

Aminosilane cross-linked poly ether-block-amide PEBAX 2533: Characterization and CO₂ separation properties

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Abstract—Commercial poly (ether-block-amide) (Pebax[®]) copolymers are thermoplastic elastomers that have attracted attention as membrane materials due to their high performance in CO₂ separation. In this study, a cross-linking reaction is reported as a viable strategy to improve the gas separation performance of a highly permeable but low selective Pebax 2533 membrane. To this end, a new bi-functional aminosilane cross-linker (3-aminopropyl(diethoxy)methylsilane (APDEMS)) was applied. Cross-linked Pebax 2533 membranes were prepared via solution-casting with different amounts of APDEMS ranging from 0.5 to 4 wt%, to investigate the effect of the aminosilane concentration on the membrane performance. Gas separation with prepared membranes was studied for CO₂/N₂ at the feed pressure ranges of 2-10 bar. Instrumental analyses were applied to investigate the effect of the cross-linking reaction on the structure and properties of the membranes. The results showed that a 2 wt% APDEMS cross-linked Pebax 2533 membrane has the best gas separation performance. The CO₂/N₂ ideal selectivity of the cross-linked Pebax 2533 increased twice compared to the neat Pebax 2533 membrane at the feed pressure of 2 bar, while the CO₂ permeability experienced a slight decrease by cross-linking, but still remains higher than the permeability of other Pebax grades.

Keywords: Cross-linked Membrane, Cross-linking Agent, Pebax 2533, Aminosilane, Gas Separation

INTRODUCTION

The emission of greenhouse gasses (GHGs), which causes global warming, is one of the most important environmental challenges in recent years. Fossil fuel combustion, industries and human activities are the main sources of CO₂ emissions, the most abundant GHG in the atmosphere [1-4]. Among the gas separation technologies, membrane separation has become a suitable choice due to its advantages over conventional separation methods such as amine absorption and distillation. Their lower environmental effect, lower cost, high energy efficiency and operation simplicity are some prominent advantages of membrane processes [5-13].

The gas permeability and selectivity of the membranes are the two main characteristics determining the membrane efficiency for gas separation. It should be considered that intrinsically highly permeable polymers usually have a lower selectivity, while less permeable polymers typically have a higher selectivity. This permeability-selectivity trade-off was expressed by an upper bound limit for specific gas separation performance of membranes by Robeson [14, 15]. Many efforts have been made to simultaneously increase the

permeability and selectivity, in order to surpass upper bound and improve the membrane performance in separations [16-20]. A large number of polymeric materials with different chemical and physical characteristics have been suggested for CO₂ separation applications [21-26]. Poly (ether-block-amide) (PEBA) copolymers with the trade name of Pebax[®] have been widely used for CO₂ separation from light gases due to their good performance in CO₂ separation [27-32]. Pebax[®] copolymers have a crystalline/amorphous structure consisting of rigid segments scattered in soft ones. The rigid segment is an aliphatic polyamide (PA), which provides the mechanical strength. The soft segment makes continuous pathways for gas diffusion and is usually a polyether (PE) such as poly tetramethylene oxide (PTMO) or poly ethylene oxide (PEO) [33,34]. Bondar et al. [34] studied gas separation properties of various grades of Pebax including 2533, 4033, 1074 and 4011 which contain 80, 53, 55 and 57 wt% of PE, respectively. The CO₂/N₂ separation results revealed that the permeability increases with the amount of PE blocks in the copolymers. Pebax 2533, with 80 wt% PTMO and 20 wt% PA 12 (nylon-12), has the highest CO₂ permeability (i.e., 221 Barrer), which is owing to the strong affinity between polar carbonyl linkages in the PE blocks and CO₂ gas molecules (CO₂ is a highly polarizable gas compared to N₂). However, other grades exhibited a better selectivity for CO₂/N₂ separation.

The low selectivity of the Pebax 2533 membrane for CO₂/N₂ separation (about 23) prevents its utilization as a suitable polymeric mate-

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rial for industrial gas separation applications. Different methods have been applied to improve the low selectivity of Pebax based membranes. The introduction of low molecular weight additives [35,36] and solid fillers in order to form mixed matrix membranes (MMMs) [37–41] are some of these approaches. Moreover, cross-linking is an effective method that has been widely used in recent years [42]. Cross-linking modification could increase the membrane resistance against aging and plasticization, while it improves the membrane efficiency [43–45]. The fractional free volume (FFV) of a polymer and the mobility of the polymer chains have been affected by cross-linking reaction through the covalent bond formation between the polymer chains [46]. Sridhar et al. [47] cross-linked a Pebax/PVDF (poly vinylidene fluoride) composite membrane using 2,4-toluylene diisocyanate (TDI) as the cross-linker agent. They showed that as the cross-linking reaction time increases, more interactions occur between the TDI and PE units, which lead to an enhancement in the membrane selectivity and an improvement of the mechanical strength. The CO_2/CH_4 selectivity of Pebax membrane increased from 21.2 to 43.1 after 5 minutes of cross-linking reaction, while the CO_2 permeability decreased from 3.7 to 0.75 GPU (1 GPU (gas permeation unit) = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ (cmHg)}^{-1}$). Liu et al. [48] prepared glutaraldehyde cross-linked chitosan/Pebax blend membranes and observed that a higher cross-linked concentration leads to a higher gas permeability and a lower selectivity. This was explained by a decrease of hydrogen bonding interactions between chitosan chains, which leads to an increase in diffusion of gas molecules. In another study, Wang et al. [49] prepared a Pebax/polyacrylonitrile (PAN) composite membrane and designed a cross-linked amino silicon gutter layer using polydimethylsiloxane (PDMS) as the cross-linking agent. The presence of a PDMS cross-linking agent in the gutter layer structure improved the CO_2 permeance but reduced the CO_2/N_2 selectivity. This is due to the hydrophobicity of PDMS, which has a low affinity to hydrophilic Pebax. A CO_2 permeance of 350 GPU and a CO_2/N_2 selectivity of 50 in the presence of a gutter layer with 2 wt% PDMS were obtained. Physical and chemical properties of cross-linker agents should be considered as the most important factors to achieve a perfect modification.

