Environmental Science and Pollution Research (2021) 28:38274–38291
https://doi.org/10.1007/s11356-021-13447-y

RESEARCH ARTICLE

CO_2-selective poly (ether-block-amide)/polyethylene glycol composite blend membrane for CO_2 separation from gas mixtures

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Received: 23 August 2020 / Accepted: 10 March 2021 / Published online: 17 March 2021

Abstract

This work focuses on the preparation of composite blend membranes based on poly (ether-block-amide) (Pebax-1657) by incorporating polyethylene glycol (PEG) for gas separation applications. The influence of PEG with different molecular weights (PEG600, PEG1500, and PEG4000) at loading content in the range of 10%wt. to 40%wt. was investigated on the microstructure and gas separation performance of the prepared blend membranes. The fabricated membranes were characterized using SEM, XRD, and water contact angle analyses. Based on the experimental results, the blending of low molecular weight PEG (PEG600) into the Pebax-1657 matrix increased the chain mobility of the membrane, led to a smooth microstructure, and improved the hydrophilicity of the blend membranes, as well as enhanced the gas permeability of N_2, O_2, CH_4, and CO_2, but only slightly affected the ideal selectivity of O_2/N_2, CH_4/N_2, CO_2/N_2, and CO_2/CH_4. In contrast, the incorporation of PEG1500 and PEG4000 meaningfully increased the membrane crystallinity, decreased chain mobility, resulted in a rough microstructure, and reduced the blend membranes' hydrophilicity. For CO_2/N_2 mixture, the Pebax/40%PEG600 membrane had CO_2 permeability of 62.9 Barrer and selectivity of 83.8, while the Pebax/20%PEG600 showed the CO_2 permeability of 63.12 Barrer and selectivity of 23.6 for CO_2/CH_4 separation.

Keywords CO_2 separation · Blend membranes · Poly (ether-block-amide) (Pebax-1657) · Polyethylene glycol (PEG) · Microstructure

Introduction

The uncontrolled CO_2 emission is one of the environmental challenges, and augmenting the volume of CO_2 among greenhouse gases results in global warming (Xie et al. 2019; Sarmadi et al. 2020). The development of an environment-friendly and energy-efficient technology for CO_2 separation is ever urgent. The membrane-based gas separation process can be an attractive and efficient candidate for CO_2 separation from flue gas and natural gas (Dai et al. 2019a; Xie et al. 2019; Saeed et al. 2020). The membrane technology has significant advantages, such as less compression cost, easy achievement, less energy consumption, and operation at mild temperatures. Recently, polymers have widely been used to prepare membranes for gas separation applications because of their ease of procurement, low material cost, good membrane process-ability, and energy-efficient (Xie et al. 2019). However, the polymeric membranes' fundamental challenge is the inverse relationship between permeability and selectivity, restricting their industrial applications. Various design strategies such as grafting, co-polymerization, cross-linking, mixed-matrix-membrane, and blending (Han and Ho 2018; Wang et al. 2016) have been employed to enhance the gas separation performance of the polymeric membranes and to overcome the trade-off between permeability and selectivity. Among these modification techniques, polymer blending is a unique method because it offers a cost- and time-effective approach to tuning the membrane properties (Feng et al. 2013a).

A polymer blend is a mixture of at least polymers that are blended to create a new product with different properties. In polymer blending, a continuous range of performance is achievable by changing the mixture composition, which on the miscibility of the polymer pairs. Likewise, the choice of

Responsible editor: Angeles Blanco

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polymers is crucial to develop a polymer blend with desired superior properties. In the case of using polymer blends to prepare membrane for the CO_2 separation, the polymers containing polar ether oxygen (EO) units in their backbones reveal high CO_2 permeability and high CO_2/light gas solubility selectivity due to the interaction between the CO_2 and EO groups (Car et al. 2008; Quan et al. 2017). Thus, the use of PEO-based polymers such as poly-ether-block-amide (Pebax) can be promising. Pebax, which is a rubbery block copolymer with immiscible flexible polyether (PE) segments and a rigid block of polyamide (PA), has appropriate perm-selectivity over CO_2 (Ren et al. 2012).

On the other hand, poly (ethylene glycol) (PEG) and PEG-derivatives are the most important polymer additives for the membrane preparation in various membrane processes because of their unique physical, chemical, and mechanical characteristics (Kargari and Rezaeinia 2020; Wong and Jawad 2019). PEG contains EO groups that show a strong affinity towards CO_2, although the high crystallinity of PEG impedes gas diffusion (Liu et al. 2016). Therefore, the addition of PEG to various polymers has a strong effect on their gas transport property (Azizi et al. 2017; Feng et al. 2013b). There are several studies which used PEG with different molecular weight as an additive to prepare CO_2-selective membranes. For example, Feng et al. (2013b) examined the effect of PEG on the gas permeability and selectivity of Pebax-1074/PEG1500 blend membranes. They reported that in the crystalline region, the blending of PEG1500 to Pebax-1074 led to enhance in the permeation activation energy of CO_2. However, in the amorphous region, the activation energies of CO_2, N_2, and CH_4 are lower than the activation energies in the crystalline region. Feng et al. (2019) used PEG with different molecular weights to prepare blend membranes based on the Pebax-1074. They observed that for the blend membranes containing PEG with low molecular weight (MW ≤ 600), the permeability enhanced with the rise of MW and led to a reduction in the activation energy of permeation and improvement of the separation performance. For Pebax1074/PEG with high MW of PEG (MW ≥ 1500), the gas permeation property is described within three regions, crystalline, transition, and amorphous, that the permeation activation energy in the crystalline region was higher than that of the amorphous region. Azizi et al. (2017) prepared the blend membranes by adding PEG with two different MW (PEG400 and PEG1000) into three different grades of Pebax (1657, 2533, and 1074). Their gas separation results showed that low MW PEG significantly increased the permeability of CO_2 and CH_4 gases but had little effect on the CO_2/CH_4 selectivity. However, increasing PEG with high MW reduced the permeability of two gases and increased the CO_2/CH_4 selectivity. Also, Reijerkerk et al. (2010) used PEG and poly (dimethylsiloxane) (PDMS)-PEG), which consists of 80%wt. of PEG and 20%wt. of PDMS, to prepare blend membranes based on Pebax-1657 and observed that for the separation of the CO_2/H_2 and CO_2/He gas mixtures, the PDMS-PEG/Pebax-1657 blend membranes had better performance than the neat Pebax-1657 membrane, while the PEG/Pebax-1657 blend membranes showed better separation performance for the CO_2/CH_4, CO_2/N_2, and CO_2/O_2 mixtures. In addition, the PEG has been used to modify other polymeric membranes poly(ether sulfone) (PES) (Akbarian et al. 2018), polycarbonate (PC) (Hamrahi and Kargari 2017), polyactive (Rahman et al. 2015), polysulfone (PSf) (Jujie et al. 2017), polyvinylidene fluoride (PVDF) (Naim et al. 2014), and polymers of intrinsic microporosity (PIMs) (Halder et al. 2017). Hamrahi and Kargari (2017) investigated the permeation of CO_2 and CH_4 through the PC/PEG-300 blend membranes. They indicated that the PC/PEG blend membranes were miscible/partially miscible without considerable micro-phase separation. The permeability of CO_2 and CH_4 decreased, as PEG loading increased. Loloei et al. (2015) investigated the influence of PEG-200 on structure and gas separation performance of Matrimid®5218 polymer, and observed that the CO_2 permeability and CO_2/CH_4 selectivity of the optimum blend membrane (Matrimid/PEG (95:5)) increased related to the neat Matrimid membrane.

Furthermore, PEG has been used as an additive in the preparation of three-phase mixed matrix membranes based on the Pebax polymer. Noroozi and Bakhtiari (2019) incorporated amino-functionalized titanium oxide nanotubes into the Pebax/PEG blend matrix for the CO_2/CH_4 separation and reported that the separation performance of the resultant nanocomposite membranes increased as the PEG content enhanced. Shin et al. (2019) prepared graphene oxide (GO)/Pebax-1657/PEG membranes for the CO_2/N_2 separation. The observed that blending PEG derivatives into the Pebax-1657 matrix led to a dramatic increase in the CO_2 permeability, while the CO_2/N_2 selectivity was almost constant. Dai et al. (2019b) used PEG functionalized carbon nanotubes (CNT-PEG) were as nano-additives to prepare hybrid membranes based on the Pebax-1657 and found that the permeability of CO_2 first increased and then decreased by enhancing the CNT-PEG content.

Besides, the performance of the Pebax membrane was improved by combining it with other polymers. Abdollahi et al. (2017) fabricated blend membranes based on the Pebax-1657 and polyvinyl acetate/dibutyl maleate copolymer (P(VAc-co-DBM)). They observed that the blend membranes are homogenous, and by addition of P(VAc-co-DBM) into the Pebax up to 30wt.%, the CO_2 permeability and CO_2/CH_4 selectivity significantly decreased and increased, respectively. Wu et al. (2021) investigated the effect of blending three different glycerides, including tripropionin (TPP), tributyrin (TBT), and tricapronin (TCP) triglycerides, with Pebax-2533 for gas separation. They revealed that Pebax had relatively high compatibility with these triglycerides, and the CO_2 permeability of all blend membranes was almost twice that of the pure Pebax membrane, but the CO_2/N_2 selectivity did not change, significantly.

This literature survey reveals that the addition of PEG into the Pebax matrix had different effects on the gas separation performance of the obtained blend membranes. Therefore, it needs to conduct further researches on the Pebax/PEG blend membranes. This work aims to investigate the effect of adding PEG with different molecular weights (PEG600, PEG1500, and PEG4000) and the influence of the additive content (10–40%wt.) on the gas separation performance of the Pebax-1657/PEG composite blend membranes. The fabricated blend composite membranes were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and water contact angle (WCA). The gas permeation efficiency of the fabricated membranes was evaluated by measuring the permeability of N_2, O_2, CH_4, and CO_2 gases as well as the CO_2/N_2, CO_2/CH_4, CH_4/N_2, and O_2/N_2 gas selectivities. The main innovative aspect of this study is the analysis and evaluation of the influence of the PEG molecular weight and content on the microstructure and gas permeation property of the PEG/Pebax-1657 blend membranes.

