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Modification of ABS Membrane by PEG for Capturing Carbon Dioxide from CO_2/N_2 Streams

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Carbon dioxide capture and storage (CCS) has been propounded as an important issue in greenhouse gas emissions control. In this connection, in the present article, the advantages of using polymeric membrane for separation of carbon dioxide from CO_2/N_2 streams have been discussed. A novel composition for fabrication of a blend membrane prepared from acrylonitrile-butadiene-styrene (ABS) terpolymer and polyethylene glycol (PEG) has been suggested. The influence of PEG molecular weight (in the range of 400 to 20000) on membrane characteristics and gas separation performance, the effect of PEG content (0–30 wt%) on gas transport properties, and the effect of feed side pressure (ranging from 1 to 8 bar) on CO_2 permeability have been studied. The results show that CO_2 permeability increases from 5.22 Barrer for neat ABS to 9.76 Barrer for ABS/PEG20000 (10 wt%) while the corresponding CO_2/N_2 selectivity increases from 25.97 to 44.36. Furthermore, it is concluded that this novel membrane composition has the potential to be considered as a commercial membrane.

Keywords blend membrane; CO_2/N_2 separation; greenhouse gas; permeability; selectivity

INTRODUCTION

Greenhouse gas emissions are generally made by industries. In this connection, fossil fuels (coal, oil, and gas) burning is the most important section of commercial energy supplies. The flue gases resulted from the combustion of the fossil fuels are generally consist of N_2, O_2, H_2O, CO_2, SO_2, NO_x, and HCl. A forcible issue in this area is greenhouse gas emissions that contribute significantly to global warming; a temperature increase between 1.4 to 5.8°C by 2100 is predicted which will have unpleasant effects of rising sea levels, loss of biodiversity, transition of ecosystems, and reduction in value and variety of agricultural products. Figure 1 depicts the distribution of the flue gases produced by these fuels showing that the major part of the effluent gases is N_2, H_2O, CO_2, and O_2, respectively. Since CO_2 possesses the most greenhouse effect, attention has been focused on capturing CO_2 from N_2 (1–5).

The UN Framework Convention on Climate Change (UNFCCC) of 1992 has provided a framework for controlling the emission of greenhouse gases (GHGs). In addition, the Kyoto Protocol of 1997 has established a set of quantified limitations in GHG emissions and reduction commitments which have the objective of mitigating emissions of the relevant countries by at least 5% below the 1990 levels to the commitment period during 2008 to 2012 (6).

Greenhouse gas emissions control can be performed in several ways such as improvements in energy efficiency and conversion to renewable energy sources such as the use of solar energy, increasing the use of non-fossil fuel power sources, improving the soil management, and the geological sequestration of carbon dioxide from significant greenhouse gas producing point sources (7). Some of the conventional techniques that are used for carbon dioxide separation are chemical absorption, physical absorption, pressure swing adsorption, temperature swing adsorption, and cryogenic distillation. Membrane gas separation, as a proceeding technique, is an attractive alternative. Because of its simplicity and lower energy consumption (8), it has been recently established in the power stations. For membrane, to be used in fossil fuel combustion process, two different strategies could be considered (9):

a. Air separation: producing oxygen enriched air streams via O_2/N_2 membrane separation process.
b. Exhaust gas separation: CO_2/N_2 membrane separation from the produced flue gas at the post-combustion situation.

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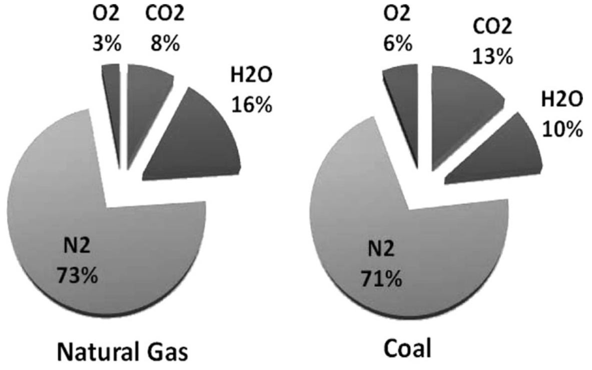


FIG. 1. A typical power station flue gas composition (4,5).

The flue gas line for a conventional pulverized coal combustion power plant has been shown in Fig. 2.

CO_2/N_2 separation in the post-combustion is involved in some challenges (10,11):

- Because of the low CO_2 molar fraction and ambient pressure level of the flue gas, using one-stage gas separation membrane in the post-combustion is not sufficient for the CO_2 purity requirement (>95 mol%).
- Due to the meet of the trade-off relation between membrane permeability and selectivity, attention was mostly drawn to multi-stage gas separation membrane systems instead of single-stage ones.
- From the engineering point of view, understanding the separation properties, the limiting step, mass transfer resistances, for CO_2 permeation, implications of operating conditions (existence of recycle streams, flow type: cross, co-, or counter-current), operating mode (sweep and vacuum), is highly important.
- Comparing the single and multi-stage systems has shown the higher energy consumption of the latter one and using a single-stage system having the membrane with high permeability and selectivity is advised.

Captured CO_2 has special applications for CO_2 flood EOR (enhanced oil recovery) and purging in natural gas project pipelines (5,12). Recent works have investigated the performance of various membranes and polymers in order to meet the desired permeability/selectivity. Polymers, such as polyimides, polysulfones, polycarbonates, polyarylates, polypyrrolones, polyamides, polyetherimides, poly(ethylene oxide) and poly(phenylene oxide), have been more investigated (4,13,14).

Kazama et al. (15) have investigated the cardo polyimide membranes for CO_2 capturing from flue gases. They found that the polyimide membrane systems are less cost-effective for capturing CO_2 from power plant exhausts than the amine process. Gas transport properties of polyallylamine–poly (vinyl alcohol)/polysulfone composite membranes, were investigated by Cai et al. (16). They concluded that in the membranes with various PAAm contents tested by the CO_2/N_2 gas mixture, the CO_2 permeance follows a facilitated transport mechanism whereas N_2 and CH_4 transport follows the solution-diffusion mechanism. Also, CO_2 permeance shows a maximum with increasing PAAm (in 10 wt% content).