Amine-containing units are CO_2 favored materials due to the high affinity for CO_2 molecules [46,50]. On the other hand, silane-containing units enhance the flexibility, in view of a better diffusion of active penetrants, and hence increase the permeability [51,

52]. The Si-O linkage decreases the energy barrier of gas diffusion due to its local mobility, which enhances the diffusion coefficient of gas molecules [53,54]. Aminosilane agents with chemical structure of $\text{R}-(\text{CH}_2)_n-\text{Si}-\text{X}_3$ (R and X represent amino and hydrolysable groups, respectively) contain both amine and silane groups, having both characteristics mentioned above simultaneously. This makes them suitable choices as cross-linking agents to modify polymeric membranes for CO_2 separation. Different types of aminosilanes such as 3-aminopropyl(diethoxy)methylsilane (APDEMS) [55,56], 3-aminopropylmethyldiethoxysilane (APMDES) [57], N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AAPTMS) and 3-(2-(2-aminoethylamino) ethylamino) propyltrimethoxysilane (AEPTMS) [58] are commonly applied for improving the adhesion between inorganic fillers and the polymer in the MMMs fabrication, but the aminosilanes utilization for cross-linking of purely organic polymer membranes has been rarely reported.

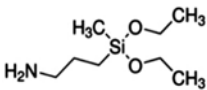
The aim of this work was to enhance the CO_2/N_2 selectivity of the highly permeable Pebax 2533 membrane. To this end, novel cross-linked Pebax membranes were prepared via a solution casting method, employing different amounts (0.5 to 4 wt%) of 3-aminopropyl(diethoxy)methylsilane (APDEMS) as cross-linking agent. To the best of our knowledge, this is the first study on cross-linked Pebax membranes using APDEMS as cross-linker for gas separation applications. The physico-chemical properties of the neat and cross-linked membranes were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), differential scanning calorimeter (DSC) and X-ray diffraction (XRD) in order to better investigate the effect of cross-linking reaction on morphology, thermal property and crystallinity of the fabricated membranes. The CO_2/N_2 gas separation performance of the membranes was analyzed. The effect of the APDEMS concentration on the performance of the resulting Pebax membranes was investigated at different operating pressures (2–10 bar).

EXPERIMENTAL

1. Materials

Pebax 2533 (80 wt% PTMO and 20 wt% PA 12 (nylon-12)) in pellet form was acquired from Arkema (Colombes, France). 3-Aminopropyl(diethoxy)methylsilane (97%, APDEMS) was purchased from Sigma Aldrich (Saint Louis, MO, USA). 1-Butanol (99.5%) was acquired from Merck (Darmstadt, Germany). Carbon dioxide

Table 1. Chemical structures and properties of materials

| Name | Chemical formula | Structure | Abbreviation | Molar mass | Density [g/cm ³] |
|--|---|---|--------------|------------|------------------------------|
| Poly (ether-block-amide) (Pebax 2533) | Poly tetramethylene oxide (80 wt%) | $\text{-(CH}_2\text{)}_4\text{-O-}_n$ | PTMO | | |
| | Polyamide 12 (20 wt%) | $\text{-(NH-(CH}_2\text{)}_{11}\text{-C(=O)-}_n$ | PA 12 | - | 1.01 |
| 3-Aminopropyl(diethoxy) methylsilane | $\text{CH}_3\text{Si(OC}_2\text{H}_5\text{)}_2\text{(CH}_2\text{)}_3\text{N}_2$ |  | APDEMS | 191.34 | 0.916 |

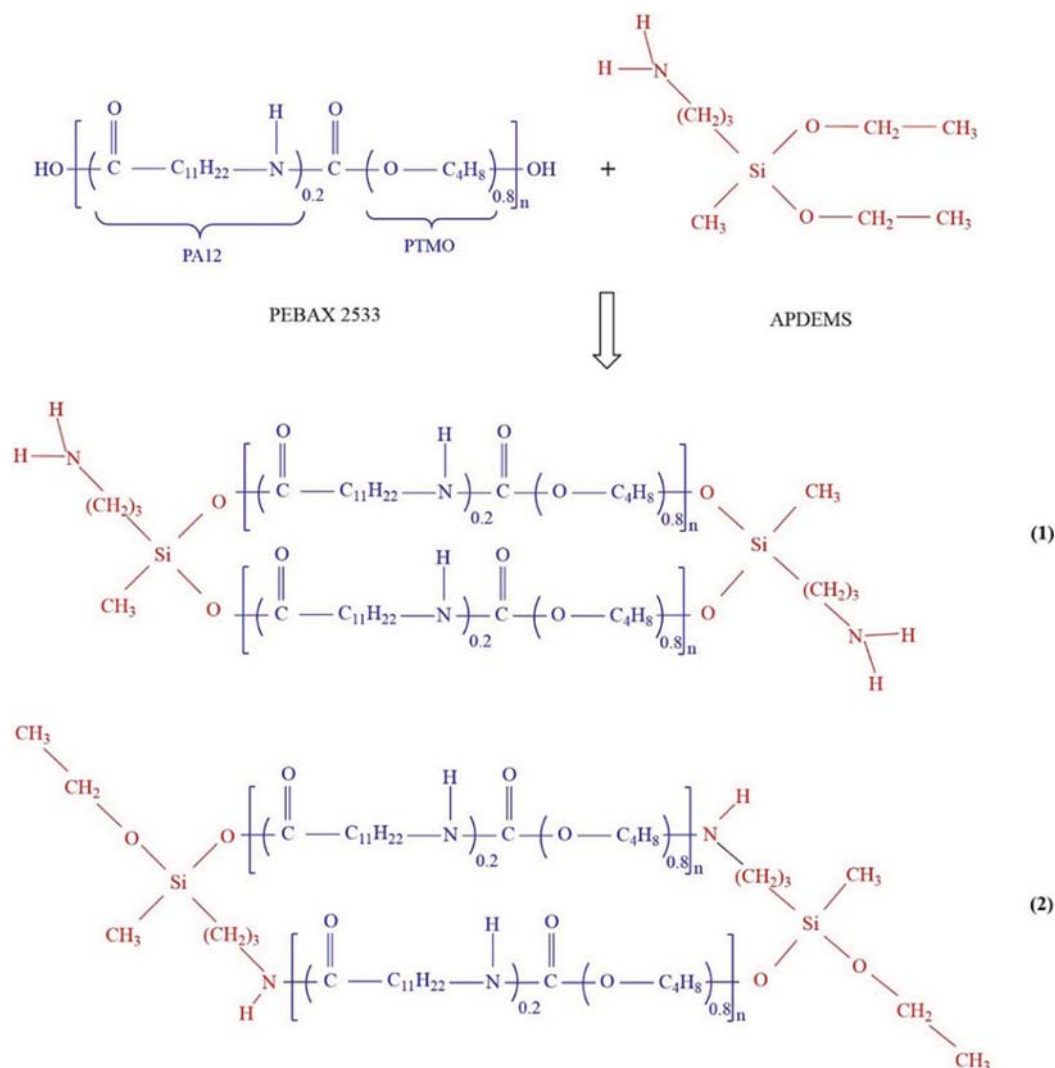


Fig. 1. Chemical structure of Pebax 2533 and APDEMS cross-linker (top), and the possible reactions between Pebax 2533 and APDEMS (bottom).

and nitrogen with 99.99% purity were supplied by Oxygen-Yaran Co., Mahshahr, Iran. The chemicals were used with no excess purification. Table 1 shows chemical structures and properties of the materials.