Experimental

Materials

The membrane materials consist of Pebax-1657 copolymer (60 %wt. PEO and 40%wt. PA) and polyethersulfone (PES, MW = 58000 g/mol) were purchased from Arkema (Paris, France) and BASF (Ludwigshafen, Germany) companies, respectively. Ethanol and N,N-dimethyl-formamide (DMF), which were purchased from Merck Co. Ltd. (Darmstadt, Germany), were used as solvents. The deionized (DI) water was used in experiments. PEG with molecular weights of 600, 1500, and 4000 g/mol was purchased from Merck Co. Ltd. The CO_2, CH_4, O_2, and N_2 gases with purities of 99.99% were applied for the gas permeation experiments.

Membrane preparation

The dual-layer composite membranes consist of a dense Pebax-1657/PEG layer as a selective top layer on a porous PES support layer were prepared by the phase separation technique.

The porous PES membrane as a substrate of the composite membrane was fabricated by the immersion precipitation phase separation method (Salehi Maleh and Raisi 2019a). A 16%wt. of clear homogeneous polymeric solution was prepared by dissolving 16 g of the PES granules in 84 g of DMF for 24 h at room temperature. The final solution vacuumed for 2 h until all of the air bubbles were removed from it. The PES solution was cast on a glass plate using a micrometer adjustable film applicator and immediately placed into a DI water bath at 30 °C, then the phase inversion process was completed, and the PES membrane was separated from the glass plate. Then, it remained in another DI water bath for 24 h. Finally, the PES membrane dried at room temperature for 24 h. The thickness of the obtained membrane was ~ 60 μm.

To prepare the selective top layer of the composite membranes, the Pebax granules were dried in an oven at 80 °C for 5 h. A specified amount of the dried granules was dissolved in a mixture of ethanol/water (70/30 wt/wt) as the solvent under reflux at 80 °C and stirring for 24 h to obtain a Pebax solution with a concentration of 5%wt. (Salehi Maleh and Raisi 2019a, 2020). After cooling the solution down to room temperature, different amounts of PEG additives were added to the Pebax solution and stirred for 3 h. To fabricate a double-layer membrane, the PES support layer was taped to a glass plate, and then a layer of bubble-free Pebax/PEG solution was cast on the PES support layer using a casing-knife. The obtained films were dried at 30 °C for 24 h to obtain the dual-layer composite membranes. To control the thickness of the membrane selective layer, a specific amount of the polymer solution cast on the PES support membrane with the same surface area. The selective layer thickness was adjusted precisely by maintaining a gap between casting blade and support with two integrated micrometers that were attached at both the ends of the casting knife. The thickness in the dry state was determined with a micrometer and confirmed by the SEM analysis. The thickness of the selective layer of the prepared membranes was 20 ± 2 μm. The composition of the casting solution for the preparation of the selective membrane layer was presented in Table 1.

Membrane characterization

XRD analysis

The XRD analysis was employed to investigate the crystalline structure of the Pebax-1657/PEG blend membranes. This

Table 1 The composition of the selective layer casting solution

Membrane	Pebax-1657 (%wt)	PEG (%wt)*	Solvents (%wt)
Neat Pebax	5	0	95
Pebax/10%PEG	5	10	94.44
Pebax/20%PEG	5	20	93.74
Pebax/30%PEG	5	30	92.86
Pebax/40%PEG	5	40	91.66

*Based on polymer

analysis was performed by the Equinox XRD instrument (Equinox 3000, Intel, France) with the CuKa X-Ray source and wavelength of 1.5542 Å at 45 kV, 40 mA, room temperature, and scanning speed 0.03° (2θ)/min. The diffraction angle (2θ) was varied from 5° to 100° to identify crystal structure and intermolecular distances of the intersegment chains. The percentage of crystallinity (X_C) of the membranes was calculated using the following equation (Ghadimi et al. 2014):

$$X_C(\%) = \frac{A_C}{A_C + A_A} \times 100\% \tag{1}$$

where A_c and A_a are the area under crystalline peaks and amorphous halos, respectively.

SEM analysis

The surface and cross-section morphology of the fabricated membranes were evaluated by a SEM device (AIS2300C, Seron Technology's, South Korea, at a high voltage of 20 kV). The samples were fractured in liquid nitrogen to examine the cross-section of the membranes. Before SEM analysis, all pieces were coated with a skinny layer (~ 100 Å) of gold particles.

FTIR analysis

Fourier transforms infrared (FTIR) analysis was used to determine the chemical structure of Pebax-1657/PEG blend membranes. The FTIR tests were performed with a Nicolet Nexus 670 spectrometer (Nicolet Instrument Co., Madison, WI, USA). The scanning frequency range was 600 cm^{-1} to 4000 cm^{-1} at the ambient conditions and with a spectral resolution of 1 cm^{-1}. A mean of 20 scans from each sample (2 × 2 cm^2) was taken.

WCA analysis

The WCA test was utilized to show the hydrophilic and hydrophobic properties of the pure and blend membranes. The lower contact angle means higher hydrophilic properties and vice versa. To perform this test, the surface of the membrane was dried, and then a droplet of DI water was dropped onto the sample surface using a micro-syringe and immediately photographed by a high-resolution camera. The WCA of several points of each sample was measured, and the mean value was reported as the water contact angle.

Density measurement

Experimental values of the density of the polymeric membrane were measured by the buoyancy method at 20 °C. In this technique, the membrane density (ρ) was calculated, as follows (Car et al. 2008):

$$\rho = \frac{M_A}{M_A + M_L}\rho_L \tag{2}$$

where ρ_L is a known density with the auxiliary liquid, M_A and M_L are the membrane weight in air and auxiliary liquid, respectively. In this experiment, the membranes were prepared in 2 × 2 cm^2 samples and were dried in a vacuum oven at 30 °C for 24 h, before weight measurement. Also, iso-octane (ρ_L = 0.692 g/cm^3 at 20 °C) is used as the auxiliary liquid, because Pebax-1657 and PEGs are insoluble in iso-octane (Feng et al. 2013b).

Gas permeation experiments

The gas separation performance of the prepared Pebax-1657/PEG blend membranes was measured by a gas permeation system with constant volume and variable pressure mode. In these experiments, the permeation of pure N_2, O_2, CH_4, and CO_2 gases was carried out at pressures of 3, 5, and 7 bar at 25 °C. A pre-calibration cross-flow flat plate module with 12.5 cm^2 active surface area was used as a membrane module. The gas permeability was determined using the below equation (Salehi Maleh and Raisi 2019a):

$$\mathrm{P} = \frac{273.15 \times 10^{10}\mathrm{Vl}}{760\mathrm{AT}\left(\frac{76\mathrm{p}_0}{14.7}\right)}\left(\frac{\mathrm{dp}}{\mathrm{dt}}\right) \tag{3}$$

where P is the gas permeability (Barrer), A is the membrane area (cm^2), T is operating temperature (K), V is the downstream volume of the membrane, l is the membrane selective layer thickness (μm), P_0 is the feed pressure (psia) and dp/dt is the rate of increase in downstream pressure (mmHg/s). In addition, the ideal selectivity ($\alpha_{A/B}$) of the membranes was calculated by the ratio of the gas permeabilities, as follows (Salehi Maleh and Raisi 2019a):

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{4}$$

Results and discussion

Membrane characterization

XRD analysis

The XRD patterns of the pure Pebax-1657 and Pebax-1657/PEG blend membranes are illustrated in Fig. S1 (in Supplementary file). The observed narrow and wide diffractions attributed to the crystalline and amorphous regions, respectively. Pebax-1657 is a semi-crystalline polymer with a diffraction peak at 2θ of ~ 20.7° (Noroozi and Bakhtiari 2019). As can be seen in Fig. S1a, the addition of PEG600 into the membranes leads to a decrease in the intensity of the crystalline peaks, and the main peak of the XRD pattern becomes weaker and broader (Azizi et al. 2017). The XRD pattern of Pebax-1657/PEG600 membranes confirmed the amorphous nature of these blend membranes. According to the XRD patterns of the blend membranes containing PEG1500 and PEG4000 (Fig. S1b and S1c), the intensity of the crystalline peak increases with an enhancement in the PEG content. The appearance of two sharp peaks at higher PEG concentration is due to the main peaks of these two PEGs. The XRD pattern of PEG4000 is presented in Fig. S2 (in Supplementary file). The combination of PEG with higher molecular weight, such as PEG1500 and PEG4000, within Pebax leads to increasing the crystallinity and reducing inter-chain spacing (Mahdavi et al. 2017).

Moreover, the crystallinity percentage of various fabricated membranes, which is calculated based on Eq. (1), is depicted in Fig. 1. As demonstrated in this figure, the crystallinity of the membranes increases by enhancing the molecular weight of the PEG. For the Pebax-1657/PEG600 blend membranes, the crystallinity percentage decreased by an enhancement in the additive concentration, whereas the crystallinity percentage increased with PEG loading for the blend membranes containing PEG1500 and PEG4000. In the neat Pebax-1657, the amide blocks can form hydrogen bonds, and it is due to the elimination of intermolecular hydrogen bonding and reduction in the cohesive energy of the membranes (Azizi et al. 2017). However, in the blend membranes, hydrogen bonding cannot be formed due to the positive interaction between the Pebax-1657 and PEG600 and resulted in higher polymer chain spacing. Besides, the merging of PEG600 as a low molecular additive leads to decreasing crystalline segments and increasing amorphous segments in the blend membranes. It can be attributed to the increasing chain mobility, decreasing intermolecular hydrogen bonding, and declining cohesive energy in the crystalline segments (Azizi et al. 2016). In contrast, PEG1500 and PEG4000, as a higher molecular PEG with low chain mobility, augments the hydrogen bonding between the polymer chains and thus cohesive energy between the crystalline segments. This phenomenon causes fractional free volume decrement in the membranes, and consequently increases the membrane crystallinity (Mahdavi et al. 2017; Xie et al. 2019).

