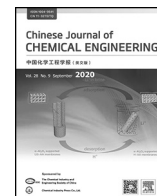




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Article

New high permeable polysulfone/ionic liquid membrane for gas separation

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ABSTRACT

In this study, the effects of 1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid on CO₂/CH₄ separation performance of symmetric polysulfone membranes are investigated. Pure polysulfone membrane and ionic liquid-containing membranes are characterized. Field emission scanning electron microscopy (FE-SEM) is used to analyze surface morphology and thickness of the fabricated membranes. Energy dispersive spectroscopy (EDS) and elemental mapping, Fourier transform infrared (FTIR), thermal gravimetric (TGA), X-ray diffraction (XRD) and Tensile strength analyses are also conducted to characterize the prepared membranes. CO₂/CH₄ separation performance of the membranes are measured twice at 0.3 MPa and room temperature (25 °C). Permeability measurements confirm that increasing ionic liquid content in polymer-ionic liquid membranes leads to a growth in CO₂ permeation and CO₂/CH₄ selectivity due to high affinity of the ionic liquid to carbon dioxide. CO₂ permeation significantly increases from 4.3 Barrer (1 Barrer = 10⁻¹⁰ cm³(STP) · cm · cm⁻² · s⁻¹ · cmHg⁻¹, 1 cmHg = 1.333 kPa) for the pure polymer membrane to 601.9 Barrer for the 30 wt% ionic liquid membrane. Also, selectivity of this membrane is improved from 8.2 to 25.8, mixed gas tests are implemented to investigate gases interaction. The results showed, the disruptive effect of CH₄ molecules for CO₂ permeation lead to selectivity decrement compare to pure gas test. The fabricated membranes with high ionic liquid content in this study are promising materials for industrial CO₂/CH₄ separation membranes.

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1. Introduction

In the past decades, natural gas has been considered a common energy source with a continuously increasing demand [1]. Low quality natural gas constitutes most of the world's gas resources which has high level of impurities or pollutants. Most of the gas reserves have been discovered during the past decades; however, they have not been developed due to lack of refining technologies that are economically feasible. To utilize these gas reserves, developing new technologies that can separate the impurities and at the same time be economically feasible for gas separation units seems indispensable [2].

Several technologies have been developed for separation of acid gas (CO₂ and SO₂) from natural gas. For example, using chemical liquid desiccants [3], solid desiccants [4], Cryogenic distillation [5], direct conversion through chemical reaction [6] and separation with membranes. Among separation techniques, membrane technology is a valuable and sustainable method in comparison with other methods such as amine absorption. This method has a few advantages over the other common methods such as economic efficiency, low energy consumption, flexible process, and being environmentally friendly [7]. Moreover, Global

warming as a result of constantly increasing greenhouse gases like CO₂ is one of the main environmental challenges which causes the climate change [8,9]. Finding economical and efficient solutions to omit or reduce this CO₂ emission is one of the future global goals. A widely used method is the utilization of membranes for CO₂ capture, in which a membrane with high CO₂ permeability and selectivity is used [9].

Most of the membrane technologies which have been used for CO₂ capture are based on polymer membranes. This is because of low cost, mechanical stability under high pressure, simplicity of fabrication in forms of sheets or hollow fibers and scalability. However, polymeric membranes have relatively low selectivity and permeability, therefore using new materials to promote their performance is the main subject of most research projects on membranes [10].

Fabrication of mixed matrix membranes comprising a polymer matrix and a proper filler with high selectivity such as metal organic frameworks (MOF), zeolites or carbon nanotube is a promising method to increase separation properties of membranes [10–12]. Sun *et al.* [13] fabricated MOF-801/PEBA membrane for CO₂/N₂ separation. A thin mixed matrix layer was formed on a porous substrate with a spin-coating process. Their membrane shows significant enhancement in permeability and selectivity compared to pure polymeric membrane. In another work, Ozen and Ozturk [14] utilized MOF-5 including various metals (Co, Ni, Cu) as a filler in polyimide matrix. Their membranes had

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high polymer/particle compatibility. Permeability of the membranes improved with the increment of particles loading. However, the highest permeability was observed in membrane with 5 wt% Cu doped MOF demonstrating 63% increase in CO₂ permeability compared to PI membrane.

Ionic liquid (IL) is a salt with a melting point less than 100 °C which contains an organic cation and an organic or inorganic anion. This material has a unique mixture of physical and chemical properties such as high CO₂ affinity, high selectivity, low volatility and a designable structure to control chemical and physical properties [15]. Unlike interesting and tunable properties of ionic liquids, their production cost in commercial scales is a major challenge. As a result, in industrial applications, combining ionic liquids with non-IL constituents to make an optimum hybrid solution is an attractive way to reduce the costs [16]. These traits provide new opportunities to use membranes based on ionic liquids for CO₂ separation techniques that are more energy-efficient and environmentally friendly than the present commercial separation technologies. Ionic liquids are divided into two categories: Room temperature ionic liquids (RTILs) and Task-specific ionic liquids (TSILs) or functionalized ionic liquids. Much like other physical solvents, most of the RTILs have more solubility in carbon dioxide than other gases like nitrogen, methane, oxygen and hydrogen. RTILs are widely used for natural gas sweetening and hydrogen purification [16].

Mannan *et al.* [17] combined the special features of polyether sulfone (PES) and the high solubility of CO₂ in 1-Ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [emim][Tf₂N] ionic liquid to prepare ionic liquid polymeric membranes (ILPM). Gas permeation studies indicated that as the ionic liquid content increased in ILPMs, both CO₂ permeability and CO₂/CH₄ selectivity increased due to affinity of CO₂ towards ionic liquids. It was observed that at 25 °C and 2.5 MPa the CO₂ permeability significantly increased from 2.42 Barrer (1 Barrer = 10⁻¹⁰ cm³ (STP) · cm · cm⁻² · s⁻¹ · cmHg⁻¹, 1 cmHg = 1.333 kPa) for PES membrane to 298.84 Barrer (~124 fold) for ILPM containing 50% ionic liquid. There was also a 3.6-fold increment in selectivity from 15.91 to 57.53.

In another work, Mohshim *et al.* [18] studied the effect of ionic liquid on CO₂ separation performance of polymer-ionic liquid membranes. To prevent void formation, a dry-phase inversion method was used in the membranes fabrication. The membranes were analyzed physically and chemically and their permeation and selectivity performance were investigated. It was found that the membranes had dense and void-free structures and had a lower degradation temperature (~410 °C) than pure PES membrane. The incorporation of ionic liquids into the

membranes significantly increased the CO₂ permeation due to the plasticization effect. However, CH₄ permeability showed an inverse trend which is related to fewer available pathways in the membrane for CH₄.

Zarca *et al.* [19] fabricated composite poly (ionic liquid)-ionic liquid membranes containing copper chloride (CuCl) *via* photopolymerization. The polymerization was conducted using an ionic liquid monomer, 1-vinyl-3-butylimidazolium bistriflimide [C₄vim][Tf₂N]), in the presence of a non-polymerizable ionic liquid 1-butyl-3-methylimidazolium chloride and CuCl that resulted in the *in situ* formation of chlorocuprate anion. The effect of the metal salt content on the separation performance of the composite gas membranes was investigated. Results showed that increasing the non-polymerizable ionic liquid content, improved the permeability of CO₂, H₂, N₂ and CO, much like neat poly([C₄vim][Tf₂N]). On the other hand, addition of copper chloride resulted in a predictable reduction of gas diffusivity. An improvement of gas permeation and ideal gas pair selectivity were observed for CO₂/N₂ and H₂/N₂ in Cu-containing composite membranes in comparison with pristine poly ([C₄vim][Tf₂N]).

