



Research Paper

Pebax-Modified Cellulose Acetate Membrane for CO₂/N₂ SeparationHamidreza Sanaeepur^{1,*}, Reyhane Ahmadi¹, Mehdi Sinaei², Ali Kargari³¹ Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 38156-8-8349, Iran² Faculty of Chemical Engineering, Islamic Azad University, Mahshahr Branch, Mahshahr, Iran³ Membrane Processes Research Laboratory (MPRL), Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), No. 424 Hafez Ave., Tehran, Iran

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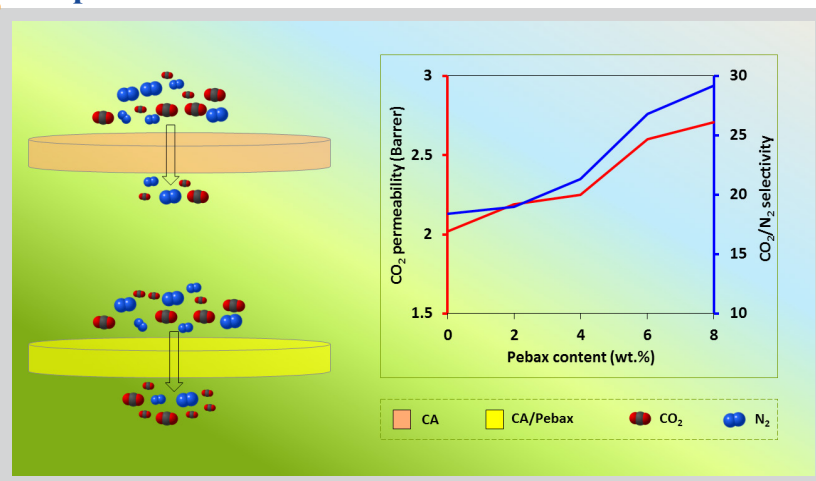
Keywords

Blend membrane
Cellulose acetate
Pebax
Gas separation
Carbon dioxide
Nitrogen

Highlights

- Blend membranes of cellulose acetate with Pebax 1657 co-polymer.
- CO₂ permeability of CA membrane increased more than 25%.
- CO₂/N₂ selectivity rises about 59% with 8 wt.% Pebax loading in the CA.

Graphical abstract



Abstract

Carbon dioxide (CO₂) releases from the exhaust gas streams of power plants that burn fossil fuels contributes the most emission of this gas, which includes more than half of the greenhouse effects. Thus, the separation of CO₂ from exhaust gases is one of the main environmental concerns. Membrane technology, due to many advantages, has attracted many research attentions among the various gas separation technologies. In this study, separation performance of cellulose acetate (CA) membrane as the most famous commercial membrane used to separate CO₂, improved through the blending method. In this regard, block co-polymer (polyether block amide), as a trade name of Pebax (Pebax® 1657), which has a proper efficiency in CO₂ separation has been used. Cellulose acetate/Pebax blend membranes are prepared by the solution casting/solvent evaporation method and their performance in CO₂ separation from N₂ was studied. The morphologies were also being investigated using SEM, FTIR, DSC and XRD. Gas permeability results showed that CO₂ permeability in CA membrane increases more than 25% and its equivalent CO₂/N₂ ideal selectivity rises about 59% with the increase in Pebax content up to 8 wt.%.

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1. Introduction

Today, climate change is one of the most important global concerns. An increase in the greenhouse gas emissions, especially for CO₂ emission, is one of the main reasons of the changes and has been led to conducting extensive researches for CO₂ separation from its emission sources at the last few decades [1, 2]. On the other hand, CO₂ can be used in various processes such as enhanced oil recovery (EOR) and gas transport to liquid (GTL). Some conventional separation technologies like chemical absorption, physical absorption, pressure swing adsorption, and cryogenic distillation in simultaneous with the newer ones like membrane separation have been used for CO₂ removal [3, 4].

Membrane separation has attracted many attentions because of low cost, modularity, low energy requirement, less space required and etc. Polymeric membranes are the common commercial membranes for CO₂ separation, but they have some limitations such as low permeability or selectivity and softening at high temperature (low thermal stability). Many researchers have been focused on finding the solutions to overcome the problems. Some ways have been tried in this case such as blending, grafting, annealing and cross-linking [4]. Polyimide (PI), poly carbonate (PC), polysulfone (PSf) and cellulose acetate (CA) are among the most common and oldest polymers that used in manufacturing the polymeric membranes for CO₂ separation [5-10].