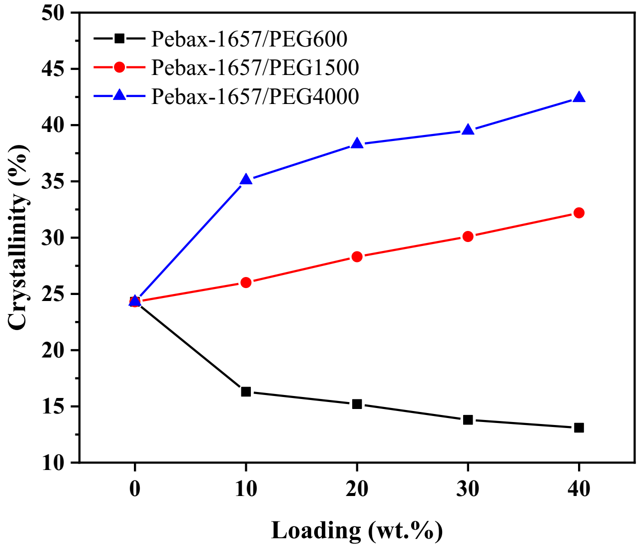


Fig. 1 The effect of incorporation of PEGs on the crystallinity of prepared membranes

SEM analysis

The SEM images of the surface and cross-section of the pure Pebax-1657 and blend membranes containing 30%wt. of PEG with different molecular weights are shown in Fig. 2. As observed in Fig. 2a, there is no defect in the top-surface of the pure membrane, and its structure is homogeneous, transparent, and uniform. Besides, the cross-sectional images of the neat membrane show a dense, smooth, and uniform layer with a thickness of 10 ± 2 μm on the porous PES substrate layer.

As illustrated in Fig. 2b, the addition of PEG600 into the Pebax-1657 is demonstrated a relatively smooth surface. Low molecular weight PEGs due to high chain mobility are acted as a plasticizer and increased the mobility of the Pebax chain, resulting in a relatively smooth surface in the blend films (Thanakkasaranee et al. 2018). In contrast, the morphological changes are more detectable for the blend membranes containing high molecular weight PEGs in Fig. 2c, 2d. In other words, the merging of PEG1500 and PEG4000 into the Pebax-1657 are indicated these PEGs with low chain mobility disrupt the Pebax-1657 chain and produce a relatively rough surface due to the presence of crystals of PEO phase (Feng et al. 2019; Thanakkasaranee et al. 2018). The combination of PEG1500 and PEG4000 into the Pebax reduces its uniform structural body due to immiscibility and phase separation. Expressly, merging of these with higher molecular weight showed that the miscibility of the two polymers could cause irregular and convoluted structures in the blended membranes, as indicated in Fig. 2b (Feng et al. 2013b; Mahdavi et al. 2017; Azizi et al. 2017). It is also apparent in the SEM images that by adding PEGs into the Pebax and increasing its loading amount, the surface roughness significantly increases.

These observations are in good agreement with the results of the XRD analysis. As shown in Fig. 1, the addition of PEG with the high molecular weight increases the crystallinity of the membranes. Therefore, the addition of PEG1500 and PEG4000 caused a heterogeneous mixture of two polymers and a hard fluidity in the Pebax-1657 matrix, resulting in a rough and complex blend membrane structure as revealed in

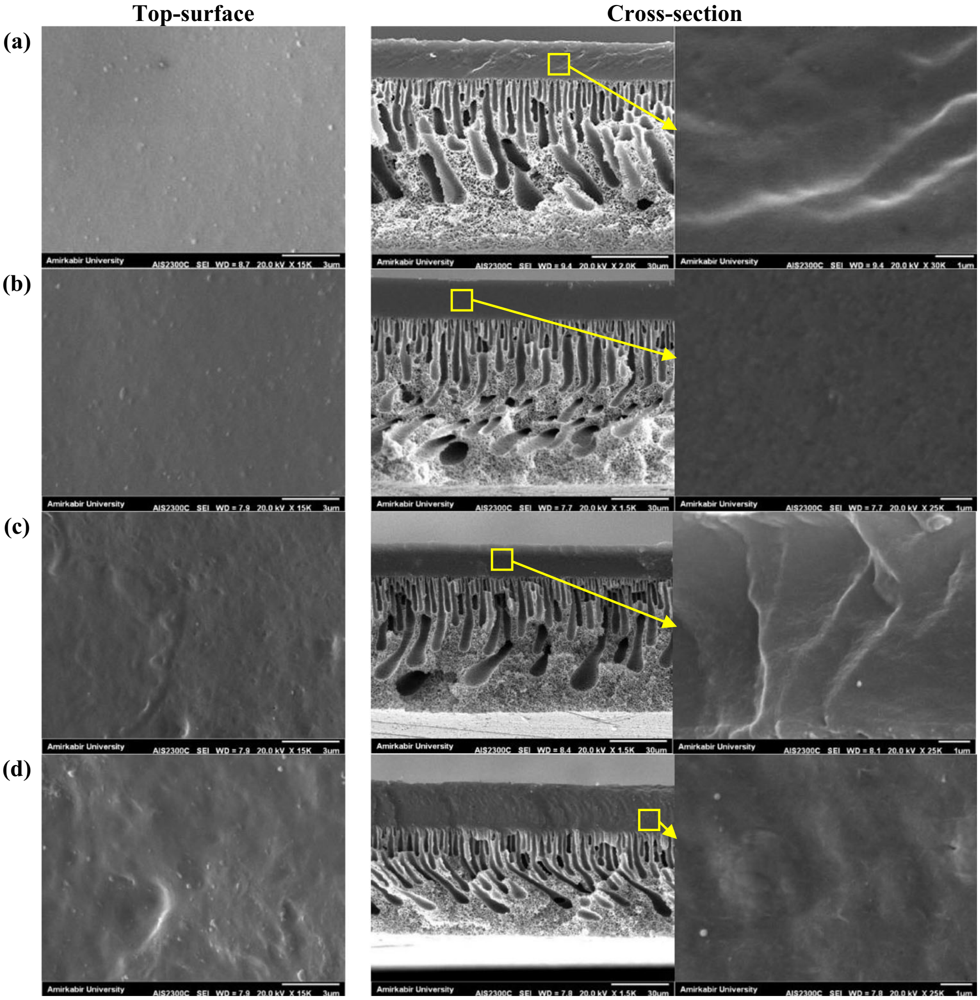


Fig. 2 The SEM images of top surface and cross-section of the pure Pebax-1657 (**a**) and blend membranes containing 30%wt. of PEG600 (**b**), PEG1500 (**c**), and PEG4000 (**d**)

Fig. 2b, c (Azizi et al. 2017). The more SEM images of the Pebax-1657/PEG4000 blend membranes are presented in Figs. S3 and S4 (in Supplementary file).

FTIR analysis

The FTIR spectra of the neat Pebax and Pebax/PEG blend membranes are depicted in Fig. 3. As can be seen, the specific groups of Pebax-1657 give characteristic peaks located at 1097 cm^{-1}, 1636 cm^{-1}, 1733 cm^{-1}, 3296 cm^{-1}, and 3500 cm^{-1} are related to the C–O–C groups in the soft PEO segment, –C=O bonds in H–N–C=O, –C=O bonds in saturated esters, hydrogen-bonded N-H, and –OH groups, respectively (Dong et al. 2016). Comparing the FTIR spectrum of the blend membranes and neat Pebax demonstrated that most of the functional groups' characteristic peaks in the pure membrane also observed in the FTIR spectra of the blend membranes. The absorption peak at 1097 cm^{-1} which is assigned to the ether group is intensified with the merging of the PEGs. It can be due to the introduction of ethylene-oxide units in PEGs (Azizi et al. 2018). Also, the combination of PEG600 intensifies the broad hydroxyl peak. At the same time, the addition of PEG1500 and PEG4000 does not significantly

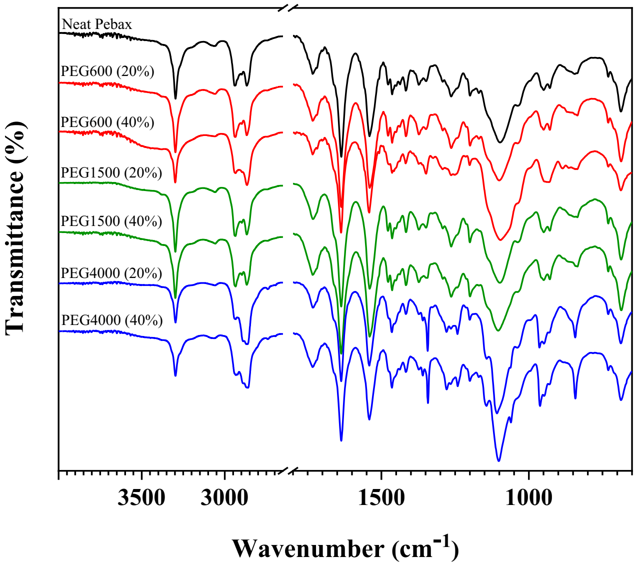


Fig. 3 The FTIR spectra of neat Pebax and Pebax/PEG blend membranes

change the broad hydroxyl peak, which indicates that in a weight equal amount of additives, PEG with a higher molecular weight offers fewer hydroxyl groups (Thanakkasaranee et al. 2018). Moreover, a comparison of the spectra of the Pebax/PEG blend membranes and that of the neat Pebax reveals that the –N–H–and the H–N–C=O peaks in the FTIR spectra of the blend membranes containing PEG1500 and PEG4000 are shifted to higher wavenumbers (shorter frequency). These changes prove hydrogen bonding between the carbonyl group of polymer and terminal –OH group of PEGs (Hamrahi and Kargari 2017).