Halder *et al.* [20] tried for the first time to blend polymers with inherent microporosity, especially PIM-1 with [C₆mim][Tf₂N] in order to improve the gas separation properties of PIM membranes. A slight reduction in permeability and an improvement in selectivity were observed in the blend membranes. However, as the IL and PIM-1 were incompatible, the polarity of PIM-1 was tuned. Blending and chemical modification of PIM-1 were investigated to gain a good distribution of the ionic liquid within the polymer matrix. First method was physical blending of PIM-1 with Poly (ethylene glycol) (PEG) as the compatibilizer. The second method was copolymerization of PIM-1 monomers with PEG containing anthracene maleimide copolymer. The copolymerization method resulted in better compatibility between the polymer and the ionic liquid in concentration range from 2.5 to 10 wt% compared to blends of PIM-1 with PEG and IL. Addition of the ionic liquid to PIM-1 (PIM-CO) copolymer led to an improvement in CO₂/N₂ selectivity from 19 to 30 at 30 °C and a relatively high CO₂ permeability coefficient (above 800 Barrer).

In the present study, a new IL with high CO₂ affinity is used to modify the separation properties of polymeric membranes. Polysulfone blend membranes containing 1-Ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) are fabricated and assessed. To the best of our knowledge, the combination of this particular polymer and ionic liquid has not been investigated in the literature. [emim][BF₄] is a imidazolium cation based RTIL with high CO₂ solubility. Therefore, it is

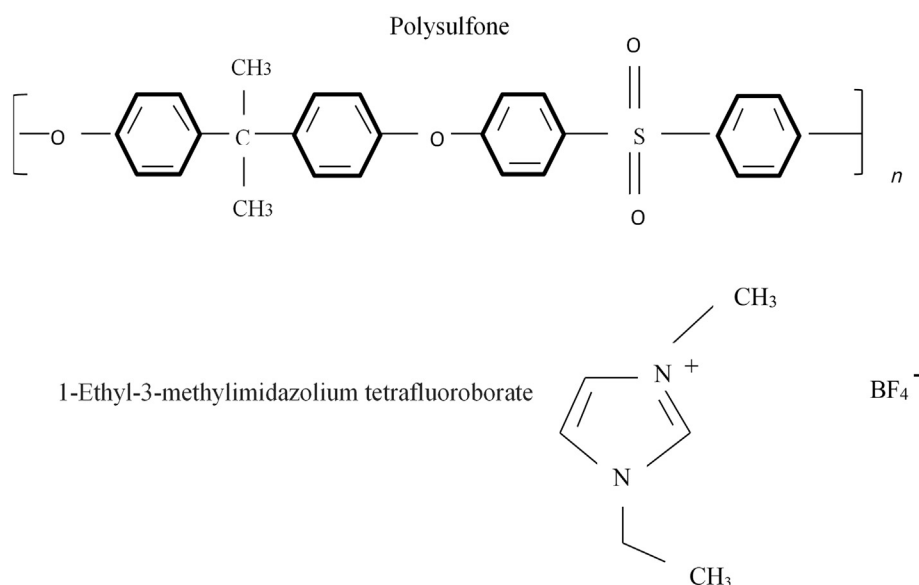


Fig. 1. Chemical structure of polysulfone and 1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid.

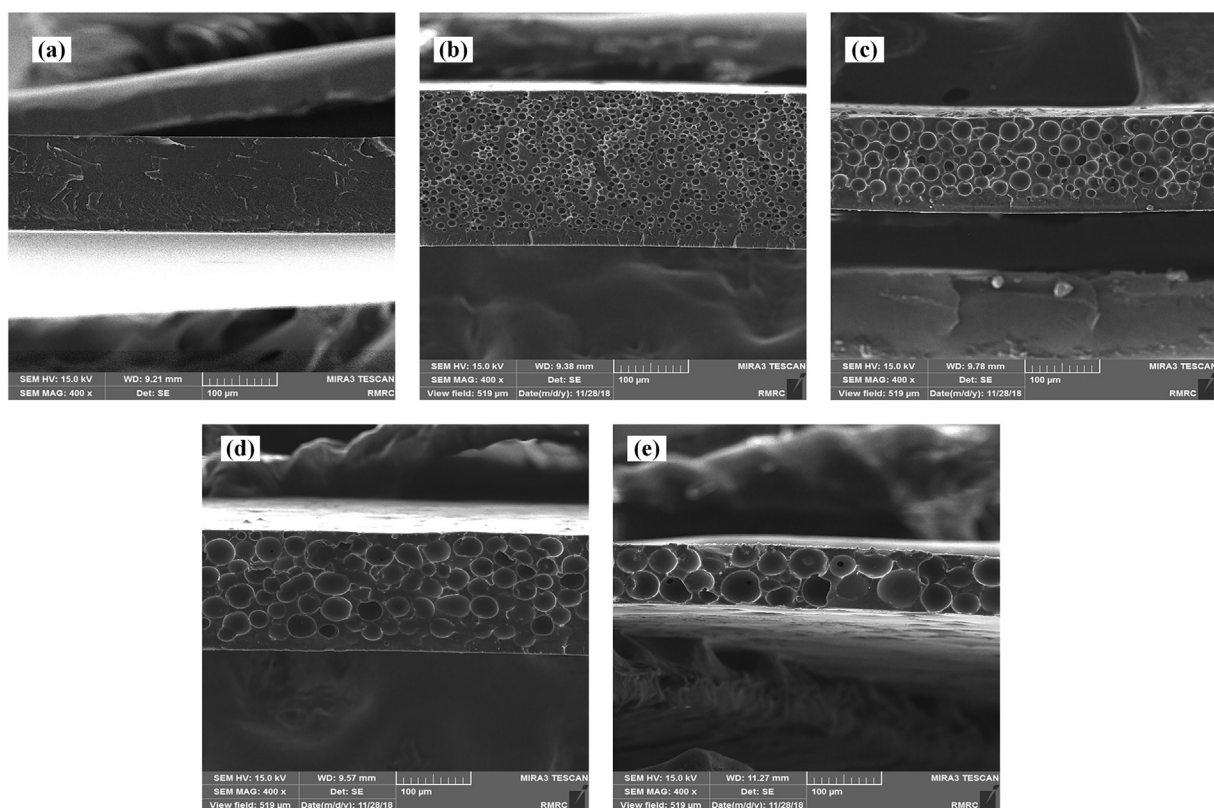


Fig. 2. Cross sectional SEM images of fabricated membranes with different IL content: (a) 0 wt% (b) 10 wt% (c) 20 wt% (d) 30 wt% and (e) 40 wt%.