2. Membrane Preparation

Cross-linked membranes were prepared via a solution casting and solvent evaporation method to form an isotropic dense structure. Pebax 2533 pellets were dissolved in 1-butanol to prepare a 3 wt% Pebax solution. The mixture turns to a homogeneous solution after 4 h stirring at 45 °C. In the next step, APDEMS as the cross-linking agent was added to the Pebax solution. To consider the aminosilane concentration effect on the membrane structure/properties, different amounts of APDEMS from 0 to 4 wt% (based on the polymer) were added dropwise to the Pebax solution at 80 °C. This solution was stirred for one hour to ensure that the crosslinking reaction was completed. The reaction conditions were selected according to the literature [48,59]. The solution was cooled to ambient temperature and left for one hour to achieve a bubble-free homogeneous solution. Afterwards, the solution was poured

into a Teflon Petri dish (7 cm in diameter) and placed at ambient temperature for 3-4 days until the solvent was evaporated. The casted membranes were put into a 50 °C oven for 48 h and then in a 50 °C vacuum oven for 2 h in order to remove the remaining solvent. The prepared cross-linked membranes were used for gas separation characterization.

Fig. 1 depicts the chemical structure of Pebax 2533, APDEMS and also the possible cross-linking reactions. The reaction between Pebax 2533 and APDEMS may occur in two possible forms. The first one is a reaction between the ethoxy group of APDEMS and the hydroxyl group of the polymer chain, with elimination of ethanol molecules (Fig. 1(1)). The second one is a reaction between the amine group of APDEMS and hydroxyl groups of the polymer chain with elimination of water molecules (Fig. 1(2)). The possibility of occurrence of these reactions will be evaluated by FTIR analysis to realize how the cross-linking reaction is performed.

3. Membrane Characterization

3-1. Scanning Electron Microscope (SEM)

The cross-sectional and surface morphologies of the synthesized

membranes were observed by scanning electron microscopy (TESCAN VEGA3 model). Before the scanning, the freeze-fractured membrane samples were coated with conducting gold to avoid electron beam charging. The measurements were carried out at acceleration voltage of 20.0 kV, magnification of 1.50-2.00 kx, with a secondary electrons (SE) detector, working distance of 7.82-9.42 mm and view field of 104-138 μm .

3-2. Fourier Transform Infrared (FTIR) Spectroscopy

The membranes' structural properties were investigated by Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflection (ATR) mode, using the OPUS software 3.0 via a Vector 22 spectrometer (Bruker Inc., Karlsruhe, Germany) in the range of 600-3,800 cm^{-1} at resolution of 4 cm^{-1} .

3-3. Differential Scanning Calorimeter (DSC)

Thermal properties of prepared membranes were investigated with a DSC1 Mettler Toledo calorimeter (Mettler Toledo, Greifensee, Switzerland). The heating rate was 10 $^{\circ}\text{C}/\text{min}$ at the temperature range of -100 to 250°C . DSC thermograms were reported from second heating run of about 13 mg membrane samples.

3-4. X-ray Diffraction (XRD)

The XRD pattern of the membranes was collected with a X'Pert Pro wide angle X-ray diffractometer from Panalytical (Panalytical Inc., Almelo, The Netherlands) using $\text{Cu K}\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation.

4. Gas Permeation Experiments

The gas permeability of the prepared membranes was measured with a constant volume apparatus using single gases (CO_2 and N_2). A simplified diagram of the gas permeation set-up was shown in Fig. 2. The membrane sample was placed in the permeation cell with the effective membrane area of 15.9 cm^2 . Pure gas was fed on the upstream side of the membrane and passed across the membrane which was collected in a constant volume downstream. The amount of gas passing through the membrane was measured by evaluating the increase of downstream pressure using an absolute

pressure transmitter (type 691, pressure range of 0-0.1 bar, accuracy of $\pm 0.3\%$ full scale, Huba Control, Würenlos, Switzerland). All the gas permeation tests for the membranes were measured at ambient temperature (about 25°C) and different feed pressures (2-10 bar).

The permeability of the membranes was calculated with Eq. (1):

$$P = \frac{273.15 \times 10^{10} V l}{A T (P_0 \times 76)} \left(\frac{dp}{dt} \right) \quad (1)$$

where P , V , l , and p are the gas permeability in Barrer (1 Barrer = $1 \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ cmHg s}$), the dead-volume of the downstream chamber (cm^3), the membrane thickness (cm), and the feed pressure (atm). dp/dt is the steady state portion of the p - t curve for the increase in pressure of the downstream side (atm/s), A is the effective membrane area (15.9 cm^2), and T is the absolute temperature (K). The reported values of permeability are the arithmetic mean of permeability data obtained from three same membrane samples to ensure the reliability of the achieved data.

The ideal selectivity of one penetrant over another one was calculated through Eq. (2):

$$\alpha_{x/y} = \frac{P_x}{P_y} \quad (2)$$

where $\alpha_{x/y}$ is the ideal selectivity, P_x and P_y show the permeability values of pure gas x and y respectively, in the same conditions.

RESULTS AND DISCUSSION

1. SEM

SEM analyses were performed on all prepared membranes to investigate the effect of the APDEMS cross-linking reaction on the morphology of Pebax based membranes. The cross-sectional (I) and surface (II) morphologies of Pebax membranes with different APDEMS content varying from 0 to 4 wt% are presented in Fig. 3.