WCA analysis

The water contact angle and water sorption behaviors of polymer films mostly affected by the chemical and/or morphological structure of the membrane surface (Seo et al. 2009; Han et al. 1998). Figure 4 shows the water contact angle of the fabricated membranes with different molecular weights of PEG. It demonstrates that the water contact angle significantly reduced by incorporating of PEGs to Pebax, indicating that the hydrophilicity of the blend membranes enhanced. This change can be due to the increase of hydroxyl and ether polar groups in the chemical structure of membranes (Kimura 2008). But as it turns out, the hydrophilicity of membranes containing PEG600 is higher than the membranes containing PEG1500 and PEG4000, which can have two main reasons. First, at an equal loading amount of PEGs, PEG600 provides more hydroxyl hydrophilic groups than the other ones (Thanakkasaranee et al. 2018). In other words, higher molecular weight PEGs revealed lower hydrophilicity because of a lower hydroxyl group's population as confirmed by the FTIR analysis. Consequently, the hydrophilicity of blend films decreased with increasing molecular weight of PEGs. Second, the trend of hydrophilicity changes depends on the morphological structure, which relates to the membrane's crystallinity (Thanakkasaranee et al. 2018). Increased crystallinity can reduce the distance between the polymer chains and, as a result, increase the water contact angle or reduce the water wettability. Therefore, by increasing the amount of PEG from 10%wt. up to 40%wt., the hydrophilicity of Pebax/PEG600 membranes increased due to the rise of hydrophilic groups and decrease of crystallinity. In contrast, the hydrophilicity of membranes containing PEG1500 and PEG4000 decreases, which can be due to the superiority of the effect of increasing crystallinity.

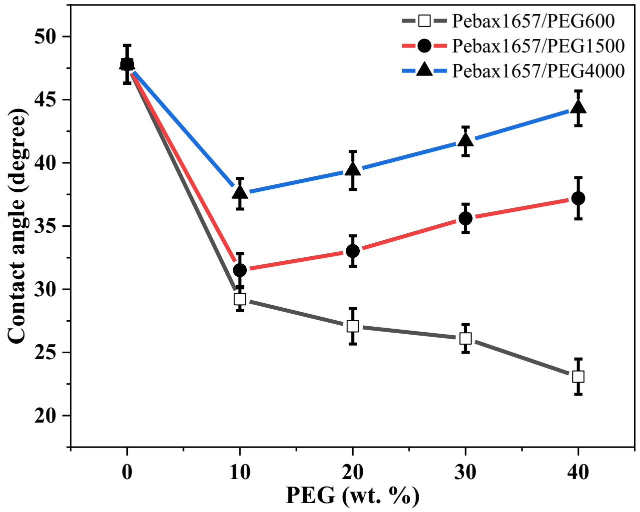


Fig. 4 The water contact angle of the blend membranes containing PEG with different molecular weights

Density and FFV

The density of the membranes was determined using the buoyancy method and the results are illustrated in Fig. 5. As can be observed, the density of Pebax/PEG600 decreases incessantly with addition of PEG600 content, which implies that the neat Pebax is denser rather than the Pebax/PEG600 blend membranes (Car et al. 2008; Rabiee et al. 2015). In opposite, blend membrane comprising PEG1500 and PEG4000 revealed denser structure than neat membrane, as PEG content increased (Feng et al. 2013b).

It is identified that fraction free volume (FFV) of polymeric membranes can be associated with their densities. Thus, the density of blend membrane can also be predicted using the additive model, as follows (Car et al. 2008):

$$\rho = \Phi_1\rho_1 + (1-\Phi_1)\rho_2 \tag{5}$$

where Φ_1 is the volume fraction of PEG, ρ_1 is the density of PEG, and ρ_2 is the density of Pebax-1657. The density of PEG600, PEG1500, PEG4000, and Pebax-1657 are 1.12, 1.2, 1.2, and 1.14 g/cm^3, respectively [Li et al. 2008; Kuttich et al. 2017; Kargari and Rezaeinia 2020; Salehi Maleh and Raisi 2019a]. Generally, the differences between results of experimental measurements and obtained data by additive model could be interpreted changes in FFV (Rabiee et al. 2015; Feng et al. 2013b). The estimated density from this model only depends of the composition of binary Pebax/PEG system, while not affected by structural changes (Car et al. 2008). As it is exhibited in Fig. 5a, this difference becomes larger at higher PEG600 loading. Hence, FFV for the Pebax/PEG600 membranes is more than the neat Pebax, and since the gas diffusion mostly happens via FFV, it is the reason for higher gas diffusivity and, as a result, higher gas permeability for the Pebax/PEG600 membranes (Rabiee et al. 2015). Figure 5b, c displays opposite trends, as the experimental density of the Pebax-1657/PEG1500 and Pebax-1657/PEG4000 blend membranes are higher than the calculated results using the additive model. This phenomenon confirmed that these blend membranes become relatively dense or, in

Fig. 5 The effect of volume fraction of PEG600 (**a**), PEG1500 (**b**), and PEG4000 (**c**) on the density of the blend membranes at 20 °C

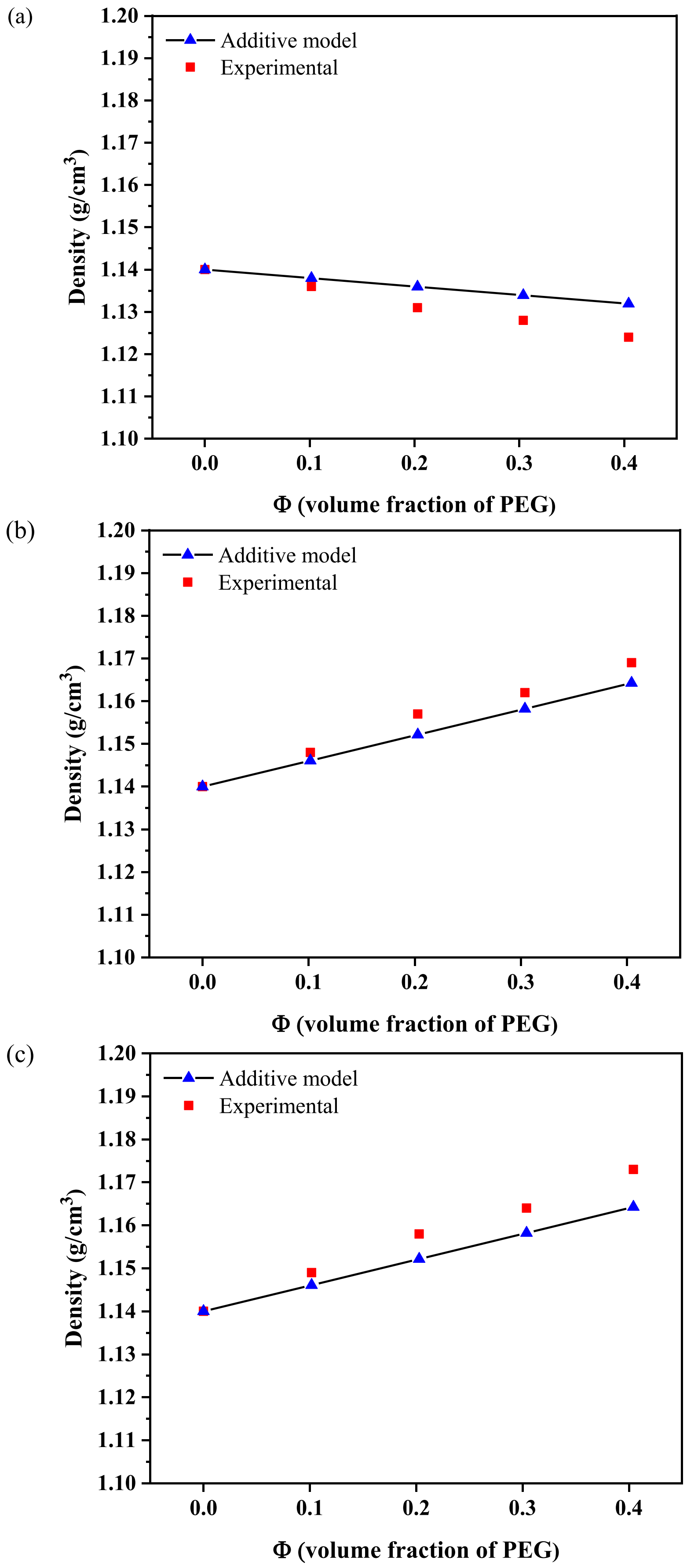


Fig. 6 The effect of loading rate of PEG600 (**a**), PEG1500 (**b**), and PEG4000 (**c**) on the gas permeability at feed pressure of 5 bar