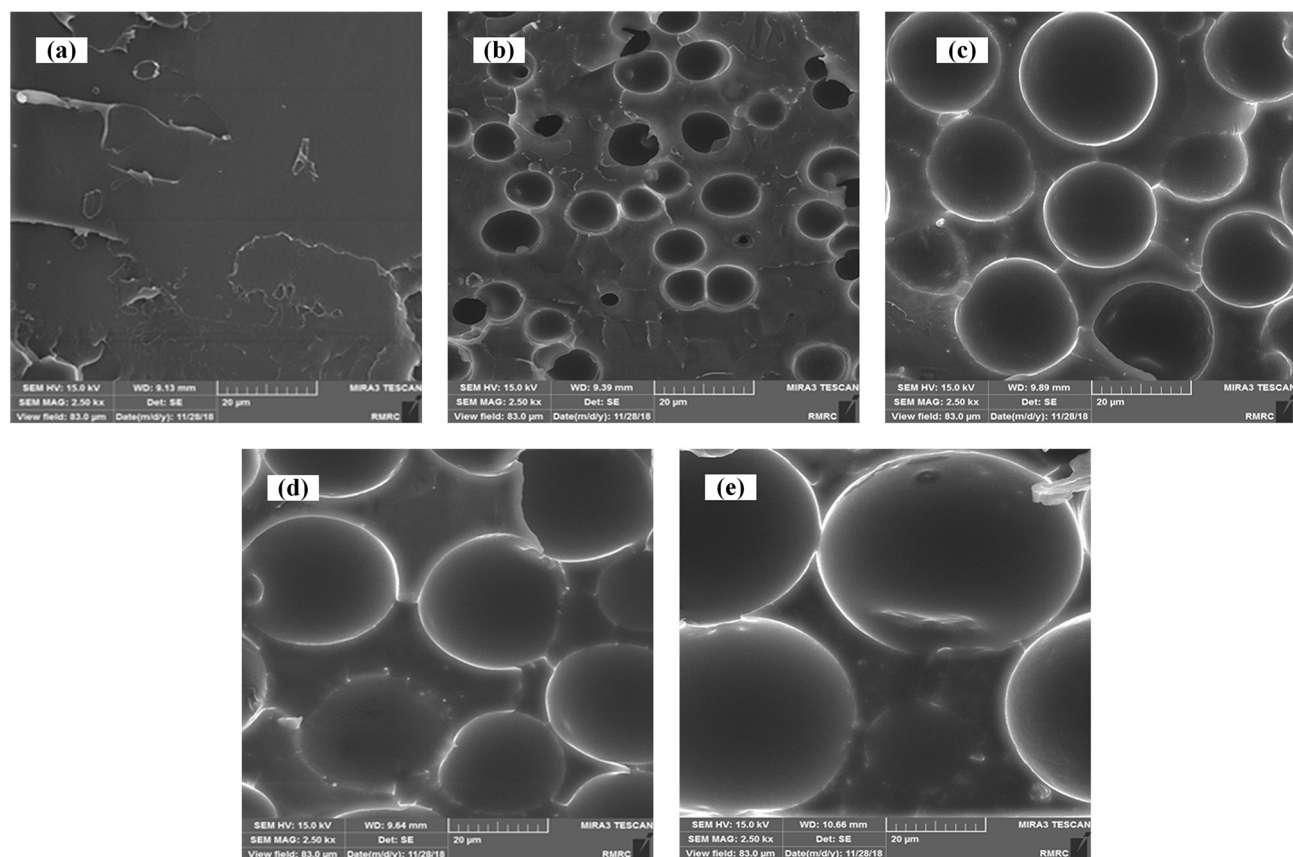


Fig. 3. Morphology of fabricated membranes with different IL content: (a) 0 wt% (b) 10 wt% (c) 20 wt% (d) 30 wt% and (e) 40 wt%.

expected that the membranes containing this polymer and ionic liquid show an increment in both selectivity and permeability towards CO₂. Polysulfone is chosen as the polymer matrix for several reasons. Carbon dioxide has higher affinity to polysulfone matrix compared to methane due to structural similarity to sulfonyl groups in the polymer and its high critical temperature. Furthermore, Polysulfone has unique properties such as thermal resistance, radiation resistance, hydrolysis resistance, high tensile strength, resistance to inorganic acids, high pressure resistance and high mechanical strength that make it an effective polymer in high pressure applications [21]. Chemical structure of polysulfone and 1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid are shown in Fig. 1.

2. Materials and Methods

2.1. Materials

Polysulfone with 99.9% purity and 1-Ethyl-3-methylimidazolium tetrafluoroborate with 97% purity are both purchased from Sigma-Aldrich, USA. *N*-Methyl-2-pyrrolidone with 99.5% purity is used as a solvent and it is obtained from Merck, Germany. CO₂, CH₄ and CO₂/CH₄ mix gases with purities of above 99.999% are provided by Tehran Farafan gas Inc., Iran.

2.2. Membrane preparation

Pure polymeric membrane and membranes with 10 wt%, 20 wt%, 30 wt%, and 40 wt% of ionic liquid are fabricated via phase inversion

Table 1

EDS analysis of the membrane samples

Element	Pure PSF membrane	Membrane with 10 wt% IL	Membrane with 30 wt% IL	Membrane with 40 wt% IL
Carbon	63.4	57.66	57.56	53.61
Nitrogen	11.8	14.49	14.95	18.49
Oxygen	19.65	19.48	11.18	12.83
Fluorine	0.12	4.31	12.46	12.62
Sulfur	5.04	4.06	3.15	2.45

method. The neat membrane with 12 wt% solid concentrations is prepared by dissolving suitable amount of polysulfone in *N*-Methyl-2-pyrrolidone and mixed overnight. For the fabrication of composite membranes, various amounts of the ionic liquid are added to the polymer solution to prepare polymer-IL membranes with concentrations ranging from 10 wt% to 40 wt% IL. These mixtures are stirred for 24 h at room temperature. In the next step, the solutions are kept at rest for 24 h at room temperature for complete degassing. Finally, the prepared solutions are cast with a casting knife and dried in an oven at 60 °C for 48 h.

2.3. Characterization

The fabricated membranes are characterized using FE-SEM, EDX, FTIR, XRD, TGA and Tensile strength.

TESCAN SEM model Mira-3 XMU microscope equipped with an EDX apparatus is used to investigate the structure and surface morphology of the membranes. Cross-sectional SEM images of the membranes are also