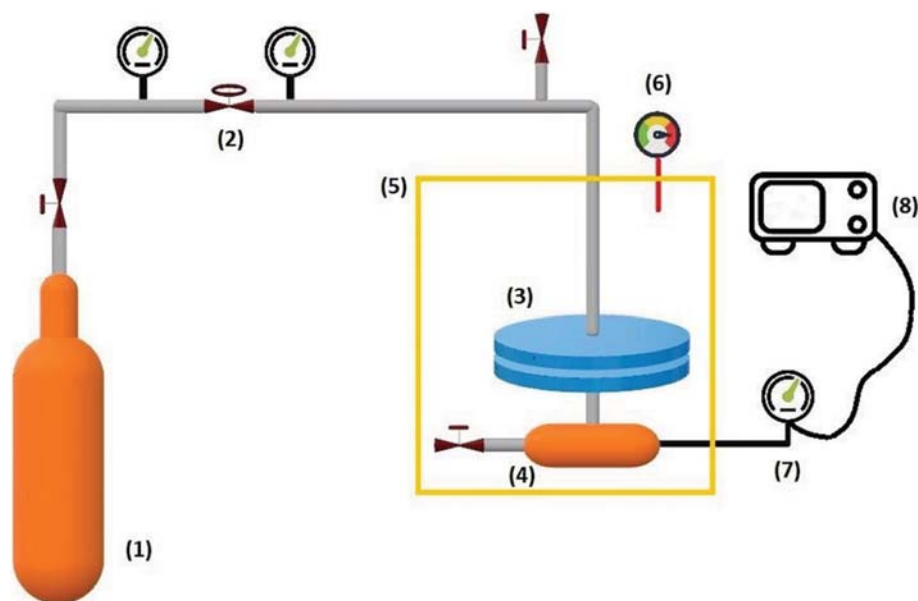


Fig. 2. Schematic diagram of gas permeation constant volume/variable pressure set-up. (1) Gas cylinder, (2) pressure regulator, (3) membrane cell, (4) permeate chamber, (5) oven, (6) temperature transmitter, (7) pressure transmitter, (8) pressure indicator.

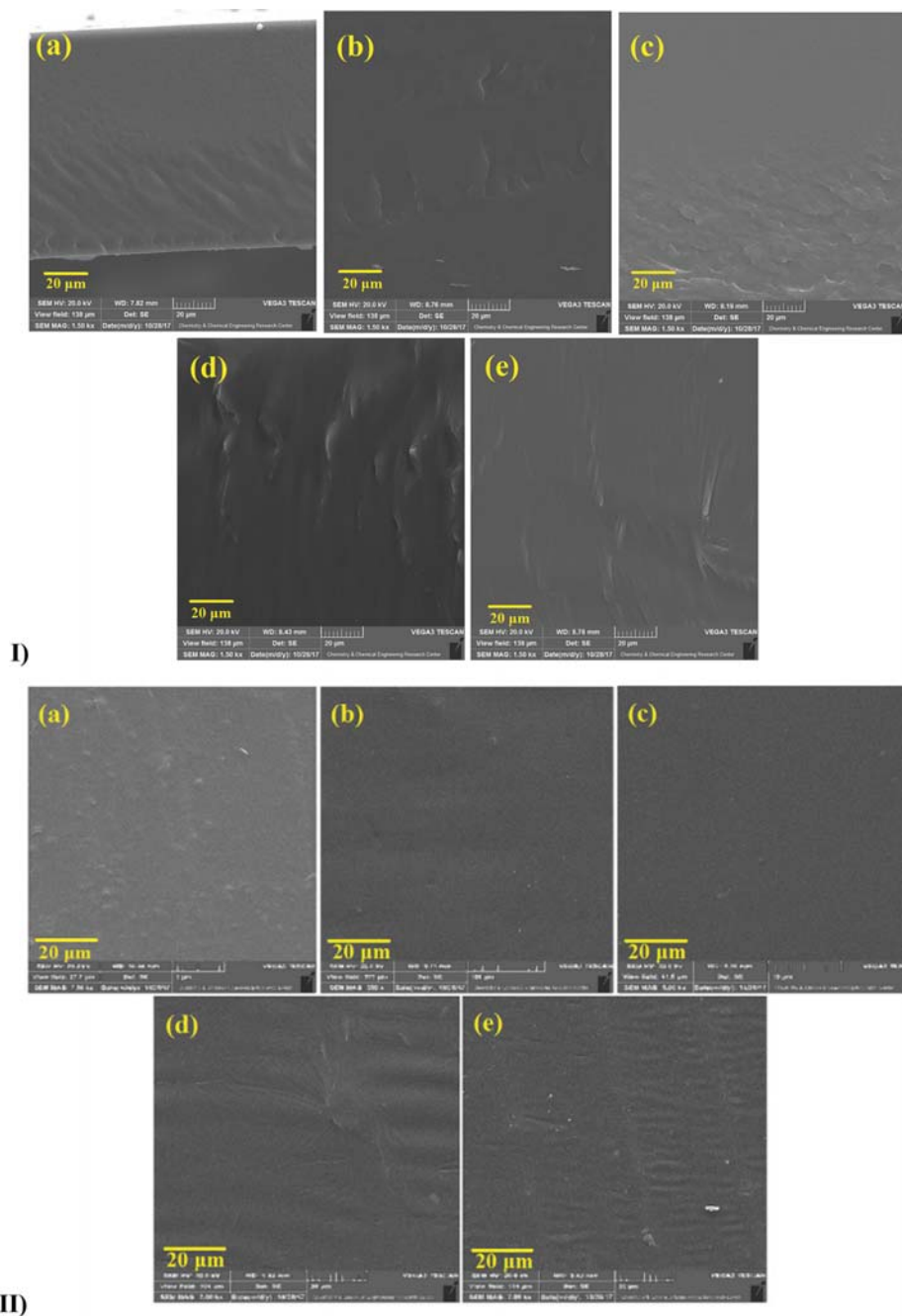


Fig. 3. (I) Cross-sectional and (II) surface SEM images of (a) Pebax 2533, (b) Pebax/APDEMS (0.5 wt%), (c) Pebax/APDEMS (1 wt%), (d) Pebax/APDEMS (2 wt%), (e) Pebax/APDEMS (4 wt%).