Sandru et al. (17), prepared composite hollow fiber membranes by coating poly (phenylene oxide) (PPO) and

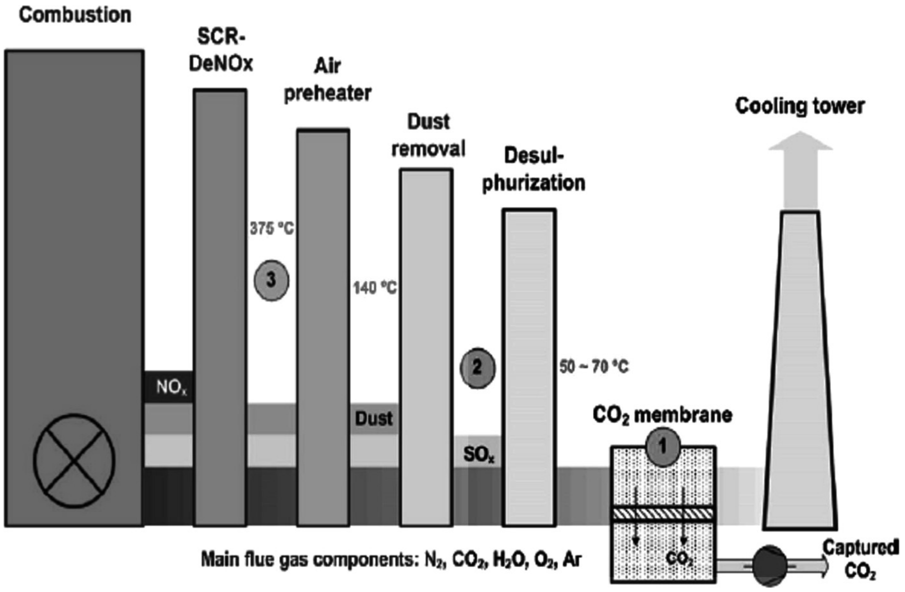


FIG. 2. Schematic diagram of CO_2 membrane position in a post-combustion flue gas line (7).

polysulfone (PSf) hollow fibers with high molecular polyvinylamine (PVAm). Both PVAm/PSf and PVAm/PPO membranes were tested with humidified and dry/wet feed gas. Their handmade PVAm/PSf membrane has the CO_2 permeance of $0.022\,m^3(STP)/(m^2 \cdot bar \cdot h)$ at a feed pressure of 1.6 bar and CO_2/N_2 selectivity of 133 (conditions: feed 100 RH%, temperature 25°C, feed 10% CO_2-90% N_2, sweep gas). Also, their PVAm/PPO membrane has the CO_2 permeance of 0.56 and $0.11\,m^3(STP)/(m^2 \cdot bar \cdot h)$ at feed pressure of 1.2 and 5 bar, respectively. The corresponding CO_2/N_2 selectivity of 209 and 517 (vacuum, 0.005 bar) achieved. They concluded that the increase in CO_2/N_2 selectivity with feed pressure indicates PVAm/PPO membranes can be tailored also for CO_2 removal at high pressure applications.

Recently, polysulfones have found many spreading applications in industrial gas separation processes, because of their desirable performance and low cost (18). Kaldis et al. (19) have examined polysulfone and polyimide membranes for capturing CO_2 form CO_2/N_2 mixtures from high pressure flue gases. They observed a significant increase in CO_2 permeability which was falling with time.

Powell and Qiao (4) in a review paper described that polycarbonates and polyarylates tend to have a carbon dioxide permeability of less than 40 and 25 Barrer and selectivity in the range of 15 to over 25, respectively. Also, they mentioned that polypyrrolones have high thermal and chemical resistance, and a more rigid structure relative to polyimides. Liang and Martin (20) prepared a poly (N-methylpyrrole) membrane which showed a CO_2 permeance of 2 GPU and a CO_2/N_2 selectivity of 17.6. Petersen and Peinemann (21) prepared a polyamide composite membrane which showed a CO_2 permeance of 54 GPU and a CO_2/N_2 selectivity of 24.

Nowadays, copolymers, due to their low cost in comparison with synthesis of new polymers, have been more taken into account. From a gas separation process characteristics point of view, they make the benefits of their constituent homopolymers up together. Piroux and co-workers (22) have studied a series of sulfonated copolyimides and found that by increasing sulfonated groups, CO_2 permeability drops dramatically.

Yoshino and coworkers (23) have investigated the CO_2/N_2 separation performance of a series of poly(ethylene oxide) segmented copolymers with polyimides, polyamides, and polyurethanes. The high selectivity of CO_2/N_2 in these membranes resulted from the high CO_2 solubility within the poly(ethylene oxide) segments. Another example of using copolymers is the work of Marchese et al. (24). They showed that in acrylonitrile-butadiene-styrene (ABS) terpolymer (Lustran® 246) membrane, CO_2 permeability increases from 2.97 at 20°C to 4.95 at 50°C and the corresponding CO_2/N_2 selectivity decreases from 28.84 to 18.75. Also, with the pressure increasing from 2 to 10 bar, no considerable changes attained in CO_2 permeability.

Zhao and coworkers (25) used a novel copolymer, poly (propylene glycol) block poly(ethylene glycol) block poly (propylene glycol) diamine (PPG/PEG/PPGDA), to chemically cross-link Matrimid5218 at room temperature. The cross-linked Matrimid membranes displayed excellent CO_2 permeability and CO_2/light gas selectivity compared with the uncross-linked Matrimid membrane. CO_2 permeability for cross-linked Matrimid5218 was 115.76 Barrer at 35°C and 2 atm that compared with uncross-linked Matrimid5218 (5.39 Barrer) has shown a very high increase with polyether addition in the Matrimid backbone structure. Also, CO_2/N_2 separation factor showed an increase from 33.47 to 52.49. Comparing CO_2 diffusivity selectivity (19.18) and solubility selectivity (1.08) for cross-linked and uncross-linked Matrimid, is resulted in more effectiveness of diffusivity than solubility selectivity.

