spun with different jet–stretch ratios (a- 1:1, b-2:1 and c-3:1).**

results for membranes spun with low to high jet–stretch value spun according to Condition C in Table 4. From the results, we were stumped by the fact that both the permeance and selectivity of stretched fibers were exceptionally poor relative to non-stretched fibers. Fig. 6 indeed shows a slight reduction in the active skin layer

thickness as a function of JS but this does not explain the declining permeance exhibited by these fibers.

Thermal properties

The thermal behavior and thermal decomposition were investigated to sketch the influence of adding the SAPO-34

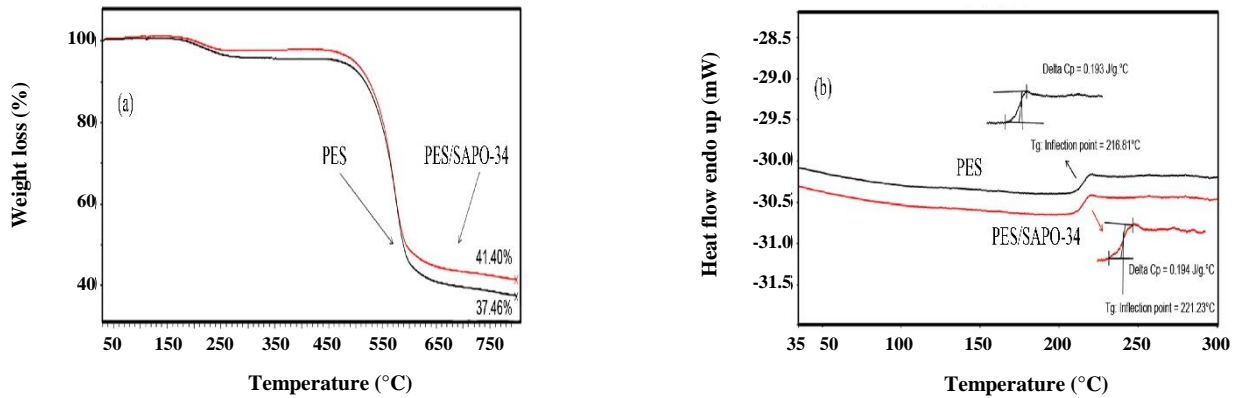


Fig. 7: a) TGA, b) DSC thermograms of nanocomposite membranes as compared to neat PS membrane.

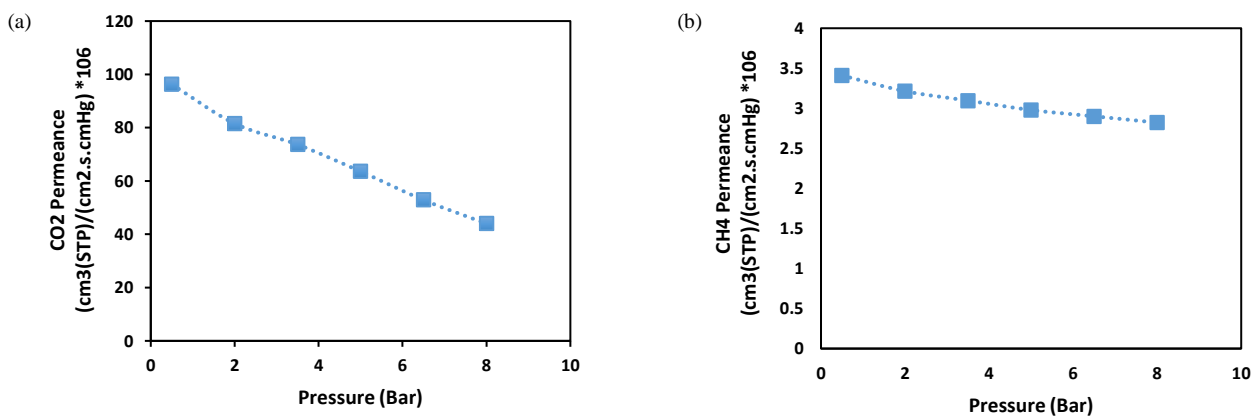


Fig. 8: Effect of feed pressure on a: CO₂ b: CH₄ permeance of the MMMs.

on the key properties of the PS membranes. The thermal behavior of the pure PS and PS/SAPO-34 MMMs was evaluated by the Thermal Gravimetric Analysis (TGA). The TGA thermograms of nanocomposites are displayed in Fig. 7 as compared to the neat PS membrane. The results show that both the neat PS and PS/SAPO-34 MMMs have two weight loss stages in the temperature range of 150–292 and 423–757 °C for the neat PS and the range of 148–270 and 433–770 °C for the nanocomposite. Fig. 7b displays the differential scanning calorimetry (DSC) diagram for the PS and PS/ SAPO-34, in which the glass transition temperature (*T_g*) of the neat PS and PS/ SAPO-34 MMMs is indicated.

Operating Factors

Fig. 8 presents CO₂ and CH₄ permeabilities of the PS/SAPO-34 MMMs as a function of upstream pressure. As observed, both permeabilities reduce with increasing

pressure. This reduction can be related to the glassy state of the polymer and the dual-mode sorption model can predict the reduced permeability with increasing pressure.