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The chemical structure of cellulose acetate has been shown in Table 1. As could be observed, it is a polysaccharide with hydroxyl (-OH) and carbonyl (C=O) groups in main chains and oxycarbonyl groups (O=C-OH) in side chains, which improve its CO₂ separation performance [5, 11, 12]. However, the glassy structure of this polymer and its low permeability make it necessary to be modified. Sanaeepur et al. [5] studied the effect of annealing on the morphology and gas permeation properties of CA membrane. They showed that simple drying of CA membrane in the fabrication process causes many fluctuations in CO₂ permeability and selectivity. But the fluctuations were almost entirely diminished by annealing the membrane under the vacuum condition. In addition, CO₂ permeability and CO₂/N₂ selectivity decreased by annealing the CA membrane. In another study by Li et al. [13], poly (ethylene glycol) (PEG) was blended with CA to increase the CO₂ separation properties of the membrane. They showed that with the incorporation of PEG, CO₂ diffusivity increases and hence the CO₂ permeability enhances. Chitosan (CS) is a polysaccharide and so lies in a category with CA. In another work, Liu et al. [14] prepared CS/Pebax blend membranes for CO₂ separation. They showed that blending the CS with Pebax results in the increase in fractional free volume (FFV) of the membrane matrix, and hence, leads to open more gas transport channels that increases the CO₂ permeability. In addition, the results showed that a considerably high CO₂ permeability (2884 Barrer) and moderate separation factors (23.2 for CO₂/CH₄ and 65.3 for CO₂/N₂) attain when the mass ratio of CS to Pebax is 1:1.

In this work, CA polymer was blended with Pebax 1657 copolymer in order to enhance the CO₂ separation performance of CA membrane. Using the copolymers such as Pebax in preparation of gas separation membranes has attracted enormous interests because of their favorable properties as well as the reduction in costs associated with the synthesis of new polymers. Pebax is a thermoplastic elastomer with two segments, a hard polyamide (PA) segment and a soft polyether (PE) segment. The former provides mechanical strength and the latter enhances the permeability due to the high movement in ether linkages [15]. As shown in Table 1, Pebax 1657 copolymer has a linear structure composed of 40% aliphatic nylon-6 as PA block and 60% poly (ethylene glycol) as PE block [16]. Special properties of this copolymer are affected by the chemical nature and the relative amounts of each PA and PE compartments. Suitable mechanical properties, good separation performance at low temperature, high dynamic properties and easy processability are the most important characteristics of the copolymer. CO₂ has a strong interaction with the carbonyl groups of the PA segments. In addition, rotation of chains at the soft PE units provides a high permeability for CO₂ [17].

2. Experimental

2.1. Materials

Cellulose acetate (M.W. ~30,000) was purchased from Sigma-Aldrich

(USA). Pebax (Pebax[®] MH 1657) was acquired from Arkema (France). The polymers were dried at 90 °C in a vacuum oven for 24 h before use. Acetic acid were purchased from Merck (Germany) and used as solvent. CO₂ and N₂ gases with 99.999% purity were supplied by Oxygen Yaran Co. (Iran).

2.2. Membrane preparation

In order to prepare CA/Pebax blend membranes, as could be observed in Figure 1, the pure CA and Pebax polymers were dissolved individually in the acetic acid solvent at 45 °C for 12 h to obtain two batches of 10 wt.% of polymer solutions. Then a certain amount of Pebax solution was added to CA solution in a glass bottle and stirred for 6 h to obtain a final solution with the desired composition. Next the solution was remained stationary at 45 °C for 6 h in order to degassing. After that a bubble-free solution was casted on a clean glass plate by a stainless steel casting knife with the clearance of 300 μm. The final blend membranes were obtained by drying the casted solution at room temperature overnight and then in a vacuum oven at 50 °C for 24 h. Therefore the CA/Pebax membranes with different amounts of Pebax (0-10 wt.%) were prepared. It should be noted that the membrane containing 10 wt.% of Pebax (CA/Pebax (10 wt.%) displayed macro-phase separation, and thus, put away from the permeability tests.