According to Fig. 3(I-a), the neat Pebax membrane has a dense, uniform and defect-free structure. By the cross-linking reaction, the polymeric matrix became more compacted and the crystallinity is increased, as confirmed by XRD analysis (see section 3.4). As observed in Fig. 3(I-b-e), the cross-sectional morphology of the modified membranes has more wrinkles, which may be randomly formed during the membrane preparation. It is assumed that the APDEMS cross-linking reaction can decrease the polymer free volume, which results in difficult and slower solvent evaporation during the membrane formation and creates a more compact struc-

Table 2. Fractional free volume (FFV) of Pebax 2533 based membranes

| Membrane | FFV (%) |
|------------------------|---------|
| Pebax 2533 | 2.97 |
| Pebax/APDEMS (0.5 wt%) | 2.76 |
| Pebax/APDEMS (1 wt%) | 2.69 |
| Pebax/APDEMS (2 wt%) | 2.56 |
| Pebax/APDEMS (4 wt%) | 2.48 |

ture. In this regard, the FFV of each polymeric membrane was determined experimentally through the density measurement approach presented in [60]. The FFV values for all the membrane samples were reported in Table 2. The values reveal that the FFV decreases from 2.97% for the neat Pebax to 2.48% for the 4 wt% APDEMS cross-linked membrane. Therefore, the transport of larger molecules through the cross-linked membrane will be limited, which increases the efficiency. Moreover, as depicted in Fig. 3(II), by increase in the cross-linking reaction the membrane surfaces become smoother up to 2 wt% cross-linker loading, and then, it can be observed a rougher surface by 4 wt% loading. Up to 2 wt% APDEMS loading, the FFV decreases and its consequent compaction of the

membrane structure governs the surface morphology that results in a smoother surface. Exceeding 2 wt%, the dominant mechanism for the formation of surface morphology is the enhanced polymer-solvent intermolecular forces; it will be followed by a difficult stress release or relaxation of the polymer chains during the casting solvent evaporation from a highly compact cross-linked structure which will lead to surface shrinkage [61]. In general, no obvious defects are observed in the SEM images, which indicates the proper membrane formations.

2. FTIR

FTIR analysis was carried out to evaluate the possibility of occurrence of the expected reactions, and to verify the effect of the

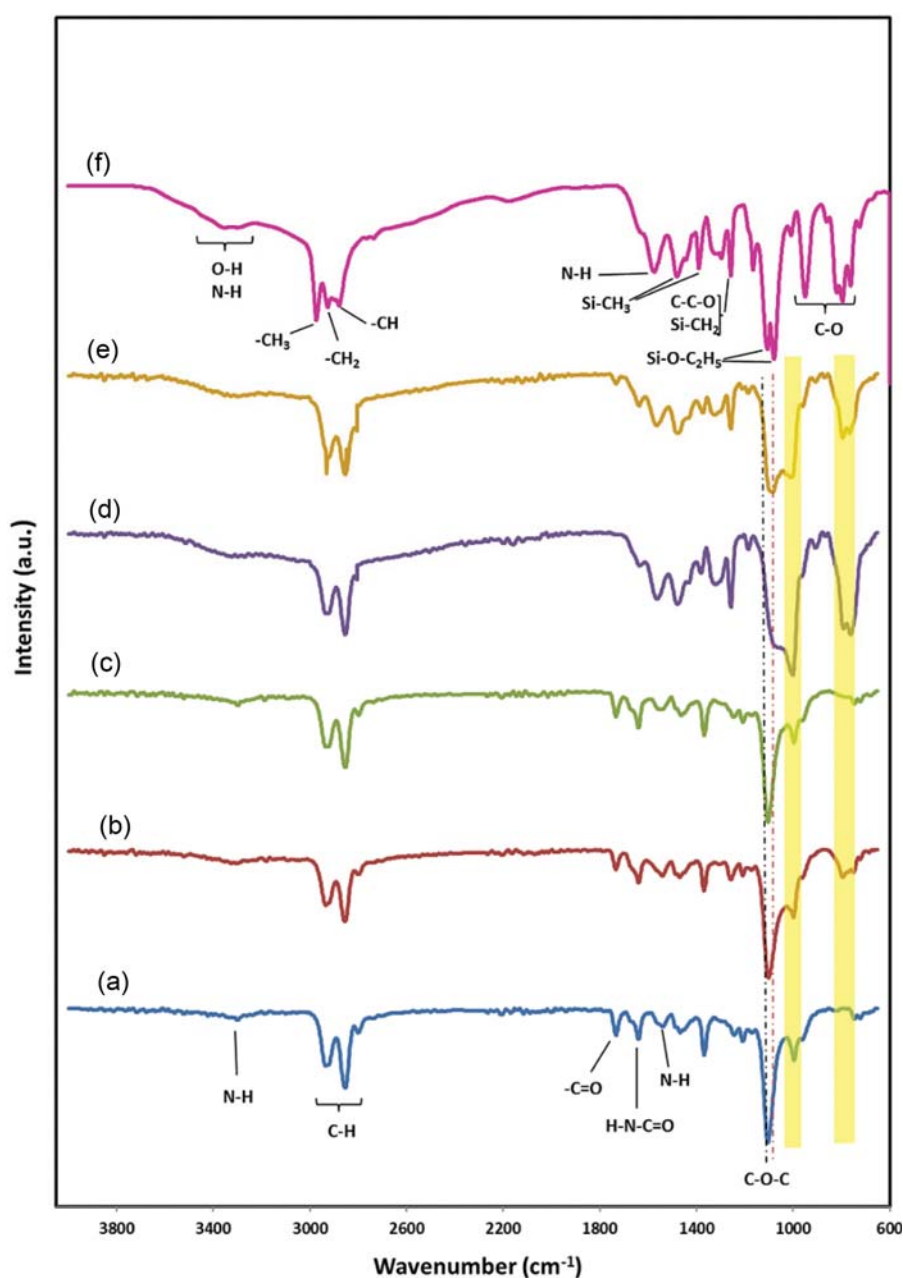


Fig. 4. FTIR spectra of (a) Pebax 2533, (b) Pebax/APDEMS (0.5 wt%), (c) Pebax/APDEMS (1 wt%), (d) Pebax/APDEMS (2 wt%), (e) Pebax/APDEMS (4 wt%), (f) APDEMS.

APDEMS concentration on the structure of the cross-linked polymer. FTIR spectra of APDEMS cross-linking agent, pristine Pebax 2533 membrane and cross-linked Pebax membranes (0.5-4 wt% APDEMS cross-linking agent) in the region of 600-3,800 cm⁻¹, are presented in Fig. 4. As can be observed in Fig. 4(a), absorption bands of pure Pebax are located at 1,103 cm⁻¹ (-C-O-C- stretching), 1,538 cm⁻¹ (bending of N-H in PA), 1,640 cm⁻¹ (stretching of -C=O in H-N-C=O), 1,734 cm⁻¹ (stretching of -C=O in PA), 2,853 and 2,935 cm⁻¹ (-C-H bending), and 3,300 cm⁻¹ (stretching of N-H in PA), which is in accordance with the literature [62,63].