Polymer blending is a useful, simple, and economical method in preparation of membranes for gas separation applications (26). Enhancement in mechanical properties, membrane manufacturing, and gas permeability are the most important advantages of blending. According to their permselectivity behavior, a large number of polymers have been used as the blending agent. Polyethers play an important role in this area. Among them, polyethylene glycol (PEG) has the most application in this field. Because of the presence of polar moieties in its main chains and high segmental flexibilities, PEG has very considerable acid gas solubility and much research has been carried out using this polymer. Hu and et al. (27) improved CO_2/N_2 selectivity by incorporation of PEG2000 and PEG475 into polyionic polymers such as poly[p-vinylbenzyltrimethylammonium tetrafluoroborate] ($P[VBTMA][BF_4]$) and poly[2-(methylacryloyloxy)ethyl-trimethylammonium-tetrafluoroborate] ($P[MATMA][BF_4]$). They showed that for PEG2000, while CO_2/N_2 diffusivity selectivity was low (close to 0.9), the corresponding solubility selectivity was high (71 for $P[VBTMA][BF_4]$-g-PEG2000 and 81 for $P[MATMA][BF_4]$-g-PEG2000, respectively). Li et al. (28), prepared blend membranes of CA/PEGs and showed that CO_2 permeability in the presence of PEG20000 (10 wt%) increases from 5.96 up to 7.49 Barrer and the corresponding CO_2/N_2 selectivity increases from 25.8 to 36.2. Car et al. (29) showed that increasing PEG content from 0.0 to 50.0 wt% in Pebax®/PEG200 blend membranes causes a decrease in T_g from −53 to −76°C. The increase in PEG200 content increases the rubbery characteristics of the blend membrane, and consequently CO_2 permeability increases from 73 to 151 Barrer while the CO_2/N_2 selectivity has no significant changes. In a review study that was carried out by Stern (13), CO_2 permeabilities of polystyrene and poly(butadiene-styrene) were reported as 12.4 and 171 Barrer and the corresponding CO_2/N_2 selectivity of 23.85 and 16.6, respectively. Increasing rubbery species content in styrene by introducing poly butadiene rubber (PBR), increases CO_2 permeability because of more flexible main chains of the butadiene rubber but has negative effect on selectivity.

ABS relative to PS has more environmental stress cracking, notch impact strength, heat distortion temperature, stiffness, processability, and less cost (30). Because of the good film-forming properties of ABS, it is used to fabricate gas separation membranes.

In this work, polymeric dense membranes have been prepared by incorporating different grades of polyethylene glycol into acrylonitrile-butadiene-styrene terpolymer via a blending process and the prepared membranes were characterized and evaluated for CO_2/N_2 separation. The selected blend is a novel blend which is used for the first time. This selected matrix has many benefits in comparison with many commercial polymers such as good film forming, more resistant to the environmental and chemical stresses and having good processability. The interaction between ABS and PEG molecules and the effect on the permeability and selectivity of the studied gas mixture shows an interesting behavior for these blends.

EXPERIMENTAL

Materials

Acrylonitrile-butadiene-styrene (ABS) terpolymer, $T_g = 108.98°C$, containing ~25% acrylonitrile, was supplied from Aldrich and was dried about 2 h at 80°C in an oven before use. Polyethylene glycol (PEG400, 1000, 1500, 4000, 10000, and 20000, all purchased from Merck) and dichloromethane (Acros) were used without further purification.

CO_2, having 99.5% purity, was purchased from Farafan Gas Corp., Tehran, Iran. N_2 with 99.999% purity was supplied by Roham Gas Corp., Tehran, Iran. These gases were used in permeation measurements. All measurements were made three times.

Membrane Preparation

In order to prepare the dense membranes, predetermined quantities of ABS and PEG dissolved in dichloromethane (5 wt%). The solution was stirred for about 5 h at room temperature. Then it was cast onto a glass plate. By solvent evaporation for 2–3 days at ambient temperature and pressure, the films were put into an oven for 12 h. Finally, the solvent-free membranes were used in permeation experiments.

Gas Permeation and Sorption Experiments

The gas permeability was measured in a permeation test setup is given schematically in Fig. 3. A high pressure stainless steel membrane holder (XX45 047 00 from Millipore Co., USA) was used with an effective area of 15.90 cm^2. This holder in its original form is well-suited for pure gas measurements (31). A glass-stainless steel rotameter (Fisher Co., USA) was used for gas flow adjusting. The pressure of the system was kept at the desired value using a pressure regulator (Parker- Hannifin Co., USA) and a back pressure regulator (GO Co., USA) both made of 316 L stainless steel. Before conducting a measurement, the gas is charged from a cylinder to the cell upstream side and transmembrane pressure kept constant using the back pressure regulator. A 0.003 micron Teflon® filter with AISI 316 L holder (Gaskleen® 6101 Series form Pall Co., USA) was used in the feed gas line in order to eliminate all of the particles before entering the membrane surface. The permeate flow rate was measured by a precision handmade volumetric flow meter.