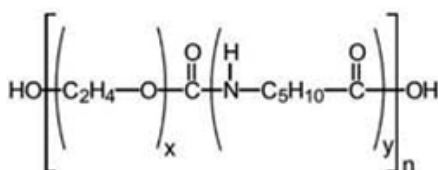
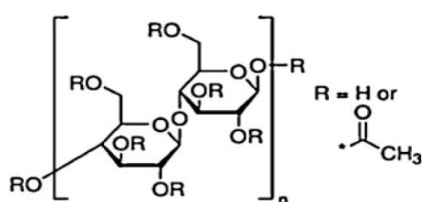
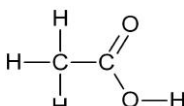
2.3. Characterization

Scanning electron microscopy (SEM) was applied to analyze the morphologies of the CA/Pebax membranes. In this case, first the membrane samples were put in liquid nitrogen and fractured. Then, they coated with metallic gold by a BAL-TEC SCD 0.005 sputter coater (BAL-TEC AG, Liechtenstein) and next were tested by SEM (KYKY-EM 3200, China). The glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) of the samples were determined by differential scanning calorimetry (DSC) analysis (second heating-cooling). It was performed by using a DSC1 (model 823 e, Mettler Toledo, Switzerland) instrument. In this case, the samples (8 mg) were heated from -100 to 250 °C at a rate of 10 °C/min under the nitrogen atmosphere. Fourier transform infrared (FTIR) spectroscopy was employed to determine the possible intermolecular interactions between CA and Pebax. It was accomplished by using a spectrophotometer (VEATOR 22 Model, Bruker Inc., USA) in the scan range of 400-4000 cm⁻¹. X-ray diffraction (XRD) patterns of the membranes was carried out by Panalytical X'pert Pro diffractometer (The Netherlands) to determine the micro-structure properties for the membranes.

2.4. Gas permeation measurements

Gas permeation test was conducted by using a constant volume /variable pressure method in the pressure range of 2-10 bar and temperature of 25 °C in order to determine the pure gas permeability of the prepared membranes.

Table 1
Chemical structure of the materials applied in this study [18, 19].

Name	Abbreviation	Molecular structure
Poly (ether-6-block amide)	Pebax 1657 X = PEO Y = PA	
Cellulose acetate	CA	
Acetic acid	AcOH	

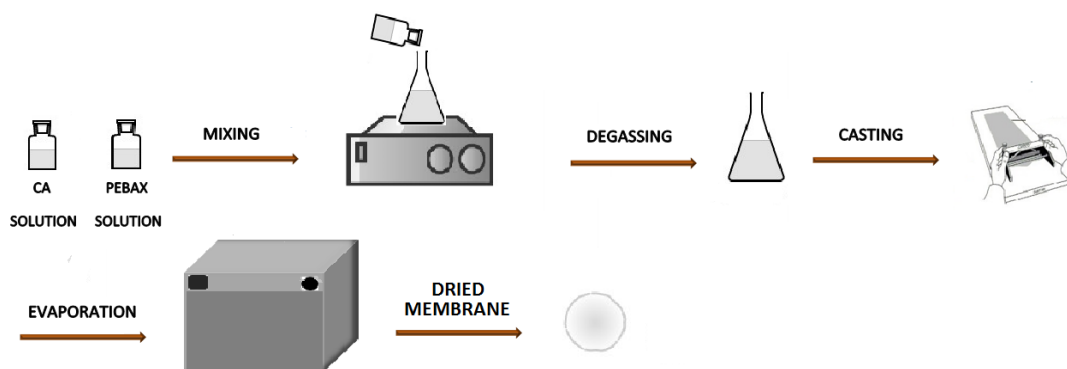


Fig. 1. A schematic representation of the membrane preparation.