Fig. 4(f) shows characteristic bands of APDEMS functional groups. The absorption bands at 1,075, 1,100 and 1,165 cm⁻¹ represent the Si-O-C₂H₅ stretching vibrations. The occurrence of absorption bands at 1,258 and 1,297 cm⁻¹ corresponds to Si-CH₂ and Si-CH₃ stretching, respectively. The N-H stretching and its bending vibrations are situated at 3,485 and 1,575 cm⁻¹, respectively. The absorption bands at 1,258 cm⁻¹ (C-C-O stretching) and near 750 to 950 cm⁻¹ (C-O stretching) are related to the ether groups of APDEMS. It has been noticed that the alkoxy C-C-O stretching frequency is similar to that of Si-CH₂. The asymmetric stretching vibrations of -CH, -CH₂ and -CH₃ are situated at 2,879, 2,926 and 2,973 cm⁻¹, respectively. Furthermore, the absorption bands at 1,390 and 1,482 cm⁻¹ are assigned to -CH₃ and -CH₂ bending vibrations [55,56,64].

FTIR spectra of cross-linked Pebax membranes (0.5-4 wt%) are illustrated in Fig. 4(b)-(e). The results were studied to investigate how the reaction occurs between the APDEMS and Pebax molecules. By increasing the APDEMS content, the absorption band at 1,103 cm⁻¹ (represents C-O stretching) shifts to a lower wave number, which confirms the covalent bond formation between the ethoxy group of APDEMS and the hydroxyl group of the PE segment. As observed, the position of both absorption bands at 1,734 and 3,300 cm⁻¹ related to -C=O and N-H stretching in PA segment is not affected by the cross-linking reaction, which allows us to conclude that there is no interaction between APDEMS and the PA segment of Pebax. It is concluded that the cross-linking reaction mainly occurs between the APDEMS and PE segments. According to the spectra in Fig. 4(b)-(e), the appearance of absorption bands in the range of 1,075-1,165 cm⁻¹ (Si-O-C₂H₅) and more intensive bands at 750-950 cm⁻¹ (C-O stretching) indicates the increased APDEMS agent value in cross-linked membranes. In addition, considering the spectrum e related to the cross-linked membranes with 4 wt% of APDEMS, a three-dimensional network of APDEMS could be created at a higher amount of APDEMS, which shows the same absorption bands as the APDEMS spectrum. This is an indication of the presence of unreacted APDEMS at this loading.

3. DSC

DSC analyses were performed to investigate the thermal properties of the neat and aminosilane cross-linked membranes. Fig. 5 shows the effect of the cross-linking reaction on Pebax membranes upon the second heating cycle of DSC thermograms. The pure Pebax 2533 thermogram displays a glass transition temperature (*T_g*) peak at -77 °C, which is related to the PE phase; however, the *T_g* of the PA phase is not observable by DSC. Moreover, two endothermic peaks are observed as well. The first one is between -18 °C and 27 °C with a maximum at 9.7 °C, which represents the melt-

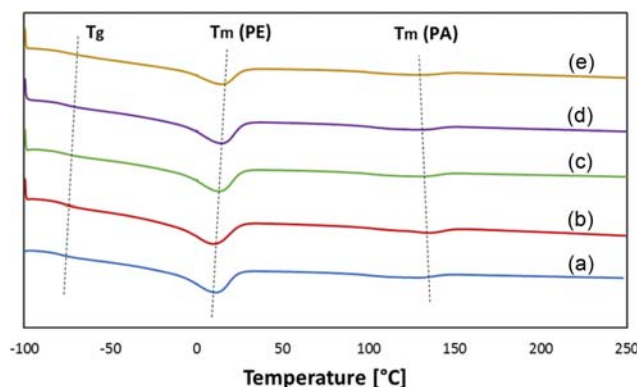


Fig. 5. DSC thermograms of (a) Pebax 2533, (b) Pebax/APDEMS (0.5 wt%), (c) Pebax/APDEMS (1 wt%), (d) Pebax/APDEMS (2 wt%), (e) Pebax/APDEMS (4 wt%).

ing temperature (*T_m*) of the PE segment. Other studies reported the values of 12.7 °C [65] and 9.56 °C [66] for the *T_m* of PE segment. The second one is between 115 °C and 150 °C, having a maximum at 134 °C, corresponding to the melting temperature of the PA segment which was reported by other studies above 100 °C [65], 136.63 °C [66] and 140 °C [67]. Therefore, the obtained results are in accordance with the DSC result of the literature for neat Pebax 2533 [65-67]. Considering the DSC thermograms of cross-linked membranes (see Fig. 5(b)-(e)), a slight increase in the melting temperature peaks of the PE segment can be observed when the APDEMS content is increased. This suggests that the interaction between APDEMS and PE blocks results in a cross-linked structure, which confirms the FTIR analysis. As the APDEMS content increases, the melting temperature peak of PA segments shifts to a lower temperature, which is explained by the reduction of the crystalline phase of PA. The reduction of interchain hydrogen bonding results in a decrease of the crystallinity and finally the melting point will be reduced.

This confirms that the presence of APDEMS is able to change the thermal properties of the PA segment, even when no chemical reaction occurs according to the FTIR analysis results. In addition, the *T_g* of the modified membranes has increased compared to pure Pebax due to the cross-linking reaction, which limits the mobility of the polymer chains.

4. XRD

The XRD patterns for pure and cross-linked membranes are shown in Fig. 6. Pebax 2533 as a semicrystalline polymer has a very intense diffraction peak at a 2θ value of 20.37°, which is related to the crystalline PA segments. The diffraction peaks at 2θ values of 10° and 23.28° with lower intensity are related to amorphous PE segments of the Pebax structure [48,68,69].