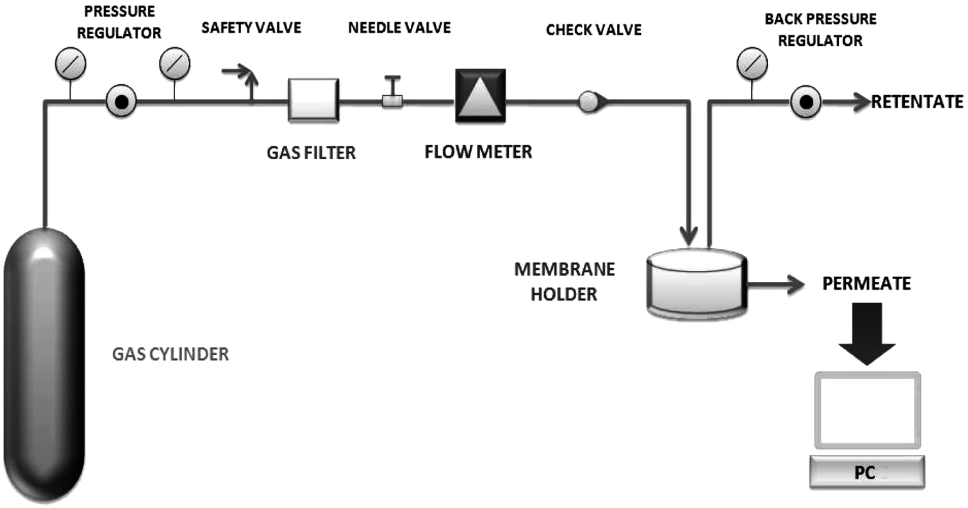


FIG. 3. Schematic diagram of the experimental apparatus.

The solubility was measured using a handmade adsorption chamber consisted of a 100 ml high pressure gas cylinder equipped with a precision pressure test gauge (Bourdon Sedem, France), an electro-polished diaphragm valve (Swagelok Co., USA) and a high pressure stainless steel membrane holder (XX45 047 00 from Millipore Co., USA).

Membrane Characterization

In order to observe the morphology (to avoid destroying the structure of the cross sections for scanning electron micrograph) of flat sheet membrane samples, they were first immersed in liquid nitrogen, fractured, and then sputtered with metallic gold to obtain an adequate contrast of the membrane fracture, using a BAL-TEC SCD 005 sputter coater. Surface and cross-section of flat sheet membrane samples were examined using a Philips XL30 scanning electron microscope. Furthermore, in order to characterize the ABS/PEG blend membranes, FTIR measurements were carried out. A Galaxy series FTIR5000 spectrometer for FTIR tests were used. The micro-structural properties of the original ABS and the selected blend of ABS/PEG membranes were analyzed on Xpert MPD wide-angle X-ray diffractometer (XRD) from Philips, Holland. The measurements were carried out at room temperature using monochoromatic radiation of α-rays emitted by Cu at a wavelength of 1.54 Å. The scan range was from 1° to 65° with a step increment of $0.025^\circ\ \mathrm{s}^{-1}$.

RESULTS AND DISCUSSION

When permeate pressure relative to the feed pressure is negligible, and Fickian diffusion constitutes the rate-limiting step in penetrant transport, in terms of a solution-diffusion process for nonporous (dense) polymer membranes and gas, the permeability coefficient can be written as:

$$P = D \times S \tag{1}$$

Here, D is the concentration-averaged effective diffusion coefficient, and S is the solubility coefficient defined as the ratio of the penetrant volume dissolved in the polymer volume relative to the upstream partial pressure in the gas phase. The solubility coefficient was measured by a manufactured adsorption chamber. In case of diffusivity calculation, from the permeability measurements by means of the so-called permeation test apparatus, it would be calculated considering the relation (1): $D = P/S$.

The ideal permeability selectivity related to the measured permeabilities of pure components A and B is defined as:

$$\alpha_{A,B} = \frac{P_A}{P_B} \tag{2}$$

Without strong gas-polymer interactions (28) (site competition (24) or plasticization effect) and pressure dependence permeability (partial pressure effect), selectivity for mixed gases can be approximated as ideal separation factor, $\alpha_{A,B}$, within 10% using the ratio of the permeabilities for pure gases A and B.

Permeability and Selectivity of Blend Membranes

Here, it is attended to the strategy of altering the composition and, hence, morphology and resultant gas transport properties of ABS-based membranes. For this reason, blend membranes of 10 wt% PEGs, with different molecular weights, in the ABS matrix were prepared and their gas separation characteristics were examined (illustrated in Fig. 4).

As observed, CO_2 permeabilities from PEG400 to PEG20000 have shown an increasing behavior, except for PEG4000. By increasing in PEG molecular weight the crystallinity increases that is leaded to a difficult condition for molecular transport. On the other hand, in polyethers, polar moiety density and main chain flexibility increase by increasing in molecular weight (28). This plays an important role in CO_2 permeability. Lin and Freeman (32), have investigated materials for the preparation of membranes that are attractive for the separation of polar penetrants from mixtures containing non-polar ones. They concluded that crystallinity should significantly decrease permeation. Preparing the more amorphous ABS terpolymer with disrupted crystallization, via incorporating a considerable amount of flexible robbery content existing in the high MW PEGs, it could be propounded as an attractive method; main chain flexibility of the high MW PEGs, can act as a hindering factor for raising the crystalline regions in the ABS structure; they hinder from coming

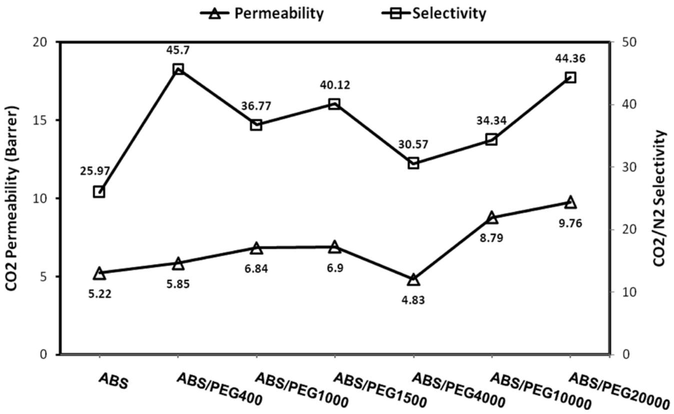


FIG. 4. CO_2 permeability and their related CO_2/N_2 selectivity of ABS and its blend membranes with (10 wt%) PEGs at 25°C and transmembrane pressure of 1 bar. The solid lines were used for connecting the data. 1 Barrer $= 1 \times 10^{-10}\ \mathrm{cm^3(STP)\cdot cm/cm^2\cdot s\cdot cm\ Hg} = 7.5 \times 10^{-14}\ \mathrm{cm^3(STP)\cdot cm/cm^2\cdot s\cdot Pa}$.

the polymer chains near to each other, being more compressed and, as a result, making crystalline regions (33).