Figure 2 shows a schematic representation of the permeation test apparatus which applied for this study. The gas permeability, diffusion coefficient, and solubility coefficient and the ideal selectivity of CA/Pebax blend membranes were calculated by using the following equations:

$$P = \frac{27315 \times 10^{10} V l}{A T (p_0 \times 76)} \left(\frac{dp}{dt} \right) \quad (1)$$

$$D = \frac{l^2}{6\theta} \quad (2)$$

$$P = D \times S \quad (3)$$

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (4)$$

3. Results and discussions

3.1. FTIR analysis

Figure 3 depicts FTIR spectra of the membrane samples: pure CA, Pure Pebax, CA/Pebax 2wt.% and CA/Pebax 8wt.% blend membranes. As seen, CA shows a broad absorption band at 3475 cm^{-1} that corresponds to $-\text{OH}$ stretching vibrations of the hydroxyl group in the CA structure. In addition, a band appears at 1639 cm^{-1} that attributes to the interlayer stretching and bending vibration modes of molecular water. The characteristic bands of CA at $1737 \text{ (C=O stretching)}$, $1367 \text{ (CH}_3 \text{ symmetric deformation)}$, $1215 \text{ (acetate C-C-O stretching)}$, and $1032 \text{ (C-O stretching)}$ cm^{-1} are clearly observed which are generally in accordance with the other literature results [20, 21]. Furthermore, absorptions at 2922 and 1431 cm^{-1} are attributed to CH_3 asymmetric stretching and CH_3 asymmetric deformation, respectively. The characteristic band of the saccharide structure of CA are observed at $1160 \text{ (stretching of the C-O- bridge)}$, 1121 and $1032 \text{ (skeletal vibrations involving the C-O stretching)}$ cm^{-1} . The absorption band at 900 cm^{-1} is attributed to the β -linked glucan structure. The absorption band at 690 cm^{-1} corresponds to the C-OH out of plane bending mode [22]. For pure Pebax membrane the characteristic bands at around 874 , 1099 , 1732 and 2867 cm^{-1} are the stretching vibrations of $-\text{OH}$, C-O , C=O and $-\text{CH}_3$ groups. In addition the bands at 1688 and 3300 cm^{-1} are attributed to H-N-C=O and N-H groups, respectively [23]. There are two new bands at 1544 and 3300 cm^{-1} in the FTIR spectra of CA/Pebax 2wt.% in comparison with pure CA, which indicate the interactions of Pebax and CA. The absorption band in 3300 cm^{-1} , which is attributed to the hydrogen bonding in $-\text{N-H}$ groups and strengthened with increasing in the Pebax content. The FTIR spectra of CA/Pebax 8wt.% shows a minor change in the band intensity, in comparison with CA/Pebax 2wt.%. Furthermore, as seen in Figure 3, no new peaks appeared in FTIR spectra of CA/Pebax blend membranes, which indicate that the blending of CA and Pebax was physically done.

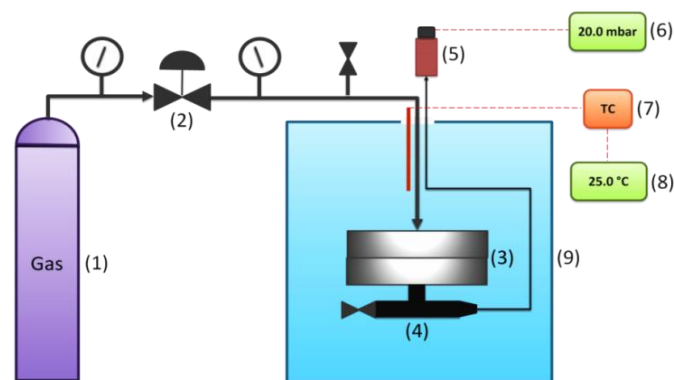


Fig. 2. A schematic diagram for the experimental apparatus applied for the gas permeability measurement: (1) gas cylinder, (2) pressure regulator, (3) membrane holder, (4) downstream chamber, (5) pressure transmitter, (6) pressure indicator, (7) temperature sensor, (8) temperature indicator, and (9) constant temperature bath.