The XRD patterns obtained from cross-linked membranes show more intense diffraction peaks at 10° and 23.28° of 2θ compared to the neat Pebax membrane; the peak intensities of PE segment are also increased by increasing the amount of APDEMS cross-linking agent. The enhanced crystallinity of the PE segments can be explained by the formation of covalent bonds between APDEMS and PE blocks, which restricts the chains mobility. On the other hand, as can be observed, an increase in APDEMS leads to a less

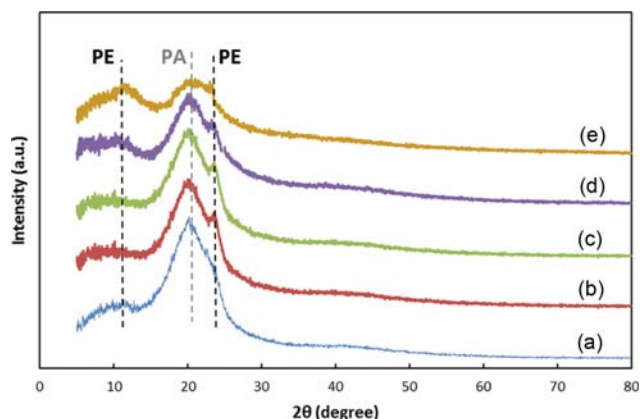


Fig. 6. XRD patterns of (a) Pebax 2533, (b) Pebax/APDEMS (0.5 wt%), (c) Pebax/APDEMS (1 wt%), (d) Pebax/APDEMS (2 wt%), (e) Pebax/APDEMS (4 wt%).

intense diffraction peak at a 2θ value of 20.37° related to the PA segment, which is due to the cohesive energy reduction between the crystalline segments. Thus, the presence of APDEMS in the polymer structure restricts the interchain interactions, although no reaction occurs between APDEMS and PA segments based on FTIR analysis results. As the 80 wt% of Pebax 2533 is composed of soft amorphous PE blocks, the Pebax crystallinity is more affected by an alteration in crystallinity of the PE blocks. The increment of PE crystallinity through the cross-linking reaction can result in an enhancement in gas separation selectivity of cross-linked membranes.

5. Gas Permeation

5-1. Effect of APDEMS Concentration

Gas permeation properties of cross-linked Pebax membranes were determined at ambient temperature and a feed pressure of 2 bar. The cross-linked Pebax membranes, with a range of APDEMS concentrations (0–4 wt%), were tested to analyze the effect of the cross-linking concentration on the permeability/selectivity of the membranes. Gas permeation results reveal that the cross-linking reaction leads to a remarkable increase in CO_2/N_2 selectivity of all membrane samples, as shown in Fig. 7. Overall, the cross-linking reaction decreases the gas molecular transports through the polymer chains by decreasing the fractional free volume of the polymer.

The CO_2 permeability decreased from 183 to 170 Barrer for the 0.5 wt% aminosilane cross-linked membrane compared to the pristine Pebax membrane, and continued to decrease to 150 Barrer by increasing the amount of APDEMS to 2 wt%. Finally, at 4 wt% of APDEMS there was a decrease of 51% in CO_2 permeability. Similarly, the N_2 permeability decreased by about 75% for 4 wt% APDEMS. In contrast, the ideal selectivity increased by 14, 43, 91 and 115%, respectively, by adding 0.5, 1, 2 and 4 wt% APDEMS. As the aminosilane concentration increased, the permeability of N_2 showed a higher reduction than the CO_2 permeability, which caused an increase in the ideal selectivity between CO_2/N_2 . The cross-linking reaction increased both the membrane compaction and crystallinity, which was confirmed by SEM and XRD analysis. As a result, the gas transport pathways decreased. Therefore, the diffusion of N_2 molecules through the membrane decreased, due to the larger kinetic diameter of N_2 molecules (3.64 \AA) com-

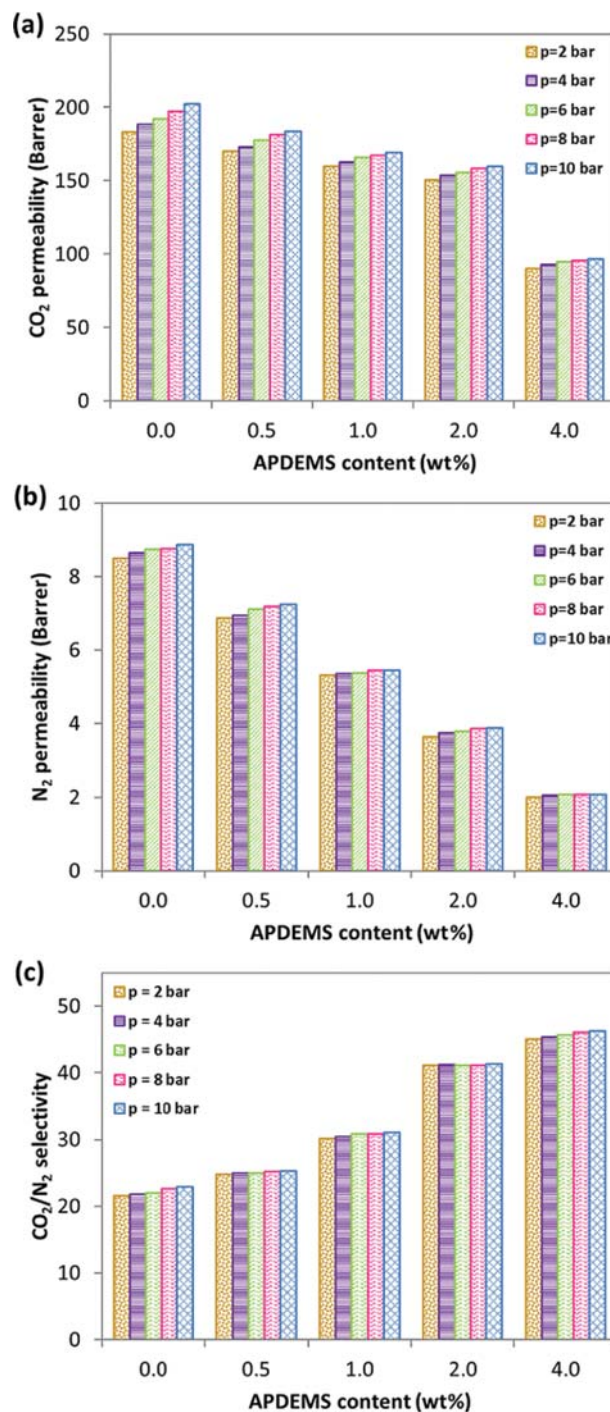


Fig. 7. The effect of APDEMS concentration on (a) CO_2 permeability, (b) N_2 permeability, and (c) CO_2/N_2 selectivity of Pebax 2533 membrane at ambient temperature.

pared to CO_2 (3.3 \AA); finally, the diffusivity-selectivity of the membrane increased. Additionally, the carbonyl groups in the ether soft segments of the Pebax structure have desirable interactions with CO_2 molecules due to their quadrupole moments. Moreover, the amine groups of APDEMS have a strong affinity for CO_2 , cross-linking could enhance the CO_2 solubility, which increased the CO_2/N_2 solubility selectivity. Therefore, the overall selectivity enhanced