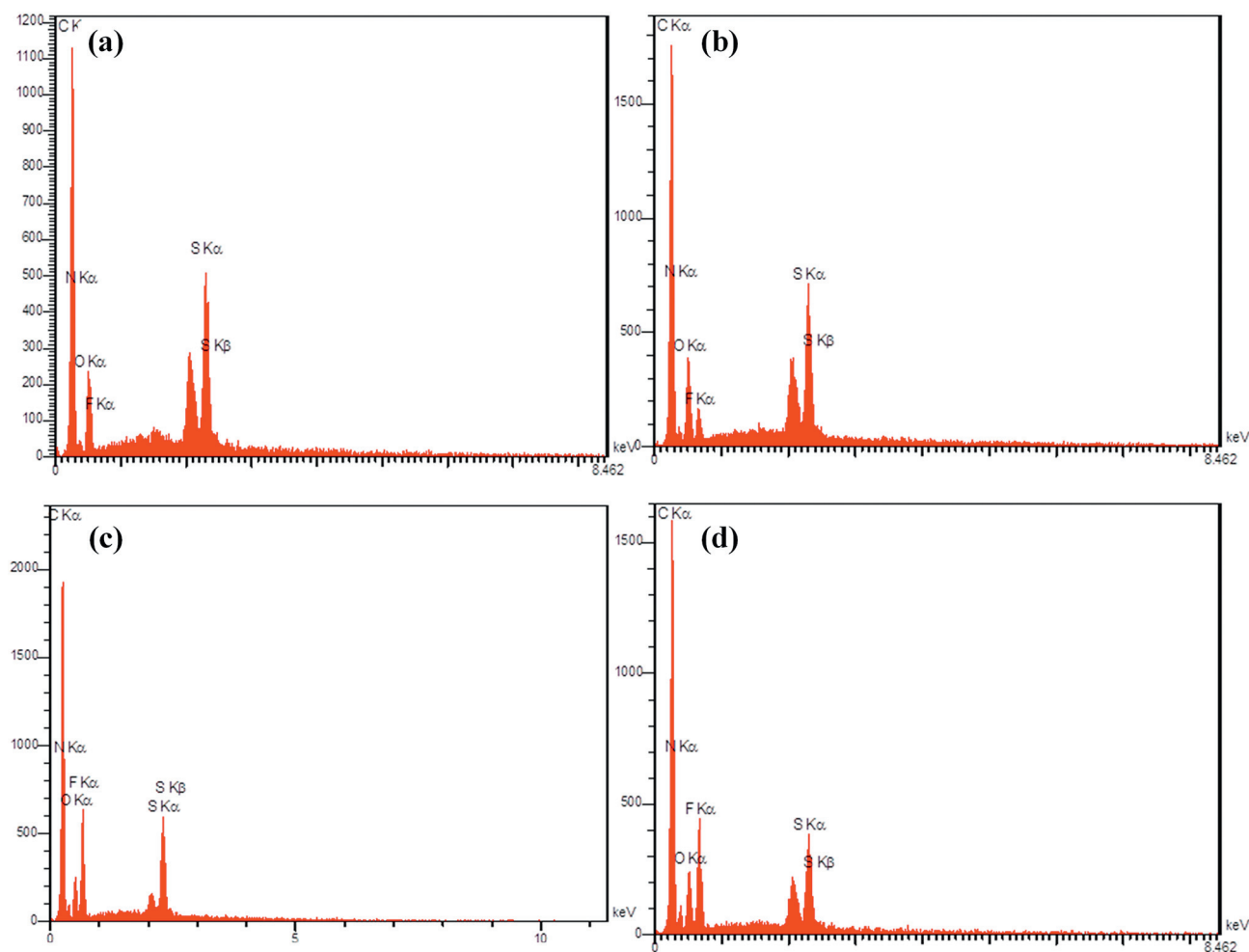


Fig. 4. EDS spectra of the polysulfone membranes: (a) pure polysulfone, (b) 10 wt% IL, (c) 30 wt% IL and (d) 40 wt% IL.

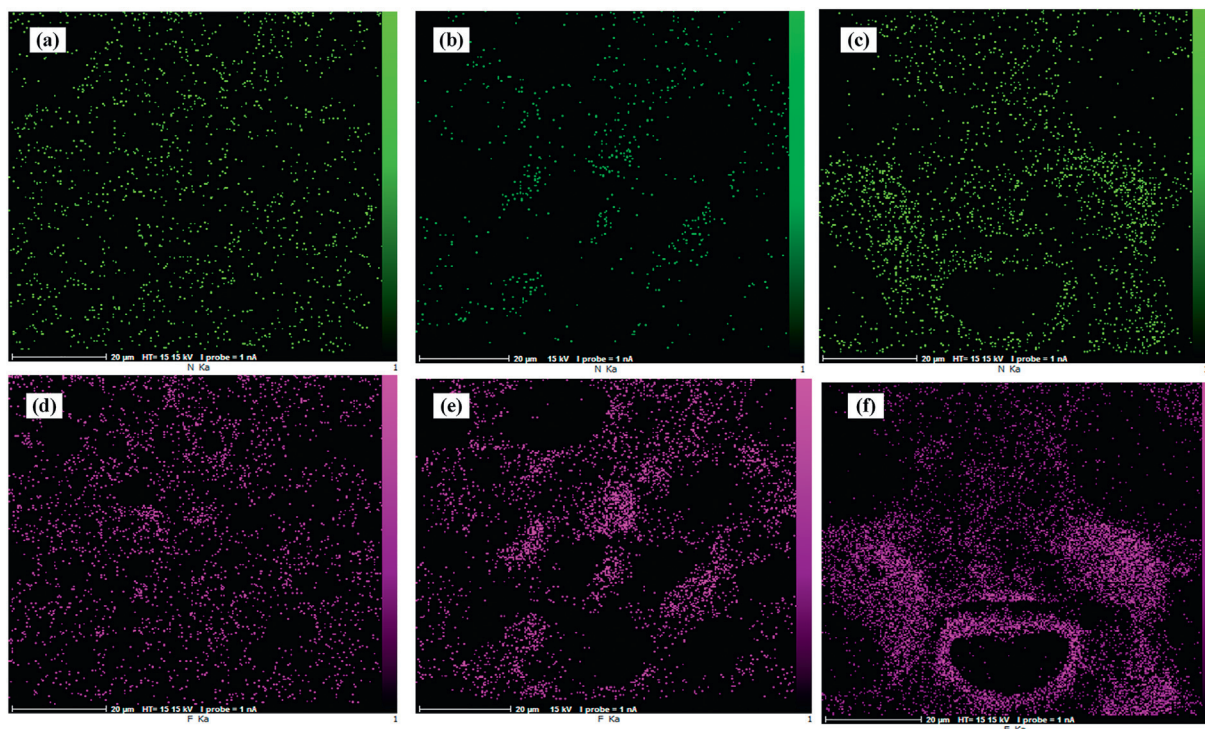


Fig. 5. elemental mapping of membranes samples: (a) nitrogen in 10 wt% IL membrane (b) nitrogen in 30 wt% IL membrane (c) nitrogen in 40 wt% IL membrane, (d) fluorine in 10 wt% IL membrane (e) fluorine in 30 wt% IL membrane (f) fluorine in 40 wt% IL membrane.

utilized to gain further information about membrane thickness which helps in permeability calculations. The samples are first fractured in liquid nitrogen and then to create conductivity they are coated with a layer of Au and placed in the SEM holder.

EDS is used to analyze the chemical composition in the samples and mapping of the elemental distribution through surface imaging. In this research, elemental analysis is conducted on three membranes containing 10 wt%, 30 wt% and 40 wt% IL using EDS and mapping.

FTIR can be used for qualitative and quantitative characterization of organic samples and to investigate functional groups and various bonds in their structures. In this work, three polysulfone membranes containing 0, 10 wt% and 30 wt% of the ionic liquid are investigated using a Shimadzu FTIR spectrometer.

To determine the effects of the ionic liquid on the structure of the polymer samples and consequently gas permeation properties, XRD analysis is utilized. The pure polysulfone membrane, PSF-10 wt% IL membrane and PSF-30 wt% IL membrane are investigated using a Rigaku ultima iv XRD diffractometer.

To assess the influence of the ionic liquid on thermal stability of the polymer membranes, three polysulfone membranes containing 0, 10 wt% and 30 wt% IL are analyzed by a Bahr STA504 TGA device.

Tensile strength test has been performed for membranes with 0, 10 wt% and 30 wt% IL concentration to investigate the mechanical resistance of membranes. A Jinjian Utm 1432 instrument are used for this test. Three samples for each membrane are tested and the average results are reported.