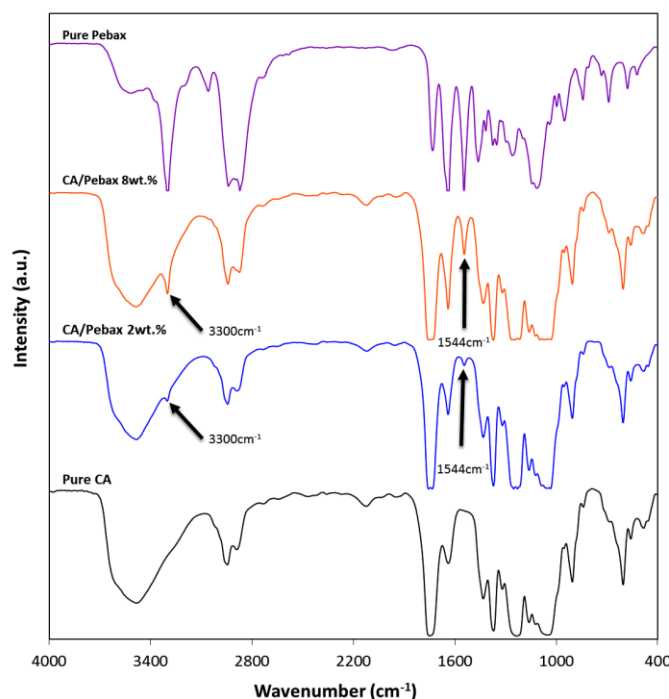


Fig. 3. FTIR spectra of the pure CA, pure Pebax, CA/Pebax 2w.%, and CA/Pebax 8wt.% blend membranes.

3.2. XRD analysis

Figure 4 shows the XRD patterns of CA, Pebax, CA/Pebax 2wt.% and CA/Pebax 8wt.% membranes. As can be observed, CA exhibits two broad crystalline peaks at around $2\theta=8$ and 17° . These are attributed to the partially crystalline areas of CA. The positions of these peaks are in accordance with the literatures [24, 25]. In addition pure Pebax membrane shows a sharp peak at around 2θ degree of 24° that is attributed to the crystalline (PA) regions of Pebax, and other peaks in different positions related to the remaining amorphous region [26, 27]. It can be observed that by the addition of 2 wt.% Pebax into the CA matrix, the peak position of the crystalline phases was reduced, that indicates the increase in d-spacing [28]. On the other hand, increasing the d-spacing can increase the amorphous region, which is led to increase in the permeability. The d-spacing of the membranes can be calculated by Bragg's equation [27]:

$$n\lambda = 2d \sin \theta \quad (5)$$

where n is the refractive index with integer values, λ is the wavelength of the incident beam (Cu $K\alpha$, $\lambda = 0.15406$ nm), 2θ is the diffraction angle between incident and scattered X-ray wave vectors and d is interlayer spacing of the lattice planes. The degree of crystallinity can be also calculated by the XRD results. In this case, the areas under crystallization peaks divide into the total sum of the areas under the crystalline and amorphous regions. The results of calculating crystallinity and d-spacing data were summarized in Table 2. As listed in Table 2, the addition of 2 wt.% of Pebax in the CA matrix leads to ~2.41% decrease in the CA crystallinity that means the CA/Pebax (2 wt.%) blend membrane shifts towards more rubbery state. However, the CA/Pebax (8 wt.%) shows ~1.34% increase in crystallinity in comparison with pure CA, which can be attributed to immiscibility of two CA and Pebax phases in this high amount of Pebax (8 wt.%) and the occurrence of micro-phase separation in this blend membrane.

Table 2

d-spacing and the crystallinity values (based on the XRD results) of the CA, CA/Pebax 2wt.%, CA/Pebax 8wt.% and pure Pebax membranes.

Membrane	Position (2θ)	d-spacing (\AA)	X _c (%)
CA	8.751	10.097	37.3
CA/Pebax (2 wt.%)	8.263	10.692	36.4
CA/Pebax (8 wt.%)	8.685	10.173	37.8
Pebax	24.0	3.705	30.42