From the above explanations, it is concluded that the incorporation of PEG20000 could has been the highest effect on CO_2 permeability; this is because of the facilitation in CO_2 transport as a result of PEG20000 flexible main chains, and also, increasing in polar moiety densities and their interaction by CO_2 molecules, although the ratio of crystalline to amorphous domains in polymer matrix has been increased. As expected, the trade-off between the two effects—the negative effect of crystallinity and the positive effect of polar moiety density and main chain flexibility—contributes to the CO_2 transport from ABS/PEG400 to 20000. According to Fig. 4, first, the difference between the CO_2 permeability values from ABS to PEG1000 increases. Then, the difference in CO_2 permeabilities of ABS/PEG1000 and 1500, i.e., 0.06, is slightly lowered and at the next, for ABS/PEG1500 and 4000 the value is -2.07. Finally, this value increases again to positive amounts for high molecular weight PEGs. Considering the above explanation, it is not illogical that in the PEG molecular weight ranges, from liquid low MWs to high MWs solids, PEG4000 with an approximately middle molecular weight has been the lowest CO_2 permeability. It is determined that adding a semicrystalline polymer, such as PEG4000, to an amorphous dominant copolymer like ABS, promotes the lamellar swelling and, eventually, the polyether microphase remains in a semicrystalline state which is an unfavorable condition for molecular transport (34).

According to Fig. 4, CO_2/N_2 separation factors have no regular procedure. The highest selectivity value, 45.7 has been observed for PEG400 which is an amorphous liquid at ambient temperature. Adding PEG400 to ABS would cause a decrease in crystallinity. A reduction in crystallinity improves CO_2 solubility and the molecular mobility (34). From the other side, N_2 molecule is smaller relative to CO_2 (the effective molecular diameter of 3.04 and 3.50 Å for N_2 and CO_2, respectively) (24,35). Also, it has no effective polar moment to interact with polymer polar chains. Therefore, N_2 transfer has a diffusion dominant mechanism. As a result, the CO_2/N_2 separation factor of the ABS/PEG400 membrane was becoming high. For the case of the CO_2/N_2 selectivity, the reflection of that mentioned above for trade-off between the two existing effects on CO_2 permeabilities, is in majority of the effective phenomena. Furthermore, the size sieving effect has been important in promoting the N_2 permeation rather than the CO_2, at the region where the crystallinity is arisen.

As it is noted in Fig. 4, the blend membrane with 10 wt% PEG20000 content has the highest CO_2 permeability relative to other molecular weights of PEGs. Therefore, the subsequent sections focus only on the blend membrane with PEG20000.

Diffusivity and Solubility

A comparison between solubility and diffusivity of neat ABS and its blend with PEG20000 was shown in Table 1. Incorporation of high molecular weight PEG, i.e., PEG20000, causes an increase in diffusivity and solubility of CO_2 in respect to neat ABS. The effect of the PEG molecular weight on the solubility is more considerable rather than the diffusivity. Indeed, the solubility ratio (1.66) for ABS/PEG20000 respect to neat ABS is more than the corresponding diffusivity ratio (1.13), which indicates the more effectiveness of solubility. Solubility has a dependency on the chemical structure of the penetrant and membrane and their interactions. Incorporation of PEG20000 causes the increase in electro-negativity and the amount of polar moieties of the polymer matrix that enhance CO_2 solubility. On the other hand, the existence of polar side groups in the blend membrane increases diffusion of the CO_2 polar molecules. Also, the increase in compressibility due to the high molecular weight PEG20000, can lead to trapping the CO_2 molecules because of the decrease in the amount of free volume which existed in the polymer matrix. This phenomenon plays as a hindering factor in CO_2 diffusion (36).

Membrane Characteristics

Figure 5 presents SEM (Scanning Electron Microscope) photographs of the top surfaces and cross sections of the blend membranes. Figures 5a, 5b, 5c, and 5d show the top surface images of ABS/(10%) PEG400, 1000, 4000, and 20000, respectively. As observed, by increasing the PEG molecular weight, the membrane surfaces became smoother, except for ABS/PEG20000 that has a rather rough surface that is suitable for trapping gas molecules and consequently facilitating transport through the membrane. Also, no crack or defects were observed and blending the polymers resulted in a homogenous pattern in the distribution of constituent species. The cross-section views of the described membranes were shown in Figs. 5e, 5f, 5 g, and 5 h. It should be noted that in the cross-section images, by increase in PEG molecular weight the resultant polymer blend structure tends to be denser (the magnifications have been increased for the better detection). It could be seen that by PEG molecular weight increasing, not only no

TABLE 1

CO_2 diffusivity, solubility and their related ratios, for ABS (1) ABS/PEG20000 (10 wt%) (2) at 25°C and 1 bar

	$D_{CO_2} \times 10^8$ [cm^2/s]	$S_{CO_2} \times 10^3$ [cm^3(STP)/cm^{3}cmHg]	D_2/D_1	S_2/S_1
1	0.222	235	1.13	1.66
2	0.250	390		