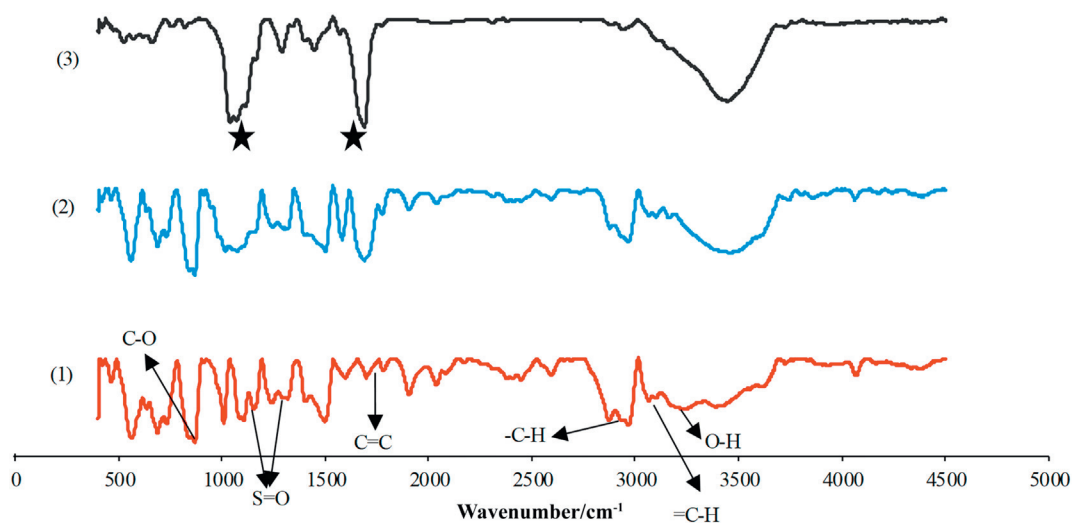


Fig. 6. FTIR spectra of the membranes (1) pure polysulfone (2) polysulfone containing 10 wt% IL and (3) polysulfone containing 30 wt% IL.

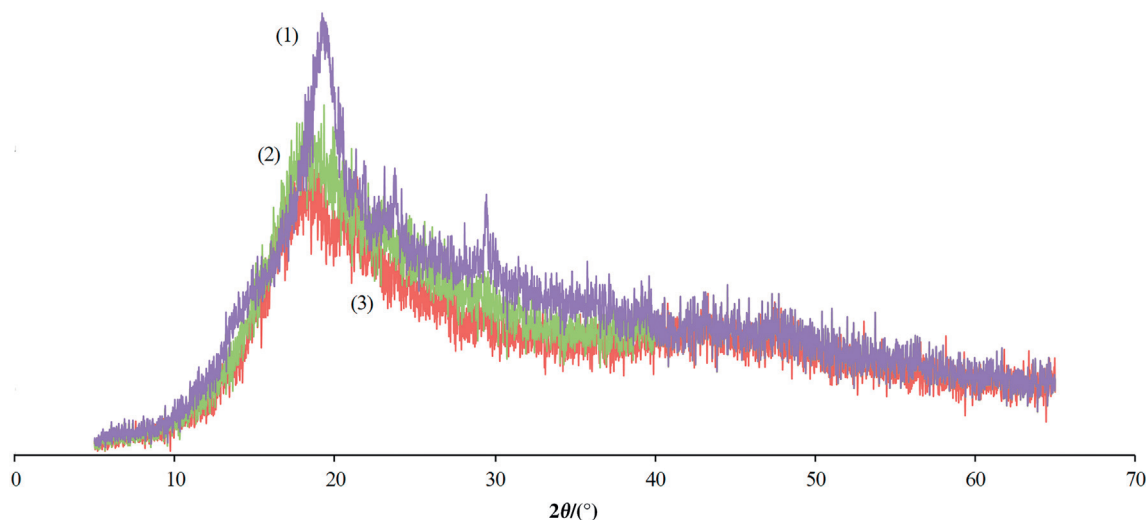


Fig. 7. XRD patterns of membranes: (1) pure polysulfone (2) polysulfone containing 10 wt% IL and (3) polysulfone containing 30 wt% IL.

2.4. Permeability measurements

Gas permeability of the fabricated membranes are measured using a constant volume method. The permeation apparatus consists of a permeation cell and a constant volume high precision pressure sensor chamber. The feed gas runs through a stainless steel cell with the effective permeation area of 3.14 cm². The permeate from the membrane is collected in a constant volume and the increase in the pressure is measured. The illustration of utilized setup for permeability measurement is mentioned in previous work study [11].

Gas permeation and ideal selectivity are calculated using the following equations:

$$p = \frac{83.14 \times 273.15 \times V \times L \times dp/dt \times 10^{10}}{6.23 \times 10^3 \times T \times A \times P} \quad (1)$$

$$\text{selectivity} = \frac{p_{\text{CO}_2}}{p_{\text{CH}_4}} \quad (2)$$

where L is the thickness of membranes in cm, V is the constant volume of the system in cm³, A is the membranes surface area in cm², T is the operating temperature in K, P is feed pressure in mmHg, dp/dt is the pressure change gradient in mm Hg·s⁻¹ and p is the gas permeability in Barrer.

To investigate the effect of CO₂ and CH₄ interaction in membranes permeability, mixed gas permeation test has been performed by using a gas mixture of 10%/90% CO₂/CH₄ with high purity of 99.999 for all membranes. All tests repeated for two times.

Eqs. (3) and (4) has been used to calculate permeability and selectivity of membranes in mixed gas test.

$$p_A = \frac{83.14 \times 273.15 \times V \times L \times dp/dt \times 10^{10} \times y_A}{6.23 \times 10^3 \times T \times A \times P \times x_A} \quad (3)$$

$$\text{selectivity} = \frac{y_A/y_B}{x_A/x_B} \quad (4)$$

In the above equation x and y are mole fraction of each gas in feed and permeate side respectively. A and B are corresponded to CO₂ and CH₄ in this work respectively. p_A is the permeability of CO₂ gas in Barrer.

3. Results and Discussion

3.1. FE-SEM

Cross-sectional SEM images of fabricated membranes are shown in Fig. 2. The images indicate that the thickness of the layers is approximately 200 μm. The pure polysulfone membranes are void-free and dense but increasing ionic liquid concentration results in larger pores which can prove the ionic liquid presence in the samples. At lower ionic liquid concentrations, no pores are detected at lower parts, but according to SEM mages when ionic liquid concentration reaches 20 wt%, small pores are uniformly distributed. This trend increases with the addition of ionic liquid to the blend system those results in larger pores and membranes with higher opaqueness.

Fig. 3 depicts the morphology of polysulfone-IL membranes containing 10 wt%, 20 wt%, 30 wt% and 40 wt% of [emim][BF₄] ionic liquid. As it can be seen in the images, the structural bulk of the pure membrane is uniform and regular.

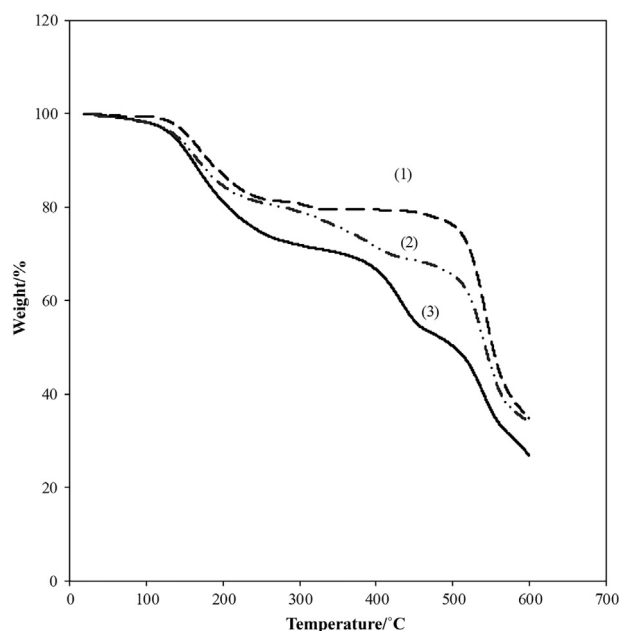


Fig. 8. TGA thermograms of: (1) pure polysulfone membrane, (2) 10 wt% ionic liquid membrane, (3) 30 wt% ionic liquid membrane.