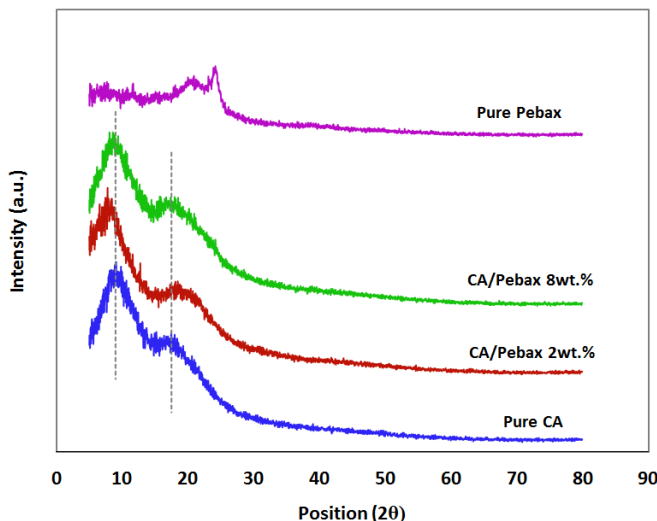


Fig. 4. XRD spectra of the pure CA, pure Pebax, CA/Pebax 2wt.%, and CA/Pebax 8wt.% blend membranes.

3.3. DSC analysis

DSC analysis was also carried out to investigate the glassy transition temperature (T_g), melting point (T_m), and crystallinity of the membranes. By investigation of the changes in T_g of a binary mixture, it can be evaluated the miscibility of the constituents. Thus, if a single T_g for a binary mixture is located between the T_g s of each constituent species, it represents the high miscibility of them. The pure CA membrane shows a T_g at 193.18°C which indicates the glassy nature of this membrane at room temperature. In addition, the pure Pebax has a T_g at -52°C that attributes to rubbery PEO segment [29]. After incorporation of 2 wt.% of Pebax, the T_g of CA reduces to 190.64°C , which indicates the miscibility of this blend in low content of Pebax. On the other hand, the CA/Pebax 8wt.% membrane shows two T_g around -54.37 and 194.77°C (lower than the T_g of pure Pebax and higher than the T_g of CA), which indicate that increasing in the Pebax content leads to a micro-phase separation. As can be seen in Figure 5, neat Pebax has two sharp peaks at 16.21 and 203.04°C , which respectively attribute to melting points of PEO and PA segments. In addition, the pure CA membrane had a T_m at 218.13°C that increases slightly to 218.80 and 221.80°C for CA/Pebax (2 wt.%) and CA/Pebax (8 wt.%), respectively. This indicates the better thermal stability of blend membranes in comparison with pure CA membrane. Crystallinity of the membranes was calculated by using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H^o} \times 100 \quad (6)$$

where ΔH_m is the integration of area under the melting peaks and ΔH^o determines the enthalpy of melting when the polymer is 100% crystalline that is 166.4 , 230 and 58.8 (J/g) for PEO, PA, and CA respectively [30-35]. As listed in Table 3, the addition of 2 wt.% of Pebax in CA matrix leads to ~10.26% decrease in CA crystallinity that means the CA/Pebax (2 wt.%) blend membrane shifts towards more rubbery state. However, the CA/Pebax (8 wt.%) shows ~0.52% increase in crystallinity in comparison with pure CA, which can be attributed to immiscibility of two CA and Pebax phases in high content of Pebax and the occurrence of micro-phase separation in the blend membrane.

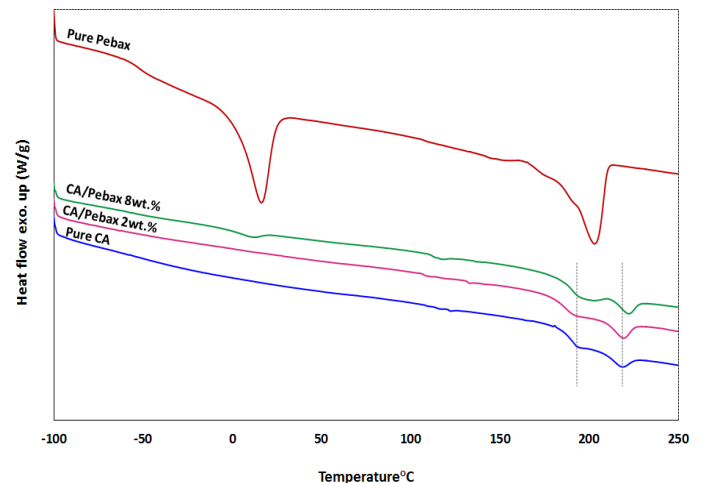


Fig. 5. DSC test results from the second heating cycles of pure and blend membranes.

Table 3

Thermal property and crystallinity (X_c) of the membrane samples.