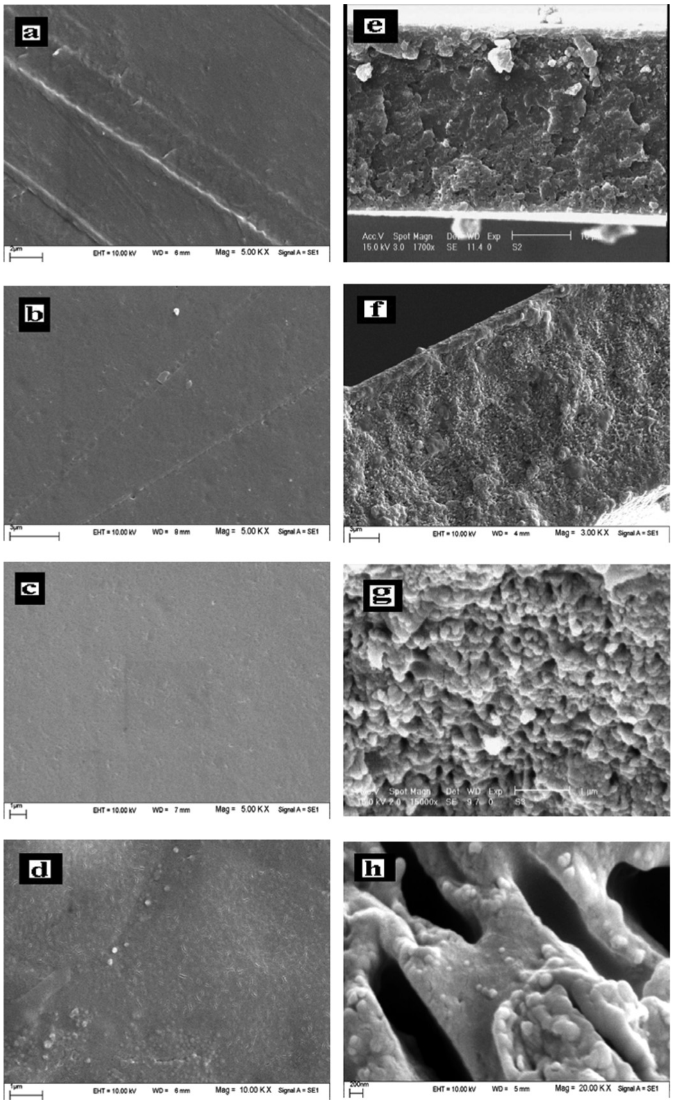


FIG. 5. SEM pictures of the cross-sections and the top surfaces of the membranes. (a) ABS/PEG400 (10%) surface; (b) ABS/PEG1000 (10%) surface; (c) ABS/PEG4000 (10%) surface; (d) ABS/PEG20000 (10%) surface; (e) ABS/PEG400 (10%) cross-section; (f) ABS/PEG1000 (10%) cross-section; (g) ABS/PEG4000 (10%) cross-section; (h) ABS/PEG20000 (10%) cross-section.

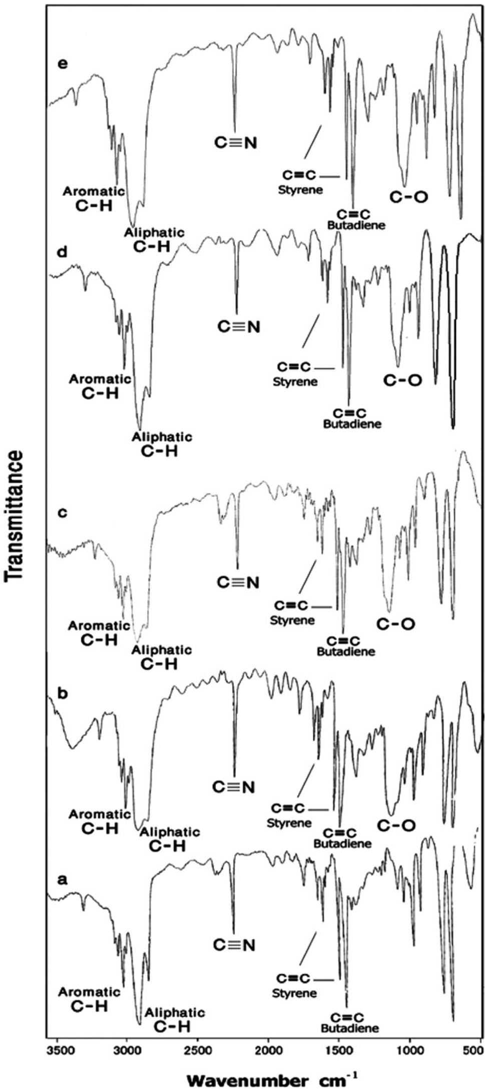


FIG. 6. FT-IR spectra of (a) ABS (b) ABS/PEG400 (10%) (c) ABS/PEG4000 (10%) (d) ABS/PEG10000 (10%) (e) ABS/PEG20000 (10%).

macro-voids are observed, but also the created polymer matrices have become more homogeneous with very fine pores. It should be noted that the stretched pores shown in the images are ascribed to the tensions in the casting stage of the membrane preparation process. Furthermore, a few light spots dispersed in the polymer matrices show that two constructive polymers of the blend membranes are partially miscible; this phase behavior to a large extent confirms the described separation characteristics of the membranes.

FTIR spectra of the ABS and its blends with (10 wt%) different PEGs were shown in Fig. 6. In the spectrum (a) for ABS, an absorption peak was occurred in the 2237 cm^{-1} that is related to nitrile groups in the ABS. Also, absorptions in the 1494 and 1602 cm^{-1} are attributed to the double bonds of styrene blocks in the ABS terpolymer. In the 1454 cm^{-1}, absorption is related to double bonds of butadiene blocks. Also, absorption in 2926 and 3028 cm^{-1} are referred to vibrations of aliphatic and aromatic C–H bonds, respectively. FTIR spectrum of ABS/PEG400 (10 wt%) in spectrum (b) is shown an excessive absorption in 1111 cm^{-1} in comparison with ABS spectrum, which is related to C–O bonds of polyether. This behavior is repeated for the other blends in spectrums (c), (d), and (e). In addition, no new absorption is observed except for the one which exists in the ABS or PEGs.