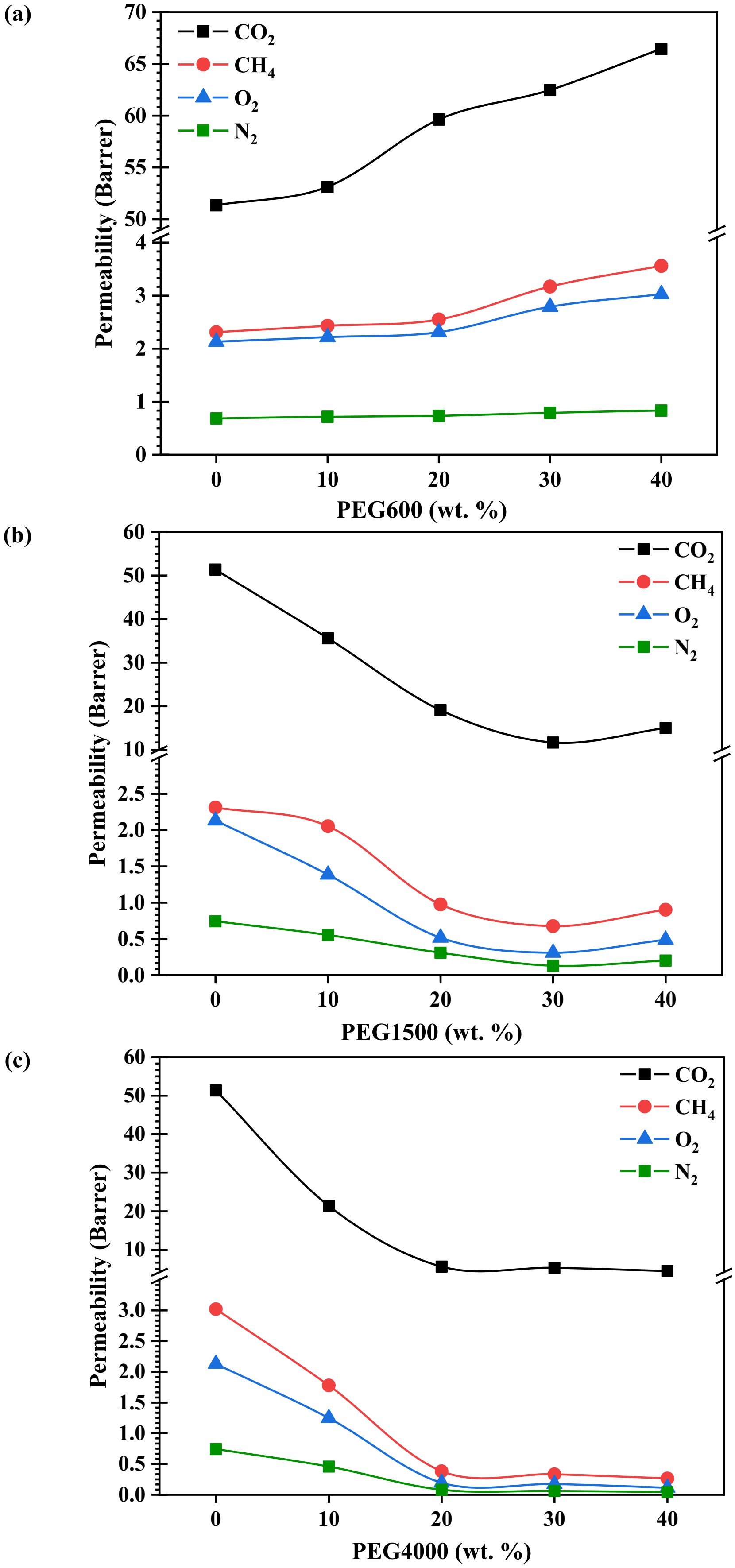
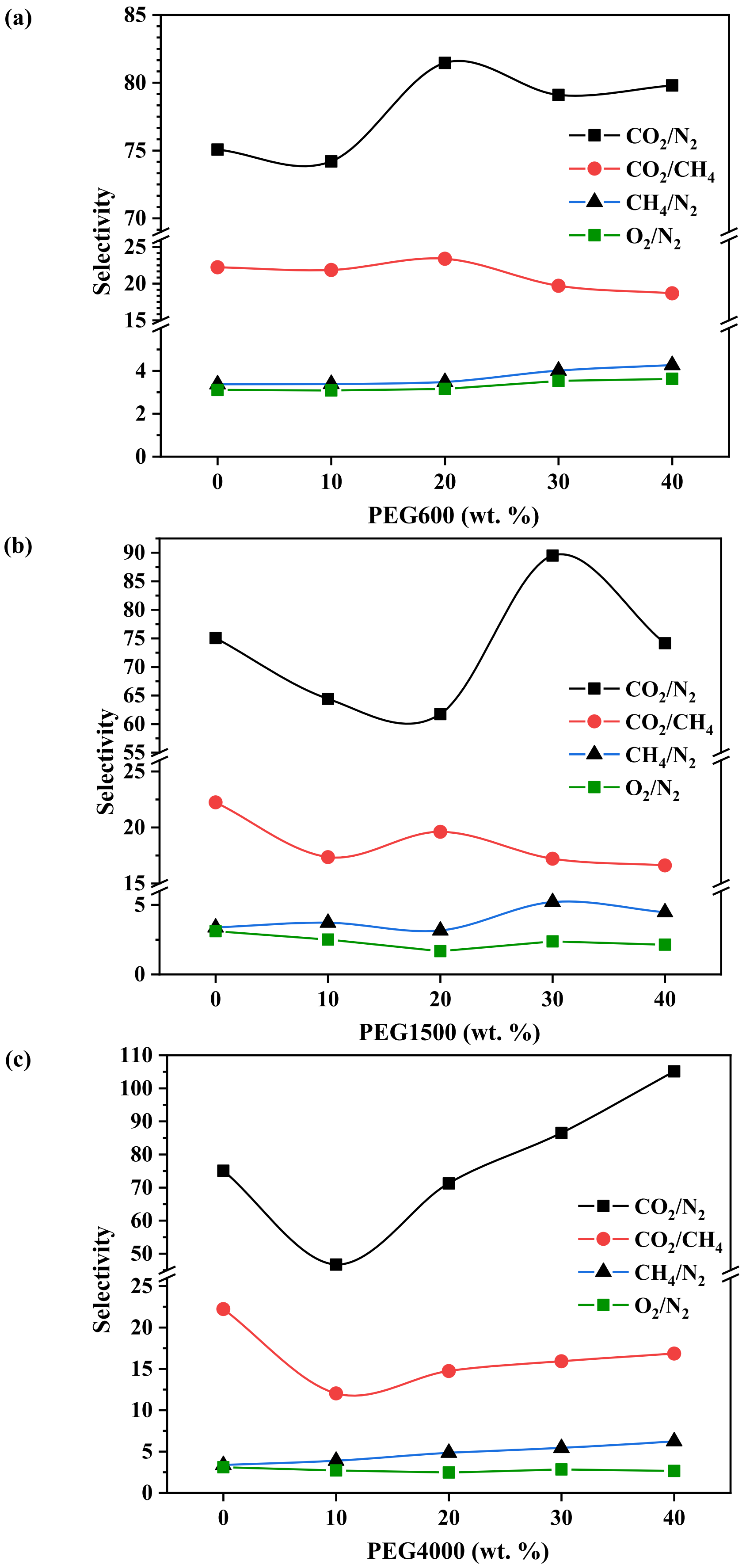


Fig. 7 The effect of loading rate of PEG600 (**a**), PEG1500 (**b**), and PEG4000 (**c**) on the gas selectivity at feed pressure of 5 bar



other words, implies that the FFV of these membranes decrease (Feng et al. 2013b). Accordingly, reducing FFV can reduce the permeability of gases, as discussed in details in the next section.

Gas permeation of membranes

The gas transport through a dense polymeric membrane follows the solution-diffusion mechanism. Based on this theory, the gas molecule will be firstly adsorbed at the feed/membrane interface, diffuses across the membrane, and then desorbs at the permeate-side (Prasetya et al. 2019; Wang et al. 2017). In this model, the permeability is affected by two parameters: solution and diffusion. The gas diffusivity and gas solubility depend on the gas and membrane properties (Salehi Maleh and Raisi 2019a). The gas solubility can be affected by gas condensability (gas critical temperature (T_c)) and gas/polymer-chain interaction. In addition, the gas diffusivity can be affected by the size of the gas molecule (gas kinetic diameter (D_K)), fractional free volume of the membrane, gas/polymer-chain interaction, and polymer-chain flexibility (Salehi Maleh and Raisi 2019b). CO_2 (T_c = 31.05 °C and D_K = 0.33 nm) has a higher critical temperature and lower kinetic diameter, so it reveals higher solubility and diffusivity than CH_4 (T_c = − 82.45 °C and D_K = 0.38 nm), O_2 (T_c = − 118.55 °C and D_K = 0.346 nm), and N_2 (T_c = − 147.05 °C and D_K = 0.364 nm) (Salehi Maleh and Raisi 2019a). The higher CO_2 solubility and diffusivity in the Pebax-1657 membrane results in higher permeability of CO_2 through the prepared membranes (Mousavi et al. 2020; Sutrisna et al. 2017). Nevertheless, the permeability coefficient of gases through the neat Pebax-1657 membrane obeys the following order: $CO_2 > CH_4 > O_2 > N_2$. The lower permeability of O_2 and N_2 can be attributed to the lower solubility and diffusivity of these gases compared to the CO_2 and CH_4 gases. Oxygen and nitrogen are non-polar gases, which have low solubility (Lin and Freeman 2004). The permeability behaviors of O_2 and N_2 gases, which do not have significant condensability and solubility, are often based on their diffusivity differences. Moreover, N_2 and O_2 have larger kinetic diameter than CO_2 and CH_4, which leads to lower gas diffusivity. Thus, the O_2 and N_2 permeabilties are lower than CO_2 and CH_4.

Effects of PEGs loading

The effect of loading rates of PEGs with different molecular weights on the gas permeability is exhibited in Figs. 6 and 7. According to Fig. 6a, by increasing the PEG600 content of the blend membranes, the permeability of all gases increases. At higher PEG600 loading, there is more chain mobility in the polymer matrix. Because the low molecular weight PEGs acts as a plasticizer between the Pebax chains, resulting in polymer-polymer interaction, and it generates the additional intermolecular space for small Brownian motion (Azizi et al.