Membrane	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	X_c (%)
CA	193.18	218.13	32.742
CA/Pebax (2 wt.%)	190.64	218.8	29.384
CA/Pebax (8 wt.%)	-54.37, 194.77	221.8	32.912
Pebax	-52.00	16.21 (PE), 203.04 (PA)	24.71

3.4. SEM observation

SEM images of the cross sectional morphology of the prepared membranes are presented in Figure 6. The cross section images of pure CA membrane and a prepared Pebax film show the uniform surfaces, without any cracks and defects. However, CA membrane has a rough cross section while a smoother cross section observes for the Pebax. The spots in the images can be

produced by small pieces of polymer that created during membrane fracturing, or by unsolved clods of polymer and also dust particles. The images of blend membranes show the bigger clods form when the Pebax content increases in the membranes. In addition, the blend membranes have rougher surfaces with more cavities than pure CA membrane, which can improve the gas permeability.

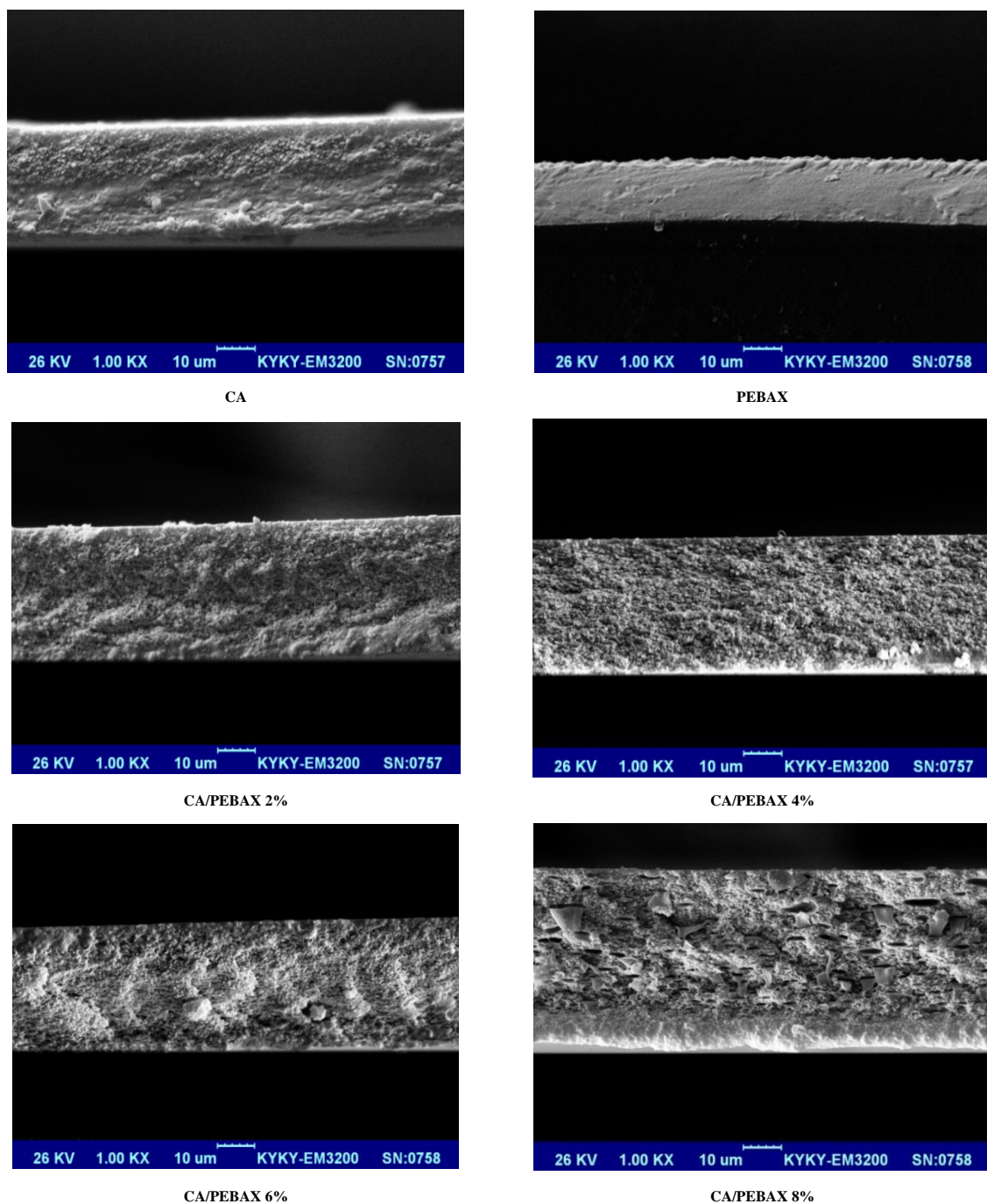


Fig. 6. SEM images of pure and blend membrane samples.

3.5. Gas separation performance

3.5.1. The effects of Pebax loading and feed pressure on the gas transport properties

CO₂ and N₂ permeability of the fabricated membranes were measured at room temperature via a constant volume/variable pressure experimental setup.

The results are reported in Figure 7. As could be observed in Figure 7(a) and (b), by adding the Pebax into the CA matrix, CO₂ permeability increases while N₂ permeability shows an increase at low Pebax content (2 wt.%) and then decreases with the further increase at Pebax contents. The good interaction between CO₂ gas and the soft segment (PE) of Pebax increases the CO₂ permeability in comparison with N₂. Increasing the free volume in low

Pebax content (see Table 2) enhances the N_2 permeability. However, by increasing the dispersed molecules of Pebax in CA matrix in the high Pebax content, the negative effect of spatial hindrance becomes higher than the positive effect of free volume increase. In fact, N_2 is an inert gas and has not any interaction with polymer matrix, therefore the solubility coefficient of N_2 , and in turn, its permeability decreases about 15%. As a result, by the addition of Pebax content, CO_2/N_2 ideal selectivity increases. CA/Pebax (8wt.%) blend membrane has the most selectivity, about 59%, higher than the selectivity of neat CA membrane.