Figure 7 shows the XRD spectra of the neat ABS membrane and the blend membrane containing 10 wt%

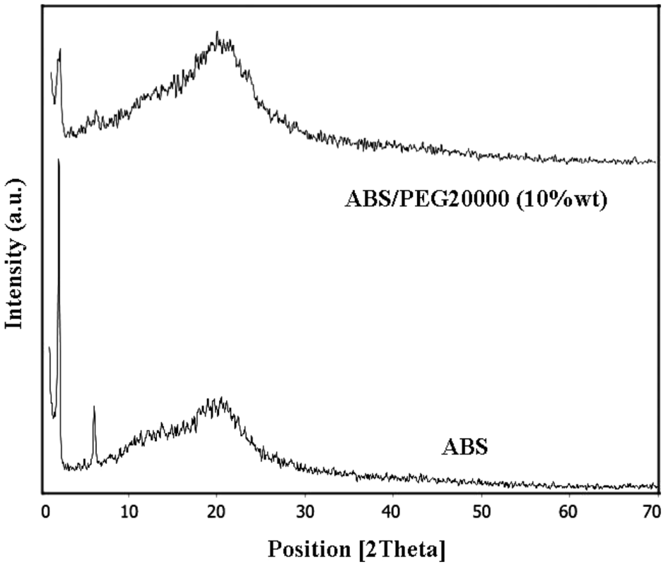


FIG. 7. XRD spectra of the neat ABS and the ABS/PEG20000 (10 wt%) blend membrane.

PEG20000, the membrane with the highest specification studied here. It can be clearly seen for ABS that shows two sharp peaks in a low angle range. The semi-crystalline nature of the polymer is suggested by these sharp peaks. However, adding PEG20000 in the polymer, the spectra show variation in intensity; the sharpness of the peaks was lowered and, also, the peaks were widened. Qualitatively, these variations indicate the amorphous nature of the blend membrane. Amorphous nature is directly related to permeability; therefore, as PEG20000 added in the ABS membrane structure, the permeability could be increase.

Pressure Effect on CO_2 Permeability

Figure 8 presents the CO_2 permeability as a function of transmembrane pressures (ranging from 2 to 8 bar) for the prepared 10 wt% membranes. In all cases the permeability in the pressure of 2 bar has the higher values. At the pressure of 4 bar and higher, no considerable pressure dependence is observed in the permeability data. The slight increase for some samples may be due to the more interaction between CO_2 molecules -that their concentration has substantially increased- and the polymer polar moieties. Figure 9 shows pressure dependency of the permeability for ABS/PEG20000 blend membranes with different PEG20000 contents (pressures ranging from 1 to 8 bars). The samples with 10 and 20 wt% PEG20000 contents have almost the same behaviors. As it is observed in Fig. 9, CO_2 permeabilities of the blend membranes containing 20 and 30% PEG20000 contents in all pressures tested here, are lower than that of for 10% PEG20000 content. From the study carried out by Yampolskii et al. (37), it could be concluded that the more addition of high molecular weight PEG20000 in the ABS matrix resulted in the more efficient chain packaging. This would be the reason of decreasing CO_2 permeabilities by increasing PEG20000 content. Also, it is observed a slight increase in the permeability of the sample with 30 wt% PEG20000 content, by increase in pressure more than 4 bar; CO_2 concentration at the higher pressures can increase polymer chain flexibility, thus it could increase in gas diffusivity and, in turn, permeability. And, furthermore, the increase in solubility of the more condensable component, CO_2, with increasing pressure led to the increase in the permeability coefficient (38,39).

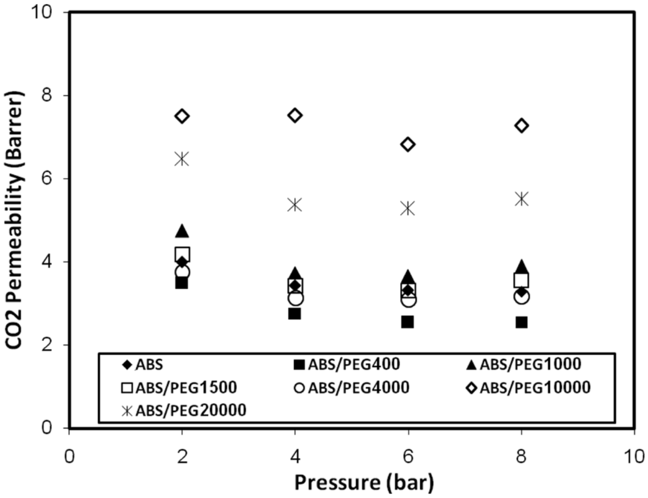


FIG. 8. CO_2 permeability as a function of transmembrane pressure.

CO_2/N_2 Selectivity

A comparison between CO_2 permeability and CO_2/N_2 selectivity as a function of PEG20000 content shows that