Table 3. Pebax based membrane performances

| Membrane | Test conditions | P CO ₂ (Barrer) | α CO ₂ /N ₂ | Ref. |
|-------------------|-----------------------------|----------------------------|--|-----------|
| PEBAX 2533 | Ambient temperature, 10 bar | 202 | 22.8 | This work |
| PEBAX/APDEMS 0.5% | | 183 | 25.3 | |
| PEBAX/APDEMS 1.0% | | 169 | 31 | |
| PEBAX/APDEMS 2.0% | | 160 | 41.3 | |
| PEBAX/APDEMS 4.0% | | 96 | 46.3 | |
| PEBAX 1074 | 35 °C, 10 bar | 120 | 51.4 | [34] |
| PEBAX 4033 | 35 °C, 10 bar | 113 | 20.4 | [34] |
| PEBAX 4011 | 35 °C, 10 bar | 66 | 56.4 | [34] |
| PEBAX 1657 | 35 °C, 10 bar | 89 | 68 | [71] |
| PEBAX 3533 | 25 °C, 4 bar | 132 | 61 | [73] |
| PEBAX 1878 | 25 °C, 4 bar | 9.6 | 4.8 | [70] |
| PEBAX 1041 | 25 °C, 4 bar | 23.3 | 33.3 | [70] |
| PEBAX 1205 | 25 °C, 4 bar | 93 | 24.5 | [70] |
| PEBAX 1657 | Ambient temperature, 10 bar | 55.85 | 40.17 | [72] |
| PEBAX 1657/TDI | | 13.38 | 55.75 | |

through increase in both the diffusivity selectivity and solubility selectivity.

The best separation performance was obtained for a Pebax membrane cross-linked with 2 wt% of APDEMS. The CO₂/N₂ ideal selectivity was dramatically enhanced, by 91%, while the CO₂ permeability slightly dropped, by about 18% compared to the pristine polymer at feed pressure of 2 bar.

For a better evaluation, the achieved results were also compared with other Pebax based membrane performances reported in the literature, as presented in Table 3. It is apparent that the 2 wt% cross-linked Pebax 2533 membrane has an acceptable performance compared to other five grades of Pebax 1074, 4011 [34], 1878, 1041 and 1205 [70]. Moreover, its permeability and selectivity are relatively about 102% and 41% higher than those for Pebax 4033 [34]. Although the selectivity of Pebax 2533/APDEMS (2 wt%) membrane is 39% lower than Pebax 1657 (which has the highest selectivity value between the other Pebax grades), it has a considerably (~79%) higher permeability [71]. Moreover, APDEMS as a cross-linker increased the CO₂/N₂ selectivity of Pebax 2533 by 91% which is about twice higher than the selectivity increment obtained by using the TDI as cross-linker for Pebax 1657 [72]. And this is also important that the TDI decreased the CO₂ permeability about four-fold higher than the corresponding decrease by the APDEMS. It could be due to the considerable chemical affinity of APDEMS towards CO₂ molecules which discussed earlier.

5-2. Effect of Feed Pressure

The operating pressure provides the required driving force for gas molecules to be transported through the membrane. Increasing the feed pressure has two contrary effects on the pure gas permeability. An increment of the feed pressure can enhance the solubility of gases by increasing the gas concentration, which leads to an increase in permeability. On the other hand, the fractional free volume of the polymer decreases by increasing the feed pressure, which leads to a decrease of transport of gas molecules through the membrane. Pure gas (CO₂ and N₂) permeation tests were carried out to illustrate the feed pressure effect on the separation per-

formance of the prepared membranes. Fig. 7 depicts the separation performance of the prepared membranes versus feed pressure: Increasing the feed pressure improves the CO₂ and N₂ permeabilities for all the prepared membranes. For example, by increasing the feed pressure from 2 to 10 bar the CO₂ and N₂ permeability of 2 wt% cross-linked Pebax increases from 150 to 160 Barrer and from 3.6 to 3.8 Barrer, respectively. This enhancement is due to the solubility enhancement, as mentioned above. The higher increase of CO₂ permeability in comparison to N₂ is due to the quadrupole moment of CO₂ molecules, which have a high affinity for polar PE segments. Hydrogen bonding occurs between polarized oxygen atoms of CO₂ and amide groups of the Pebax polymer, which improves the CO₂ solubility. Moreover, CO₂ has a higher diffusion coefficient due to the smaller kinetic diameter compared to N₂ [73-75]. Therefore, as seen in Fig. 7, the ideal selectivity of CO₂ over N₂ is slightly enhanced by the feed pressure increase.

In addition, the increase of the ideal selectivity for pristine Pebax is higher than for APDEMS cross-linked Pebax membranes. This can be explained by enhanced membrane compaction, which is produced by the APDEMS cross-linking reaction.

CONCLUSIONS

A novel cross-linked Pebax 2533 membrane was prepared by aminosilane cross-linking modification. APDEMS was used as cross-linker agent in the range of 0 to 4 wt% based on the polymer to improve the CO₂/N₂ separation performance of Pebax 2533 membranes. Gas separation tests showed the best performance for a concentration of 2 wt% APDEMS, where the ideal CO₂/N₂ selectivity at 2 bar was noticeably increased by 91%; the CO₂ permeability was slightly decreased by 18% comparing to the pristine Pebax 2533 membrane.

The presence of an APDEMS cross-linker improves the Pebax membrane efficiency in three different ways. First is the chemical reaction between APDEMS and PE segments of Pebax 2533, which restricts the polymer chain mobility, and as a result, the Pebax mem-

brane becomes more crystalline, which increases the membrane selectivity. The crystallinity increment caused by the cross-linking reaction was confirmed by XRD analysis. Second, the presence of amine groups in the APDEMS structure, with a high affinity to CO₂ molecules, increases the CO₂ solubility and improves the membrane selectivity. Third is an increase of membrane compaction, which enhances the transport of CO₂ molecules through the membrane due to the smaller kinetic diameter of CO₂ compared to N₂. It should be considered that although the cross-linking reaction decreases the permeability, the presence of Si-O linkages of the aminosilane agent with local mobility would prevent the CO₂ permeability dropping down so much. Investigating the effect of operating pressure on the membrane performance showed that the CO₂ permeability increases with feed pressure, although modified membranes are not affected as much as the pristine Pebax 2533 membrane, which is due to the more compact structure of the cross-linked membranes.

Finally, it can be concluded that the cross-linking modification using APDEMS is an effective method to enhance the efficiency of Pebax 2533 membranes, and may help in developing the utilization of Pebax 2533 as membrane material at industrial scales.

CONFLICT OF INTEREST

The authors declare there is no conflict of interest.

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