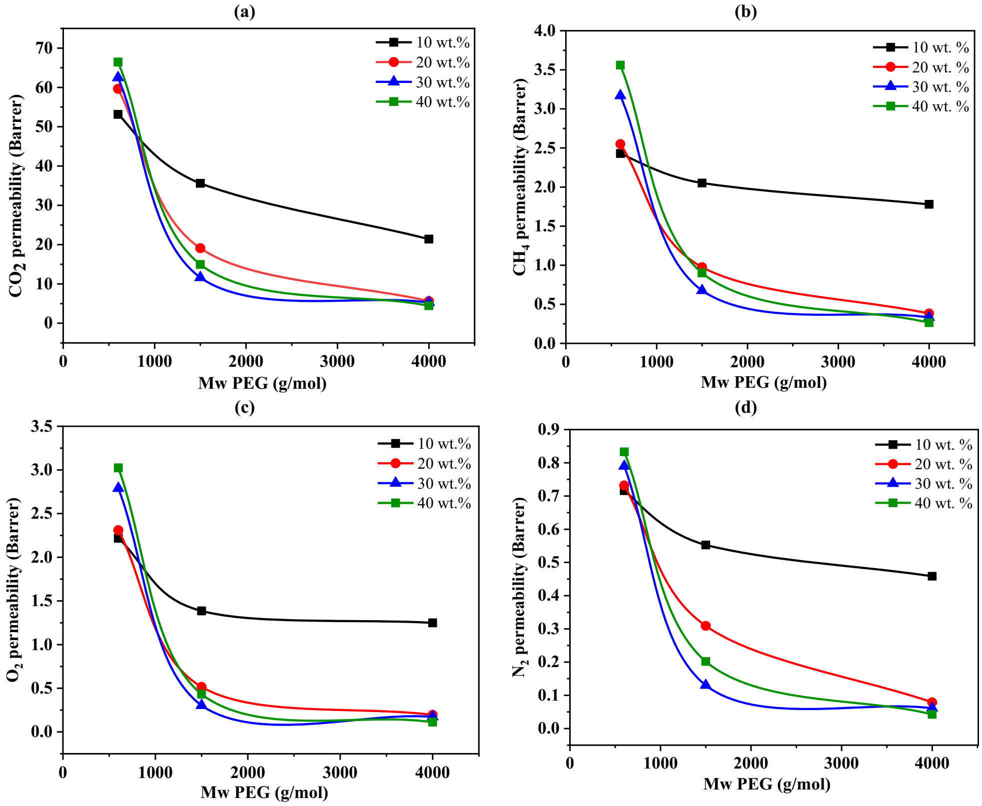


Fig. 8 The effect of PEG molecular weight on the gas permeability of the blend membranes at feed pressure of 5 bar

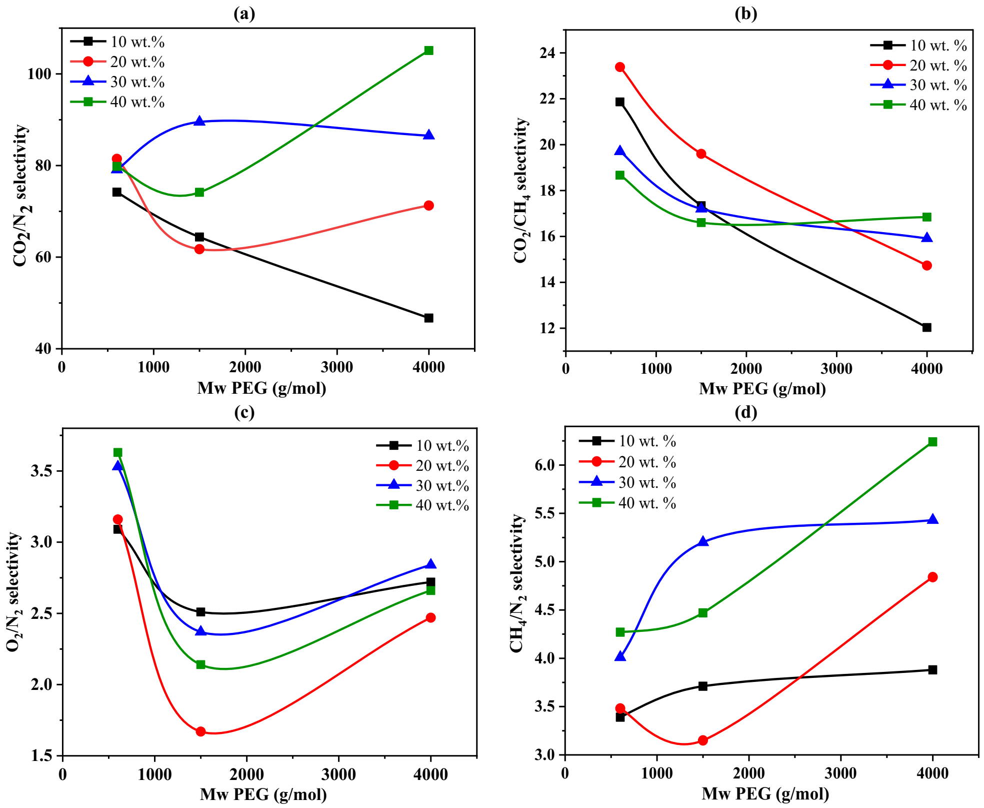


Fig. 9 The effect of PEG molecular weight on the gas selectivity of the blend membranes at feed pressure of 5 bar: **a** CO_2/N_2, **b** CO_2/CH_4, **c** CH_4/N_2, and **d** O_2/N_2

2016; Yave et al. 2009). Also, it can be seen that the CO_2 permeability is remarkably higher than the permeability of other gases. The CO_2 gas is more soluble in the prepared blend membranes than other gases due to its interaction with the ethylene oxide groups of the Pebax and PEG molecules. As the ethylene oxide content increases in the blend membranes by enhancing the PEG content, the CO_2 gas solubility goes to a higher level (Azizi et al. 2016). Moreover, due to the increase in the inter-chain space and subsequent increase in the membrane fractional free volume, the diffusivity of all gases enhances (Forsyth et al. 1995; Azizi et al. 2016; Yave et al. 2009). Also, CO_2 gas has a higher diffusivity in the membrane than O_2, N_2, and CH_4 gases, due to its smaller kinetic diameter (Sutrisna et al. 2017). Therefore, by blending PEG600 into the Pebax-1657 matrix, the sum of these effects causes the CO_2 gas permeability to increase more than other gases.

In contrast, as displayed in Fig. 6b, c, the permeability of all gases decreases by increasing the loading rates of PEG1500 and PEG4000. At higher content of these additives, the mobility of the Pebax chains reduces. Because the high molecular weight PEGs prevent the polymer-polymer interaction and play as a stiffer between the Pebax chains and diminish the extra molecular space for small Brownian motion (Azizi et al. 2017; Yave et al. 2009). On the other hand, Fig. 1 revealed that the crystallinity of the blend membrane increases by an enhancement in the loading of PEG1500 and PEG4000. The PEO chains of Pebax-1657/PEG1500 blend membranes are in the crystalline state at ambient temperature, which are regarded as impermeable domains for penetrant gases. Besides, the crystals will affect the chain mobility and sorption sites of blend membranes, which induce lower diffusivity and solubility (Lin et al. 2006; Feng et al. 2013b). Thus, at higher loading of PEG1500 and PEG4000, the crystallization of the Pebax polymer segments reduces the chain mobility, and consequently, the amorphous region for gas diffusion as well as sorption sited decreases, leading to lower gas permeability.

The effect of loading rate of PEG600, PEG1500, and PEG4000 on the selectivity of CO_2/N_2, O_2/N_2, CH_4/N_2, and CO_2/CH_4 pair gases is indicated in Fig. 7. According to this figure, the selectivity of O_2/N_2 and CH_4/N_2 slightly increased by enhancing the PEGs loading up to 40%wt., while the CO_2/CH_4 and CO_2/N_2 selectivities trend have a maximum at PEG600 content of 20 %wt. In the case of dense gas separation membranes, the dominant transport mechanism is the solution-diffusion, and due to the polar nature of the fabricated membranes, the component transfer through the membrane depends on the type of gas. Due to the high solubility of CO_2 compared to the nonpolar gas like N_2, the CO_2 permeability is higher than N_2 permeability. This will result in increasing the CO_2/N_2 selectivity. On the other hand, an improvement in the O_2/N_2 selectivity can be attributed to higher sorption and diffusion of O_2 compared to N_2, which increases

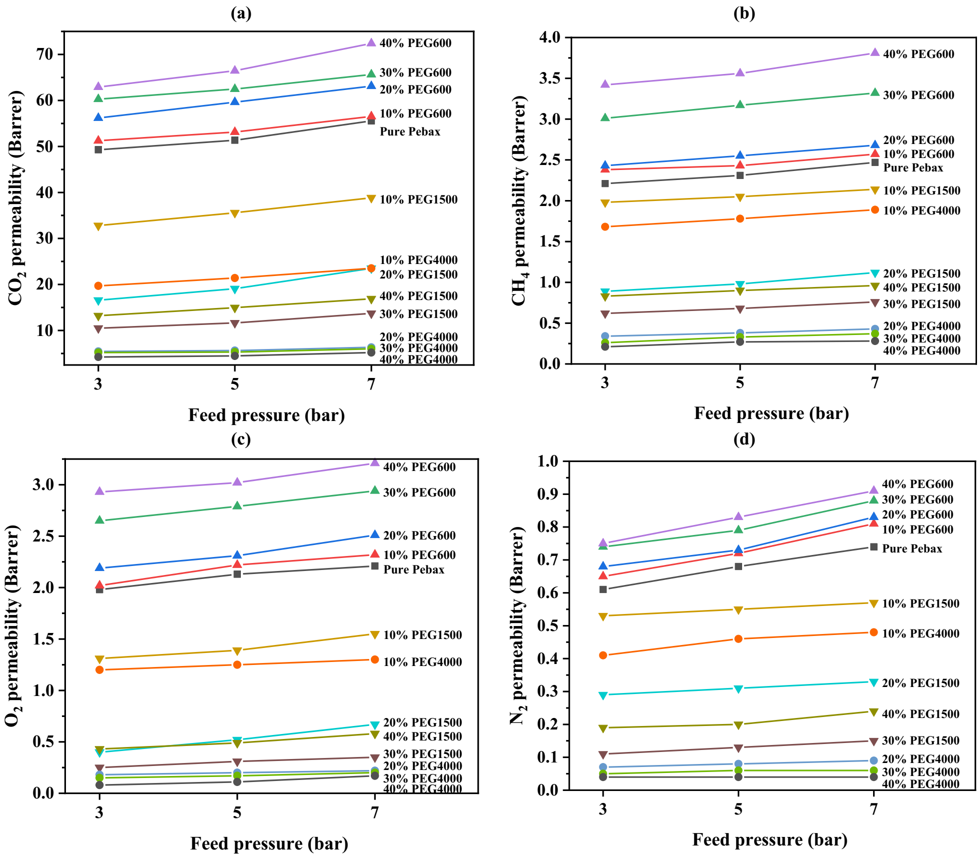


Fig. 10 The effect of feed pressure on the gas permeability of the blend membranes