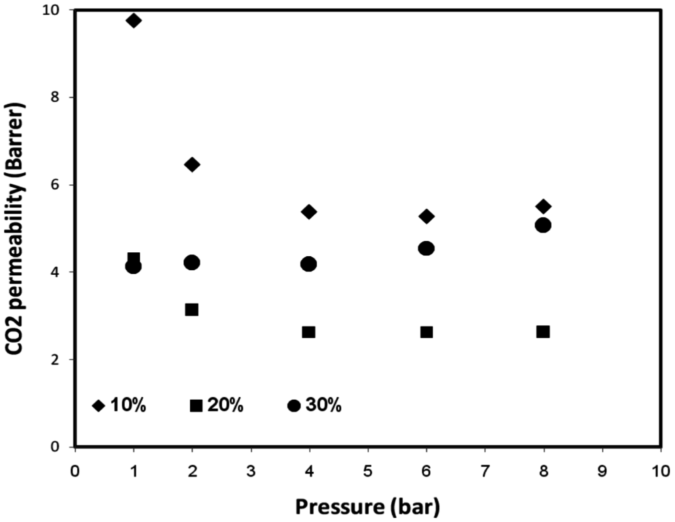
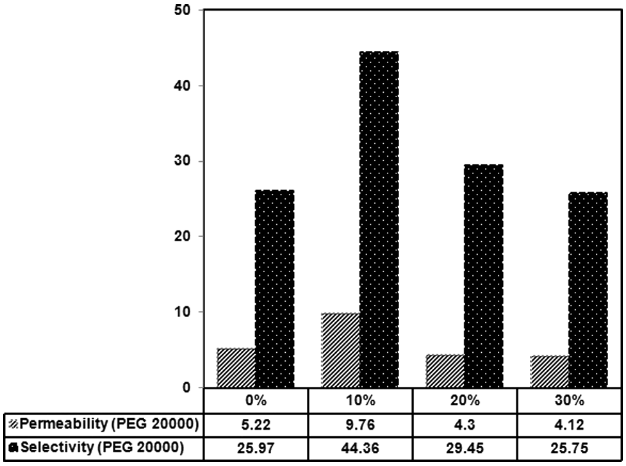


FIG. 9. CO_2 permeability as a function of transmembrane pressure for different PEG content of ABS/PEG20000 membranes.



	0%	10%	20%	30%
▨Permeability (PEG 20000)	5.22	9.76	4.3	4.12
■Selectivity (PEG 20000)	25.97	44.36	29.45	25.75

FIG. 10. Effect of PEG content on the performance of ABS/PEG20000 blend membrane at 1 bar.

the maximum values are corresponding to the trans-membrane pressure of 1 bar. Figure 10 shows the values for ABS/PEG20000 blend membrane at trans-membrane pressure of 1 bar. CO_2 permeability and CO_2/N_2 selectivity have the highest values of 9.76 Barrer and 44.36 in 10 wt% PEG20000 content, respectively. This is because of the flexibility of main chains in the PEG20000 that facilitates CO_2 transport through the membrane. On the other hand, at high PEG20000 contents (i.e., more than 10 wt%), the crystallinity increases in the blend membrane with increase in PEG20000 content which plays an obstacle role in CO_2 transfer through the membrane (28). This causes a decrease in CO_2 permeability and the corresponding CO_2/N_2 selectivity, at high PEG20000 contents. Figure 11 shows a comparison between CO_2/N_2 selectivity versus CO_2 permeability for ABS/PEG membranes (current study) with some well-known polymeric membranes (24,30, 40–41). Previously studied representative polymers have distinguished by a solid line as an upper limit (42). The membranes fabricated by blending PEG with ABS became closer to Robeson line, especially for ABS/PEG20000 (10 wt%). As it was discussed, the effective molecular diameter difference between CO_2 and N_2 is not so large that the size exclusion becomes the dominant factor for selective transfer through the membrane. But CO_2 has higher polarizability and quadrupole moment comparing with N_2, although being nonpolar; this subject and the fact that PEG has a good CO_2 selectivity because of the flexibility of the main chains and polar moieties, cause an appropriate CO_2/N_2 selectivity for ABS/PEG blend membranes.

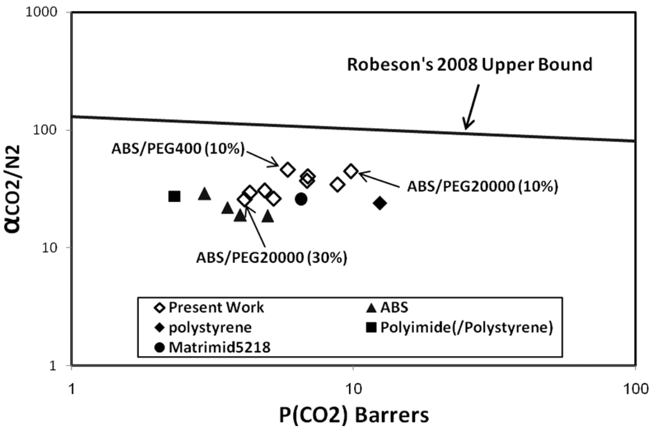


FIG. 11. A comparison between ABS/PEG blends membranes and previously studied polymers for CO_2/N_2 separation.

CONCLUSIONS

Blend membranes for separation of CO_2 from CO_2/N_2 streams was prepared by blending PEG with ABS. Different grades of PEG from PEG400 to PEG20000 were examined for CO_2 separation. The resultant membranes were tested in the pressures ranging from 1 to 8 bar and 25°C. It was found that ABS/PEG20000 has the best simultaneous permeability and selectivity than the other grades.

The effect of PEG content in ABS/PEG20000 on CO_2 permeability and the related CO_2/N_2 selectivity showed that the best values are corresponding to the membrane with 10 wt% PEG20000. Therefore, PEG20000 is an attractive grade for the desired separation properties. High selectivity of the blend membrane is due to the high solubility of CO_2 molecules because of the incorporation of the polar bonds of polyether in the polymer matrix and their strong interaction with C=O polar bonds of CO_2 molecules. A comparison between these developed membranes and previously studied membranes for CO_2/N_2 separation shows an increase in permeability selectivity of the presented membrane. It seems to be a good alternative for currently energy consuming processes for carbon dioxide capturing such as amine process (about 120°C and 65 bar).

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LIST OF SYMBOLS

a.u.	Arbitrary unit (for Intensity)
D	Apparent diffusivity coefficient (cm^2/s)
GPU	Gas permeation units ($10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$)
P_A	Permeability coefficient of gas A (Barrer)
P_B	Permeability coefficient of gas B (Barrer)
S	Solubility coefficient ($cm^3(STP)/cm^3 \cdot cmHg$)
$\alpha_{A,B}$	Ideal permeability selectivity

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