Table 2
Tensile strength test results

Membrane	Tensile stress/MPa	Young's modulus/GPa	Elongation at break/%
Pure PSF	56.79	3.8	14.97
10 wt% IL	20.42	1.89	10.62
30 wt% IL	10.54	1.58	6.87

The results demonstrate that addition of the ionic liquid as a plasticizer to the polymer matrix reduces viscosity and results in more porous and irregular structures [22]. The size and distribution of the pores depend on the type and concentration of incorporated ionic liquid in the polysulfone matrix. The pure polysulfone membrane is transparent while the membranes containing ionic liquid show different degrees of opaqueness. Membranes containing low IL concentration show a few white spots. When the ionic liquid content increases, the white spots uniformly extend throughout the surface of the membranes and the membranes gradually change from transparent to opaque. On a microscopic scale, it was found that the opacity is a result of pore formation in the membranes. These pores allow free passage of the gas in the membranes and therefore increase permeability but also can drastically reduce selectivity.

A hypothesis for the formation of these types of structures in the membranes is the difference between solvent and ionic liquid densities. Moisture has an effect on micro pores formation, since ionic liquids are hydrophilic, small percentage of water may be present in the IL.

3.2. Elemental analysis and mapping

To identify the constituent elements and analyze their ratio and distribution in the membranes, EDS spectra and mapping images were employed. The EDS spectra of pure polysulfone and polysulfone-IL membranes containing 10 wt%, 30 wt% and 40 wt% IL are represented in Fig. 4.

The elemental analysis results of the samples are reported in Table 1. It was expected that the pure polymer membrane should only consist of carbon, oxygen and sulfone, but detectable amounts of nitrogen and fluorine are also observed. This observation may be the result of liquid nitrogen that was used to fracture the membranes and to clean the tools or the apparatus during the microscopy procedure. The detection of carbon, oxygen, sulfone, nitrogen and fluorine is quite natural in polymer-IL membranes regarding the chemical structure of [EMIM][BF₄] ionic liquid.

The percentage of these elements are expectedly higher in sample containing 40 wt% IL in comparison with 10 wt% IL. In the sample containing 40 wt% IL the nitrogen content is 1.3 fold and the fluorine content is 3 fold the 10 wt% IL sample.

The distribution of each element in every sample is also analyzed through elemental mapping. Fig. 5 depicts nitrogen and fluorine distribution in membranes with 10 wt%, 30 wt% and 40 wt% IL. By loading higher IL contents an increase in the percentage of nitrogen and fluorine is observed in the samples demonstrating the presence of ionic liquid in the two membranes.

Table 3
Permeability and selectivity results

Membrane	CO ₂ permeability/Barrer	CH ₄ permeability/Barrer	CO ₂ /CH ₄ selectivity
Pure PSF	4.29 ± 0.1	0.52 ± 0.03	8.21
10 wt% IL	129.14 ± 3	7.35 ± 0.2	17.57
20 wt% IL	232.09 ± 15	9.74 ± 0.5	23.83
30 wt% IL	601.98 ± 13	23.27 ± 0.9	25.87
40 wt% IL	422.68 ± 10	18.91 ± 0.9	22.35

3.3. FT-IR analysis

FTIR spectra are used to investigate the intermolecular interactions and to make sure of proper distribution of ionic liquid in the polymer matrix. The pure polymer membrane spectrum shows a pair of peaks at 1475 cm⁻¹ and 1600 cm⁻¹ that correspond to the stretching of aromatic double bonds (C=C). The peak at 3060 cm⁻¹ indicates the stretching of aromatic = C—H group. Two peaks at 690 cm⁻¹ and 900 cm⁻¹ are related to out of plane aromatic bending vibrations. The symmetric and asymmetric vibrations of S=O band in sulfone functional group are observed at 1236 cm⁻¹ and 1150 cm⁻¹. The peaks at 1000 cm⁻¹ and 1315 cm⁻¹ indicate the asymmetric vibrations of C—O bands (Fig. 6(1)).

Fig. 6(2) and (3) shows the FTIR results of membranes containing 10 wt% and 30 wt% IL. The peaks at 1043 cm⁻¹ and 1687 cm⁻¹ (indicated by two stars in Fig. 6(3)) are assigned to the C—H bands of alkyl and imidazolium in the ionic liquid that were absent in the pure polymer membrane spectrum. These observations demonstrate the distribution of ionic liquid in the polymer matrix [23]. The broad peak at 3400 cm⁻¹ which is observed in all the three spectra is related to the stretching vibrations of O—H band in water molecules that are present in the system.

3.4. XRD studies

The XRD patterns of pure polysulfone membrane and polysulfone containing 10 and 30 wt% ionic liquid membrane are illustrated in Fig. 7. A wide peak at 2θ of 19° and a narrow peak at 2θ of 45° are observed in the XRD pattern of pristine membranes that are in agreement with the literature data [24].

Addition of the ionic liquid, results in structural integrity disruption as can be seen in Fig. 7. With the enhancement of ionic liquid concentration, the peaks intensity decreased due to decrease in polymer crystallinity.

This is in accord with the FE-SEM results. In fact, addition of the ionic liquid to the polymer matrix reduces structural integrity by increasing amorphous domains [25]. In the amorphous materials, X-rays weaken each other and diffraction does not happen, but if the atoms are placed in order and with specific distance from each other, the distance would be a multiple of the X-ray wavelength like it happens with the polysulfone membrane. Generally, adding ionic liquids and nanoparticles change the degree of crystallinity in polymeric membranes. Here, crystallinity of the membranes is reduced by incorporation of the ionic liquid as it is shown in Fig. 7. Addition of the ionic liquid to the polymer matrix leads to higher mobility of the polymer chains that is a result of reduction in hydrogen bonds. This leads to higher fractional free volume which refers to the small domains left unoccupied at the end of the polymer chains [25].

3.5. TGA analysis

To analyze the thermal degradation properties of the membranes after the incorporation of the ionic liquid, TGA analysis is performed on the samples. Fig. 8 shows the TGA thermograms of pure polysulfone membrane and polysulfone membranes containing 10 wt% and 30 wt% [emim][BF₄]. Polysulfone or poly (aryl sulfone) are a special class of engineering polymers with high mechanical and thermal strength. These thermoforming polymers are known for their strength and stability at high temperatures. Polysulfone and poly (aryl ether sulfone) consist of aromatic ether and sulfonyl groups. Phenyl and sulfonyl groups are thermally stable that results in thermal stability of the whole polymer [26]. Polymer stability can also be related to the constituent elements. Sulfonyl groups are related to the aromatic system through resonance, so the inter-polymer bonds gain strength from the resonance energy. Therefore, higher degrees of thermal or radiation energy can be adsorbed by