the O_2 permeability. Also, the CH_4/N_2 selectivity increased via an enhancement in the CH_4 sorption. As the loading rate of PEG1500 and PEG4000 increases up to 40 %wt., the selectivity of CH_4/N_2 increases relative to the pure Pebax, while the selectivity of CO_2/N_2, O_2/N_2, and CO_2/CH_4 decrease compared to the pure membrane. These behaviors for the gas selectivities can be ascribed to the sorption-diffusion behavior of gases or, indeed, the permeability trends that are stated above. As illustrated, the introduction of the polar ether groups of PEG600 augments the affinity of CO_2 molecules for the polymeric chains, improving the solubility-selectivity of the membranes. Nevertheless, it also enhances the chain spacing in the blend membranes, which reduces the molecular sieving properties as well as its diffusivity-selectivity of the membranes. Consequently, the overall selectivity, which is the product of the diffusivity-selectivity and solubility-selectivity, improves slightly. However, the incorporation of the polar ether groups of PEG1500 and PEG4000 enriches the CO_2-philicity of the blend membranes, enhancing the solubility-selectivity of membranes. Besides, these diminish the chain spacing, which boosts the molecular sieving ability in addition to their diffusivity-selectivity of the membranes. Accordingly, the overall selectivity upsurges noticeably in gas separation, especially for the CO_2/N_2 case (Wang et al. 2014; Azizi et al. 2017; Car et al. 2008). Furthermore, the wave-like trends in CO_2/N_2 and CO_2/CH_4 selectivities of blend membranes are consistent with the results presented in the literature (Hu et al. 2013; Raouf et al. 2020). These behaviors usually occur at high loading due to changes in the diffusion and solubility selectivity behavior of the CO_2 gas molecules.

Effects of PEG molecular weight

The effect of the molecular weight of PEG on the gas permeability through the blend membranes is shown in Figs. 8 and 9. As can be seen, the permeability of all gases through blend membranes decreases by increasing the PEG molecular weight. According to Fig. 8, the membranes containing PEG600 have the highest permeability. After the addition of PEG600 into the Pebax matrix, it shows good miscibility with pure Pebax and reduces membrane crystallinity due to its high chain mobility. Thus, the PEG600 increases the amorphous regions for gas permeation (Azizi et al. 2017; Yave et al. 2009), and the free volume in the blend membranes enhances, as confirmed by the density measurement in Fig. 5a. As a result, they cause increased gas permeability.

On the other hand, the PEGs with molecular weight higher than 1000 have different behaviors (Azizi et al. 2017). The Pebax1657/PEG1500 membranes revealed lower gas permeability than the membranes containing PEF600. PEG1500 is a medium molecular weight of PEGs. It has a crystalline structure with low chain mobility. The merging of PEG1500 leads

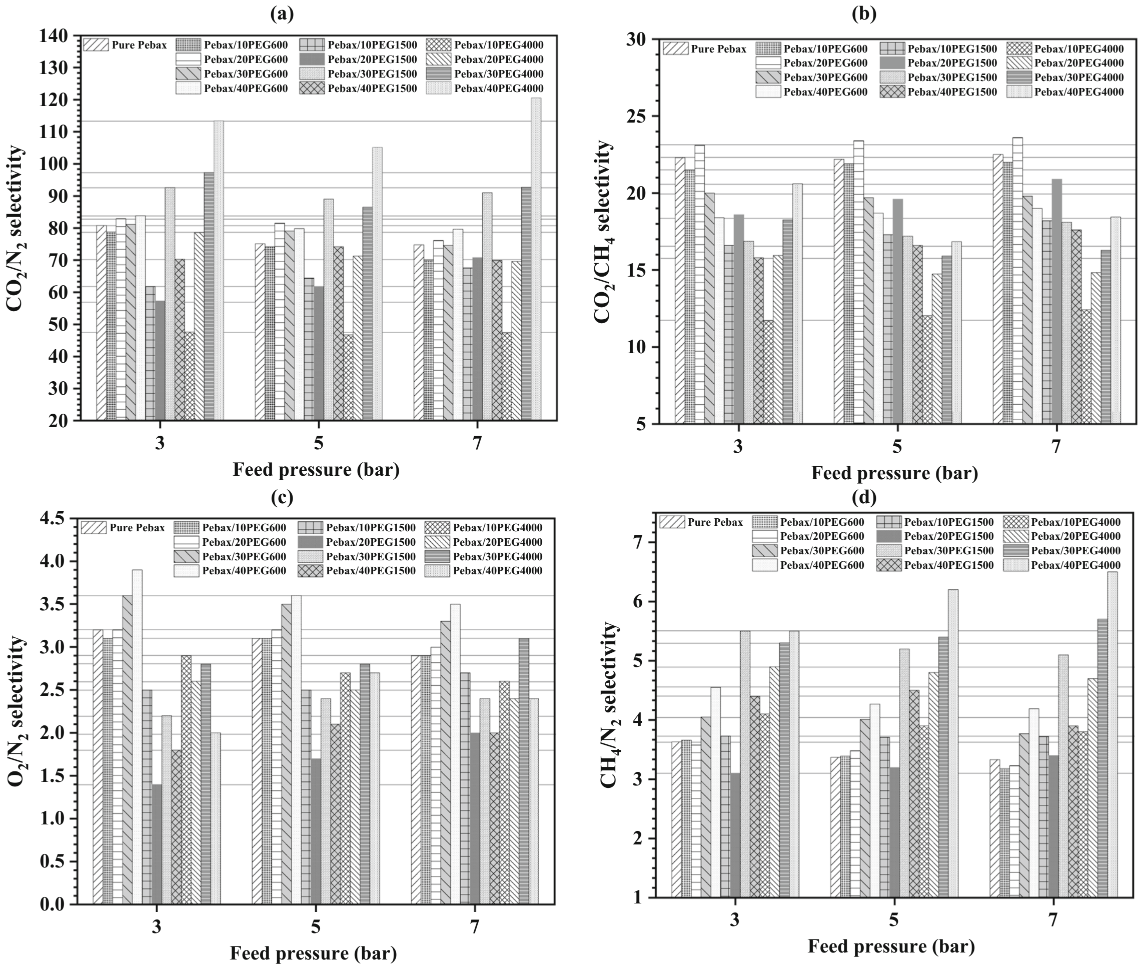


Fig. 11 The effect of feed pressure on the gas selectivity of the blend membranes

to crystallization of both hard and soft segments of Pebax. This means that it declines the quantity of amorphous EO segments and the free volume of the blend membrane (Azizi et al. 2017). Therefore, the gas permeation through the Pebax/PEG1500 blend membranes decreased. This observation is in good agreement with the density result in Fig. 5b.

Besides, the lowest gas permeability was obtained for the Pebax1657/PEG4000 membranes. PEG4000 has a higher crystalline structure and lower chain motion than PEG600 and PEG1500. Similar to PEG1500, the blending of this reduces the amorphous regions and increases the crystallinity of both segments of the Pebax-1657, thus reducing the free volume of the blend membrane that in accordance with obtained result from density analysis. In comparison, these effects are more severe for blend membranes containing PEG4000 than for membranes containing PEG1500. Therefore, Pebax1657/PEG4000 has the lowest permeability.

The effect of PEG molecular weight on the gas selectivity of the blend membranes is presented in Fig. 9. As shown in Fig. 9a, the CO_2/N_2 selectivity of the blend membranes containing 10%wt. PEG decreased by increasing the PEG molecular weight. As previously mentioned, by the addition of the high molecular weight PEGs into the Pebax-1657 matrix, the permeability of gases decreases, so the decreasing trend of CO_2/N_2 selectivity can be related to the ratio of the gas permeabilities, which reduced by enhancing the PEG molecular weight. At 20%wt. loading, by enhancing the PEG molecular weight from 600 to 4000, the CO_2/N_2 selectivity decreased and then increased. By increasing molecular weight due to the polymer chain hardening and reduction of the membrane free volume, the CO_2 permeability decreases. Also, the diffusion rate of gases with a larger molecular size, such as N_2, decreases. As a result, the permeability of CO_2 and N_2 gases decreases, so the ideal selectivity, which depends on the permeability of the gases, reduces. At the PEG content of 40%wt., the behavior of selectivity changes with molecular weight is similar to the loading of 20%wt.

Moreover, Fig. 9b shows the CO_2/CH_4 decreased at all PEG contents with an increase in the PEG molecular weight. According to Fig. 9c, the O_2/N_2 selectivity trend has a minimum at PEG molecular weight of 1500 g/mol. As inferred from Fig. 5, the fractional free volume of the membranes decreases by varying PEG molecular weight from 600 to 1500 g/mol that leads to a reduction in the sorption capacity and the gas diffusion rate of the membranes. Therefore, it reduces the permeability of both gases and subsequently reduces the ideal selectivity of O_2/N_2. On the other hand, by increasing the PEG molecular weight from 1500 to 4000 g/mol, due to better interaction of O_2 with the polymer, the O_2 gas shows higher solubility and diffusion compared to N_2, and consequently, the O_2/N_2 selectivity increases. Based on Fig. 9d, the CH_4/N_2 selectivity improved by increasing the PEG molecular weight. The increase in the selectivity of CH_4/N_2 can be related to the higher solubility of CH_4 than N_2.