The effect of operating temperature from 303 to 343 K on permeability and selectivity of the PS/SAPO-34 MMMs are presented in Fig. 9. As the operating temperature increases, permeabilities increase, while selectivity decreases. Gas permeation through dense polymeric membranes is considered an activated process which can be represented by an Arrhenius equation [27-28].

Comparison with other membranes

Table 5 has gathered the recently published CO₂/CH₄ separation performance of polysulfone-based MMM hollow fiber. Our developed SAPO34 MMM exhibited lower selectivity than that of other MMMs in the literature, but with relatively high permeance.

Table 5: A comparison of PS/SAPO 34 hollow fiber mixed matrix membranes for CO₂/CH₄ separation.

Membrane	Permeance, GPU		Selectivity	Ref.
	CH ₄	CO ₂	CO ₂ /CH ₄	
PS	2.52	78.11	31.05	[37]
PS + 0.1% fumed silica	2.75	90.04	32.74	[37]
PSF + 2% carbon black	2.16	76.25	35.40	[38]
PS + 5% μ CX	2.45	95.40	39.10	[39]
PS	2.19	60.09	27.44	[40]
PS + 0.05% Cloisite® 15A	1.41	56.25	40.26	[40]
PS/SAPO-34	3.41	96.25	28.22	Present Study

μ CX = microporous carbon xerogel.

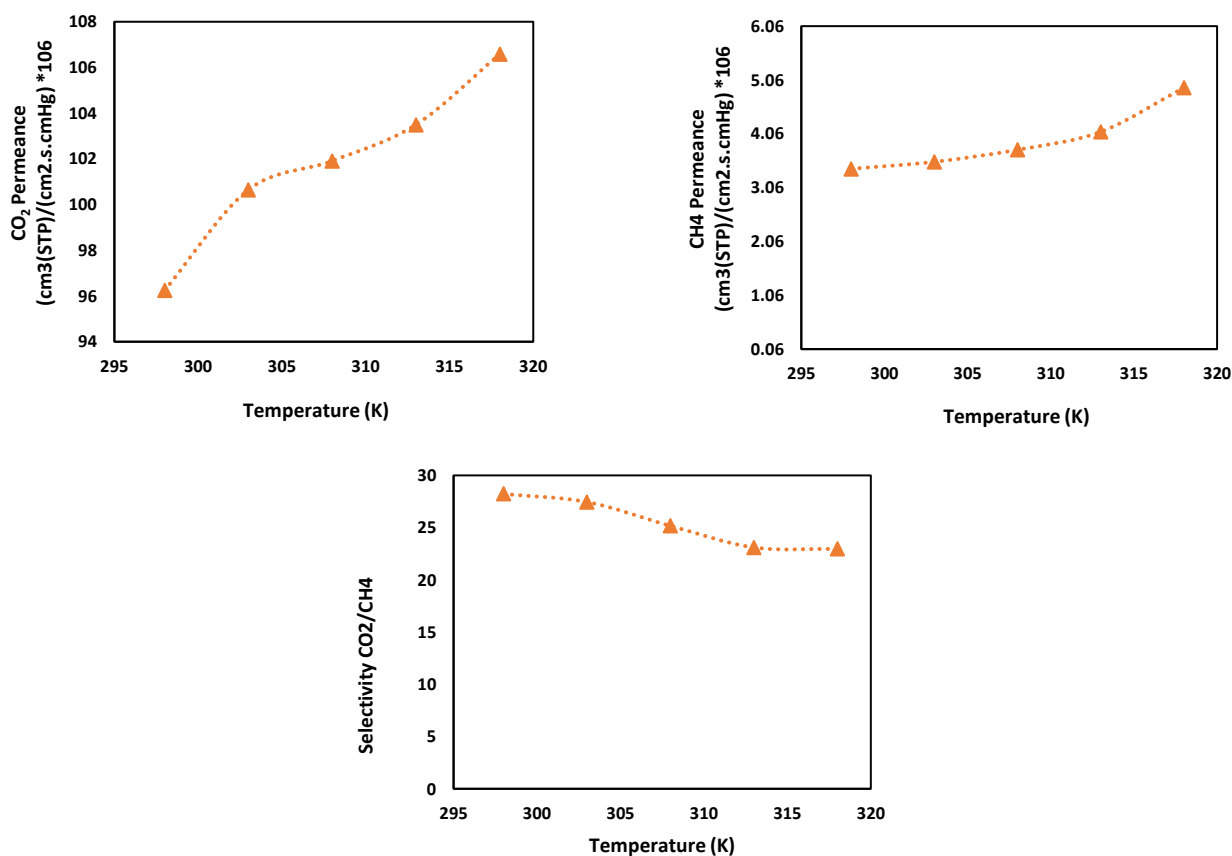


Fig. 9: Effect of feed temperature on a:CO₂ b:CH₄ permeance c: selectivity of the PS/SAPO-34.

CONCLUSIONS

The microporous and hydrophobic PS membranes incorporated with porous fillers were successfully developed in this work. It was found that the assigned air gap height for hollow fiber extrusion gave the most

influence on gas permeation properties. The stretched fibers exhibited a significant reduction in both permeance and selectivity which might be attributed to the excessive elongational stress which lead to tighter chain packing and de-bonding of clay particles from the matrix. The effects

of modified feed temperature and feed pressure on permeation and CO₂/CH₄ selectivity of membranes were investigated.

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