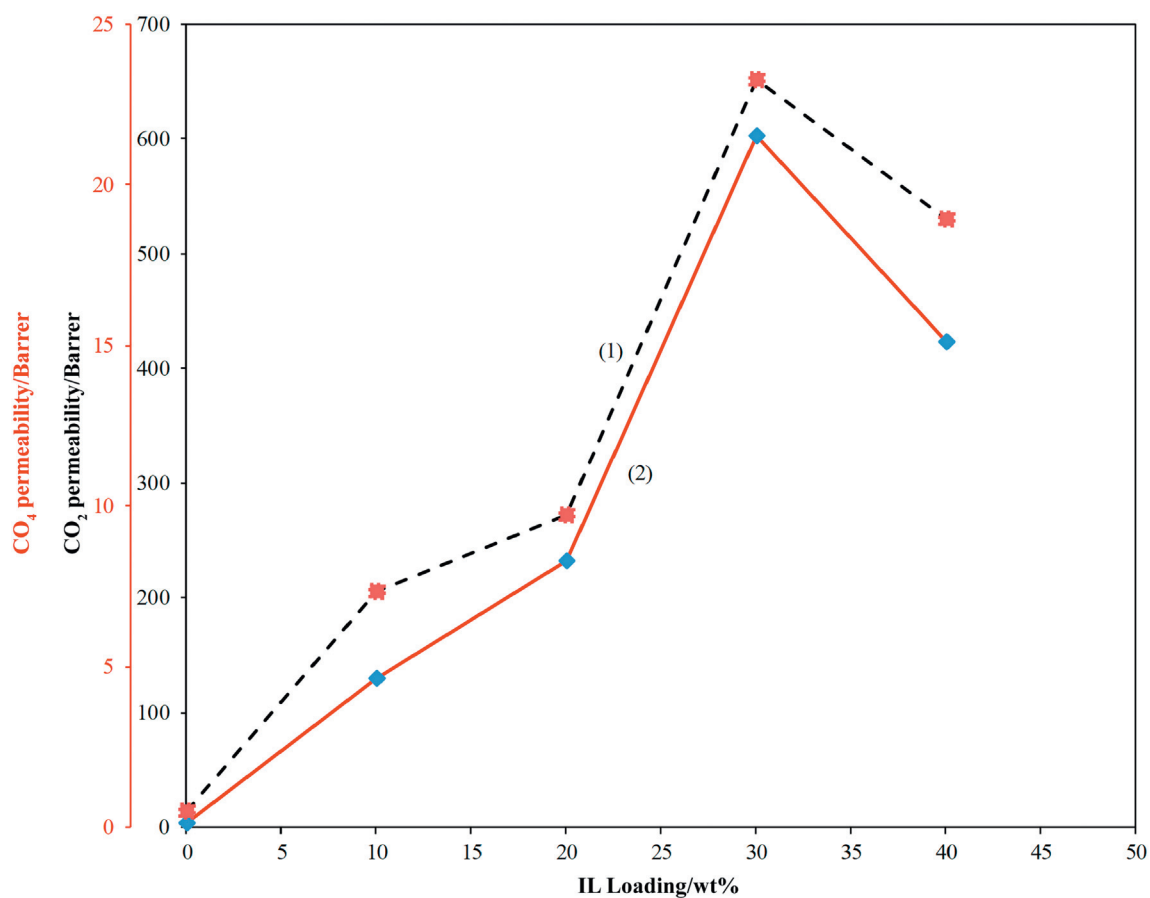


Fig. 9. Effect of the ionic liquid loading on: (1) CO₂ permeability, (2) CH₄ permeability.

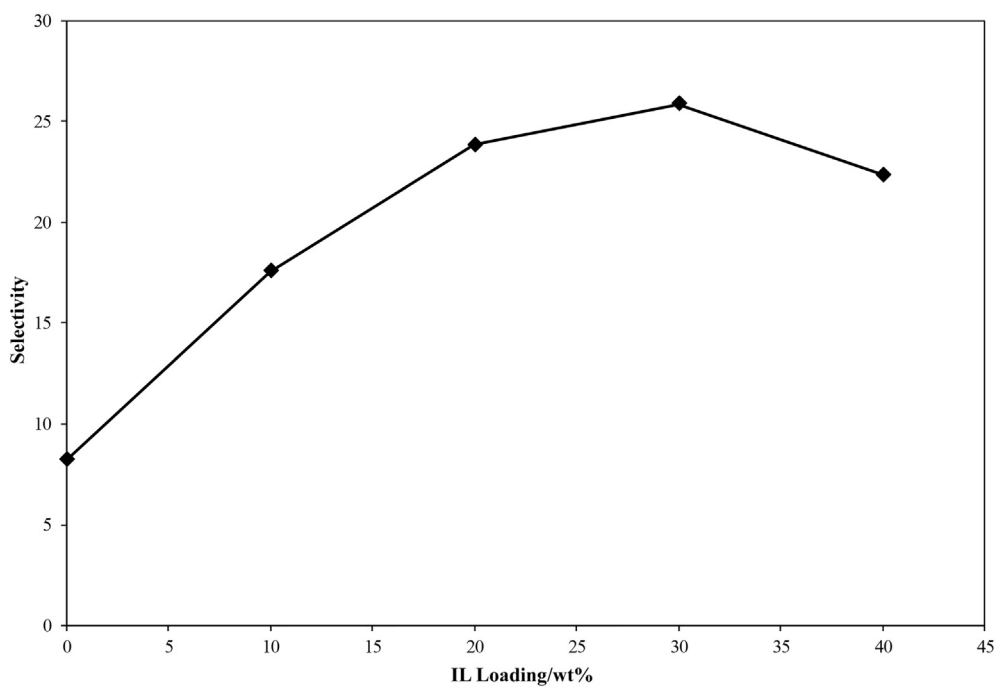


Fig. 10. CO₂/CH₄ selectivity of polysulfone-IL membranes with different ionic liquid loadings.

Table 4
Mixed gas test results

Membrane	CO ₂ permeability/Barrer	CH ₄ permeability/Barrer	CO ₂ /CH ₄ Selectivity
Pure PSF	3.65 ± 0.1	0.59 ± 0.02	6.19
10 wt% IL	115.21 ± 5	8.02 ± 0.4	14.37
20 wt% IL	208.25 ± 18	10.28 ± 0.5	20.26
30 wt% IL	550.10 ± 10	24.52 ± 0.8	22.43
40 wt% IL	395.44 ± 20	20.26 ± 0.9	19.52

the molecular structure without further reaction or decomposition [27]. The first weight loss at about 250 °C corresponds to the residual solvent evaporation. Another observed weight loss started at about 400 °C and ended at 600 °C that could be attributed to simultaneous decomposition of the ionic liquid and the polymer. Thermal stability of the membranes containing ionic liquid are less than the pure polymer membrane because the ionic liquid tends to decompose before the polymer matrix. Decomposition temperature of [emim][BF₄] is about 443 °C to 494 °C which is in agreement with the results represented in Fig. 8. The polymer-IL membranes show higher weight loss than the pure polymer membrane. Increasing the ionic liquid content in the membranes reduces thermal stability.

3.6. Tensile strength analysis

Table 2 shows the results of Tensile analysis for membranes with 0, 10 and 30% IL concentration. Young's modulus, Tensile strength and Elongation at break were calculated. All these parameters decreased with increase in ionic liquid concentration. The decrement of mechanical resistance shows that ionic liquid acts like a plasticizer in polymeric membranes, which has been reported in other works [17]. Although adding IL increased membranes flexibility and decreased its resistance, but even membrane with 30 wt% IL has still proper mechanical properties for operating conditions.

3.7. Permeability and selectivity results

The permeability results of CO₂ and CH₄ gases for all the membranes are presented in Table 3. The effect of IL content on the permeability of the membranes can also be seen in Fig. 9. All the tests are measured twice at 25 °C and 0.3 MPa. Permeability of both gases increases by incorporation of the ionic liquid. Usually mass transfer is much faster in ionic liquids compared to solid polymeric materials. Therefore, presumably higher loading of the ionic liquid would result in higher gas flux and faster separation in polymeric gel-ionic liquid membranes which our results completely comply with these expectations.

The membrane containing 30 wt% ionic liquid shows the highest permeability. The CO₂ permeation of this membrane increases about 140 times compared to that of the pure polymer membrane. The same is observed for methane permeation, where permeability increases 44.4 times. This dramatically higher permeability is mainly as a result of pores formation and the change in membrane structure. The results show that permeability increases by increasing IL content up to 30 wt%. Therefore, the sample containing 30 wt% IL is chosen as the optimum membrane.