In addition, these observations are in accordance with other works. Azizi et al. (2017) fabricated blend membranes by combining PEG400 and PEG1000 into the three grades of Pebax with different PE contents (namely Pebax-1074, Pebax-1657, and Pebax-2533). The results of their work exhibit that when a low molecular weight PEG (such as PEG 400) is merged into a membrane, its gas permeability enhances considerably; however, its CO_2/CH_4 ideal-selectivity slightly improves. Whereas the merging PEG1000 into Pebax matrix reduces gas permeability noticeably, but also enhances the CO_2/CH_4 ideal-selectivity. Feng et al. (2013b) combined PEG1500 with Pebax-1074 for preparation of blend membranes. They found that the permeability of CO_2, H_2, N_2, and CH_4 gases is reduced with the introduction of PEG1500 in the primary polymer, especially for CO_2. By increasing the loading amount up to 30%wt. PEG1500, the trend of gas permeability decreasing continues, and then in the loading amount of from 30 to 50%wt. PEG1500, the trend of changes is almost constant or slightly increased. The addition of crystalline PEG1500 can decline gas diffusivity and solubility, resulting in an evident decline in the CO_2 permeability. Therefore, the CO_2/H_2, CO_2/N_2, and CO_2/CH_4 selectivities for Pebax-1074/PEG1500 blend membranes (10%, 20%, and 30%) are lower than those of neat Pebax1074 membrane. However, for Pebax1074/PEG1500 (50%) blend membrane, the selectivities of CO_2/light gases enhance.

Effect of feed pressure

The effect of feed pressure on the gas separation performance of various prepared blend membranes was investigated in the pressure range of 3 to 7 bar, and the results are illustrated in Figs. 10 and 11. As given in Fig. 10, the permeability of all gases increased by increasing the feed pressure. In general, the influence of pressure on gas permeability through dense membranes can be related to (i) The concentration of gases in the membranes increases at higher pressures. (ii) More hydrostatic pressure affects the rubber components of polymers and compacts the membrane. (iii) The pressure is the driving force for the gas transfer through the membrane.

As the feed pressure increases, the free volume inside the polymer matrix decreases, which reduces the diffusion of gases. Pure Pebax membranes are semi-crystalline with approximately 25% and 15% crystallinity in their hard and soft parts, respectively, according to the DSC results reported by Salehi Maleh and Raisi (2019b). Therefore, the increase in pressure cannot easily compress the Pebax-1657, similar to other rubbery membranes. Consequently, increasing pressure becomes

Table 2 The gas separation performances of various Pebax/PEG blend membranes

Membrane	Additive	P_{CO_2} (Barrer)	ε_P	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$	T (°C)/P (bar)	Ref.
Pebax-1657	PEG600 (40%wt.)	72.39	1.30	79.55	19	25/7	In this work
Pebax-1657	PEG1500 (30%wt.)	13.72	0.25	91.90	18.10	25/7	
Pebax-1657	PEG4000 (40%wt.)	5.20	0.10	120.48	18.44	25/7	
Pebax-1657	PEG200 (%wt.)	151	2.07	47	15.5	30/0.6	Car et al. 2008
Pebax-1657	PEG200 (50%wt.)	172	1.76	50.5	15.7	35/4	Reijerkerk et al. 2010
Pebax-1074	PEG1500 (50%wt.)	36.4	0.22	51.9	26	35/5	Feng et al. 2013b
Pebax-1074	PEG1500 (30%wt.)	17.14	0.11	34.98	–	30/5	Feng et al. 2019
Pebax-1074	PEG400 (%wt.)	150.37	2.32	–	20.79	25/10	Azizi et al. 2016
Pebax-1074	PEG400 (40%wt.)	168.4	2.60	–	20.8	25/2	Azizi et al. 2017
Pebax-1657	PEG400 (40%wt.)	174.5	2.42	–	19.2	25/2	
Pebax-2533	PEG400 (40%wt.)	319.4	1.67	–	7.6	25/2	
Pebax-1657	PEG200	151	1.94	43.2	–	30/0.3	Yave et al. 2010
Pebax-1657	PEG200 (50%wt.)	152	2.05	–	15.2	30/0.6	Yave et al. 2009
Pebax-2533	PEG200 (40%wt.)	351.6	1.87	–	9.2	25/2	Azizi et al. 2018
Pebax-1657	PEGDA (40%wt.)	160	1.23	124	34.5	25/8	Ghadimi et al. 2014
Pebax-1657	PTMEG (40%wt.)	165	1.50	69.5	17.5	25/4	Rabiee et al. 2015
Pebax-1657	PEGPOSS (30%wt.)	170	2.21	50	–	30/1	Rahman et al. 2015

a helpful feature and amplifies the diffusion coefficients of light gases such as N_2, O_2, and CH_4. Therefore, based on the above reasons, it can be concluded that at higher pressures, the solubility of gases into the Pebax-based membranes enhances. Simultaneous enhance in the solubility and diffusion of the gases increases the permeability coefficients of incompressible gases with a slight augment in the feed pressure. Based on the permeability coefficient definition, increase the permeability of all gases is mainly due to the increase in the driving force and may be due to the enhancement in gas solubility (Ghadimi et al. 2014).

Furthermore, increasing the pressure upsurges the permeability of condensable gases such as CO_2. The observed trend for the CO_2 permeability is typical behavior for the rubbery polymers. Generally, for CO_2 gas molecules, operating pressure has a significant effect on the gas sorption within the rubbery membrane. In this way, the augment in gas sorption leads to the higher mobility of polymer chains and the production of more free volume in the membrane, and as a result, gas diffusion through the membrane promotes. Thus, increasing gas sorption and diffusion leads to higher permeability for CO_2 by increasing the feed pressure (Zarshenas et al. 2016).

Figure 11 shows the effect of feed pressure on the gas selectivity of the blend membranes containing different molecular weights of PEG. As can be perceived, by increasing pressure from 3 to 7 bar, the ideal selectivity of CO_2/N_2, O_2/N_2, and CH_4/N_2 declined, and CO_2/CH_4 selectivity remained constant. At 10%wt. and 20%wt. of PEG1500 loading, the selectivity of CO_2/N_2, O_2/N_2, and CH_4/N_2 was roughly increased and the CO_2/CH_4 selectivity enhanced at all PEG contents. On the other hand, rising in the selectivity of CO_2/N_2, O_2/N_2, and CH_4/N_2 and decreasing in CO_2/CH_4 selectivity were observed at 30%wt. and 40%wt. of PEG4000 loading. The observed trends for the gas selectivity variation with the feed pressure can be ascribed to the dependency of the gas permeabilities on the feed pressure, as discussed above.

Comparison with other studies

A variety of neat PEGs with different molecular weights and PEG-derivatives have been used by various researchers to prepare Pebax/PEG blend membranes, and different results have been reported. Table 2 indicates a comparison between the gas separation performance of the prepared blend membranes in this study and the reported results for the Pebax/PEG blend membranes in the literature. By comparing the performances of various Pebax/PEG blends, it can be found that the CO_2/N_2 and CO_2/CH_4 selectivities of the blend membranes containing 30 %wt. of PEG600, PEG1500, and PEG4000 are higher than the selectivity of Pebax/PEGs blend membranes provided by other researchers. Also, to better compare the permeability values, the relative permeability parameter (ε_p = the ratio of CO_2 permeability of blend membrane to pure Pebax), as a measure of permeability increment, was calculated (Pazani and Aroujalian 2020; Salehi Maleh and Raisi 2020). Based on the ε_p values, it is clear that the permeability of the blend membranes prepared in this work is in accordance with the results of similar studies. Besides, the gas separation performance of Pebax/30%wt. PEG600 membrane can be competitive and superior to blend membranes containing PEG-derivatives such as PEGDA, PEGPOSS, and PTMEG.

Conclusions

In this study, the effect of PEG as a blending agent on the microstructure and gas perm-selectivity of Pebax-1657/PEG blend membranes was explored. For this purpose, three molecular weights of PEGs (PEG600, PEG1500, and PEG4000) at the loading of 10–40%wt. were used. According to the XRD, the merging of PEG600 as a low molecular additive into the Pebax leads to increasing amorphous segments and chain mobility in the blend membranes. Also, the combination of PEG with higher molecular weight, PEG1500, and PEG4000, within Pebax leads to increasing the crystallinity and reducing inter-chain spacing in the blend membranes. The SEM results revealed that the Pebax-1657/PEG600 blend membrane has a relatively smooth surface. In contrast, the morphological changes are more detectable for the blend membranes containing higher molecular weight PEGs. The merging of PEG1500 and PEG4000 into the Pebax-1657 are indicated these PEGs with low chain mobility disrupt the Pebax-1657 chain and produce a relatively rough surface. Based on WCA analysis, PEG600 leads to increasing the hydrophilicity of blend membranes, and in opposite PEG1500, and PEG4000 leads to decreasing the hydrophilicity of blend membranes. The blend membranes containing PEG600 showed higher values of O_2, CH_4, and CO_2 permeabilities and, consequently, higher O_2/N_2, CH_4/N_2, and CO_2/N_2 selectivities in comparison with the pure Pebax-1657. While, the presence of PEG1500 and PEG4000 in the blend membranes decreased O_2, N_2 CH_4, and CO_2 permeabilities and increased O_2/N_2, CH_4/N_2, and CO_2/N_2 selectivities.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-13447-y.

Authors' contributions Parisa Taheri: conceptualization, methodology, data collection, writing, and original draft preparation. Ahmadreza Raisi: supervision; study design; data analysis and interpretation; writing; and critical revision and editing. Mohammad Salehi Maleh: methodology, data analysis, writing and original draft preparation. All authors read and approved the final manuscript.

Funding This research had no funding resource.

Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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