The improvement of carbon dioxide permeability is more pronounced because of its higher diffusivity and solubility in the polymer and ionic liquid. Considering the higher fractional free volume of ionic liquids compared to polymers, carbon dioxide can readily diffuse in the membranes. It is known that carbon dioxide exhibits high level of diffusivity and solubility in the ionic liquid so it is anticipated that polymer-IL membranes show higher CO₂ permeation than pure polymer membrane.

As mentioned earlier, CO₂/CH₄ ideal selectivity of fabricated membranes are calculated based on gas permeation. Increasing ionic liquid content up to 30 wt% brings about an increase in selectivity. The best result is corresponded to the membrane with 30 wt% IL which shows 140% selectivity growth compared to polysulfone membrane. It should be noted that the transport mechanism in polymeric membranes are based on solution-diffusion. One of the reasons for the selectivity improvement in polysulfone-IL membranes might be selective CO₂ adsorption by the ionic liquid which facilitates gas permeability and

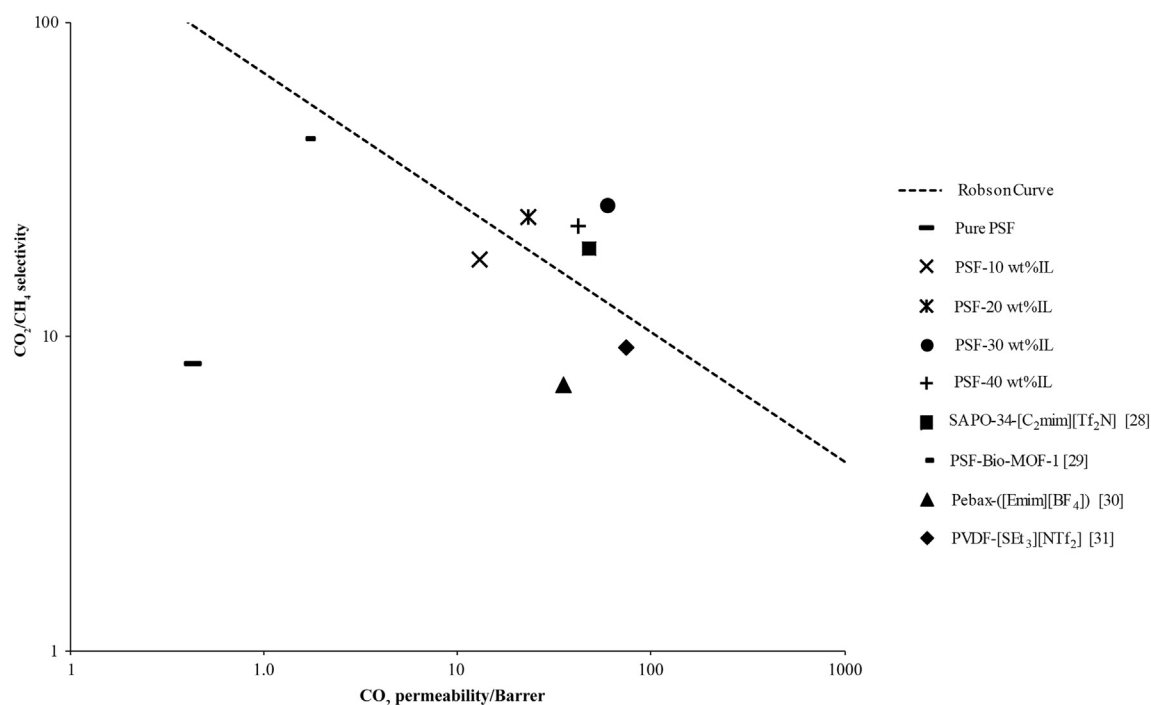


Fig. 11. Performance of fabricated membranes compared to Robeson curve [28,29].

Table 5

Comparison of our results with other studies

Membrane	Polymer	Ionic liquid	CO ₂ permeability/Barrer	CO ₂ /CH ₄ selectivity	References
PSF-30 wt% IL	PSF	[emim][BF ₄]	601.98	25.87	This work
PES-50 wt% IL	PES	[emim][Tf ₂ N]	298.84	57.53	[15]
PEBAX/IL	PEBAX	[emim][BF ₄]	350	7	[30]
PVDF/IL	PVDF	[bmim][BF ₄]	93.9	12.9	[31]
PVDF/IL	PVDF	[SEt ₃][NTf ₂]	747	9.20	[31]

leads to higher membrane selectivity. Because of the polarity of CO₂ molecules, they tend to interact with the charged ionic liquid which is not the case for nonpolar methane molecules. An increase in polymer free volume and mobility due to higher ionic liquid content is another reason for this observation. In fact, CO₂ shows higher permeability as a result of higher affinity of IL for this gas in comparison with CH₄.

Contrary to the predictions, permeability and selectivity of 40 wt% IL membrane considerably decrease in comparison with 30 wt% IL membrane which can be due to polymer aggregation or membrane degradation because of oversaturation of the ionic liquid. This membrane shows about 33% and 13.5% decrease in CO₂ permeability and selectivity respectively compared to 30 wt% IL membrane. The CO₂/CH₄ selectivity is illustrated in Fig. 10.

The results of mixed gas permeation test can be seen in the Table 4. The results show significant selectivity and CO₂ permeability decrement as well as CH₄ permeability enhancement compare to pure gas test. These results are due to disturbing effect of CH₄ molecules. Indeed, the existence of CH₄ disturb CO₂ molecules adsorption and diffusion process. Moreover, the high affinity of ionic liquid for CO₂ gas, increases the CH₄ permeability through membranes. The interaction between these two gases results CO₂ permeability decrement and CH₄ permeability growth, so the selectivity decreases compare to ideal selectivity. However, this reduction was more significant in pure PSF membrane and in membranes with low ionic liquid concentration (the decrement of CO₂ permeability in membrane with 30% ionic liquid was 9% while pure PSF membrane showed 17% reduction compare to pure gas test). The high free volume of membranes with higher amount of ionic liquid, decreases the disruptive effect of CH₄ molecules.

3.8. Robeson plot and comparison with the literature data

In order to assess gas permeability performance, plot of fabricated membranes on Robeson upper bound at 25 °C and 0.3 MPa is depicted in Fig. 11. As can be seen, the performance of 10 wt% IL membrane is close to Robeson upper bound, while membranes containing 20 wt%, 30 wt% and 40 wt% IL surpass Robeson upper bound and exhibit excellent performance. Moreover, comparison of our results with other studies can be seen in Table 5.

4. Conclusions

In this study, polysulfone blend membranes containing 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid are fabricated. Based on FESEM analysis, it is demonstrated that pristine polysulfone membrane is completely dense and void-free. Adding the ionic liquid which acts as a plasticizer to polymer matrix disrupts membrane's integrity and leads to higher porosity. EDS and Mapping analyses as well as FTIR spectra prove the existence of IL in the membranes. Using TGA analysis, it was indicated that by increasing the ionic liquid content the thermal stability and degradation temperature of ILPMs declines. Adding 10 wt% to 40 wt% of the ionic liquid to the polysulfone membrane, improves CO₂ permeation by 30.4% to 98.3% in comparison with pure polymeric membrane. This improvement is due to high CO₂ affinity of ionic liquid and the formation of uniform pores in membrane structure. Selectivity also shows the same trend with about 300%

increase in the membrane with 30 wt% IL. Based on these findings, polysulfone membrane containing 30 wt% IL is chosen as the optimum sample. The performances of membranes containing 20 wt%, 30 wt% and 40 wt% ionic liquid, surpass Robeson upper bound and demonstrate good selectivity and permeability towards CO₂.

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