The effect of feed pressure (2-10 bar) on gas separation performance of all prepared membranes was also shown in Figure 7. As could be observed, CO_2 permeability of the membranes decreases with the pressure increase, while the N_2 permeability shows a little increase. In general, an increase in feed pressure up to the pressures lower than the plasticization pressure in the glassy polymers increases the inter-chain volumes and results in swelling phenomenon [37, 38]. Therefore, the CO_2 gas molecules find an opportunity to fill the volumes and so the permeability decreases. In fact, the rate of volume increase is higher than membrane adsorption in the pressures below the plasticization pressure [39]. On the other hand, an increase in feed pressure forces the polymer chains to loose and form a closer packing density and thus decreases the gas permeability [40]. As N_2 permeation across the membrane is done without considerable interaction or sorption with polymer chains, its permeability increases with the increase in diffusion pathways. As

a result the CO_2/N_2 selectivity decreases with increasing of pressure. For example, the CO_2 permeability and CO_2/N_2 selectivity of pure CA membrane decreases respectively from 2.7 to lower than 2.4 Barrer and from 29 to 24 for CA/Pebax (8 wt.%).

3.5.2. Diffusion and solubility coefficients

Table 4 displays the effect of Pebax content on diffusion and solubility coefficients of CO_2 and N_2 gases as well as their ideal diffusivity and solubility selectivity. In addition, the data for pure Pebax was added for better interpretation of the results. As seen, with the increase in Pebax content of the blends, the diffusion coefficient of CO_2 decreases while its solubility coefficient increases. It can be demonstrated that the interactions of CO_2 with carbonyl and ether groups of PA and PE segments will increase by increasing of Pebax content [36], which results in the higher CO_2 solubility coefficient. This also coincides with a negative effect on diffusion coefficient of this gas, where the CO_2 will have a lower time for permeation from other pathways. In addition, as mentioned previously, by increase in Pebax content, N_2 solubility decreases and its diffusion increases. As a result, with the increase in Pebax content from 0-8 wt.%, ideal solubility selectivity increases from 3.77 to 27.76 and ideal diffusivity selectivity decreases from 4.88 to 1.05. Generally, with the increase in Pebax content, the structure of blend membranes becomes more rubbery and increasing the ideal solubility selectivity will dominate the increase in general selectivity [46, 47].

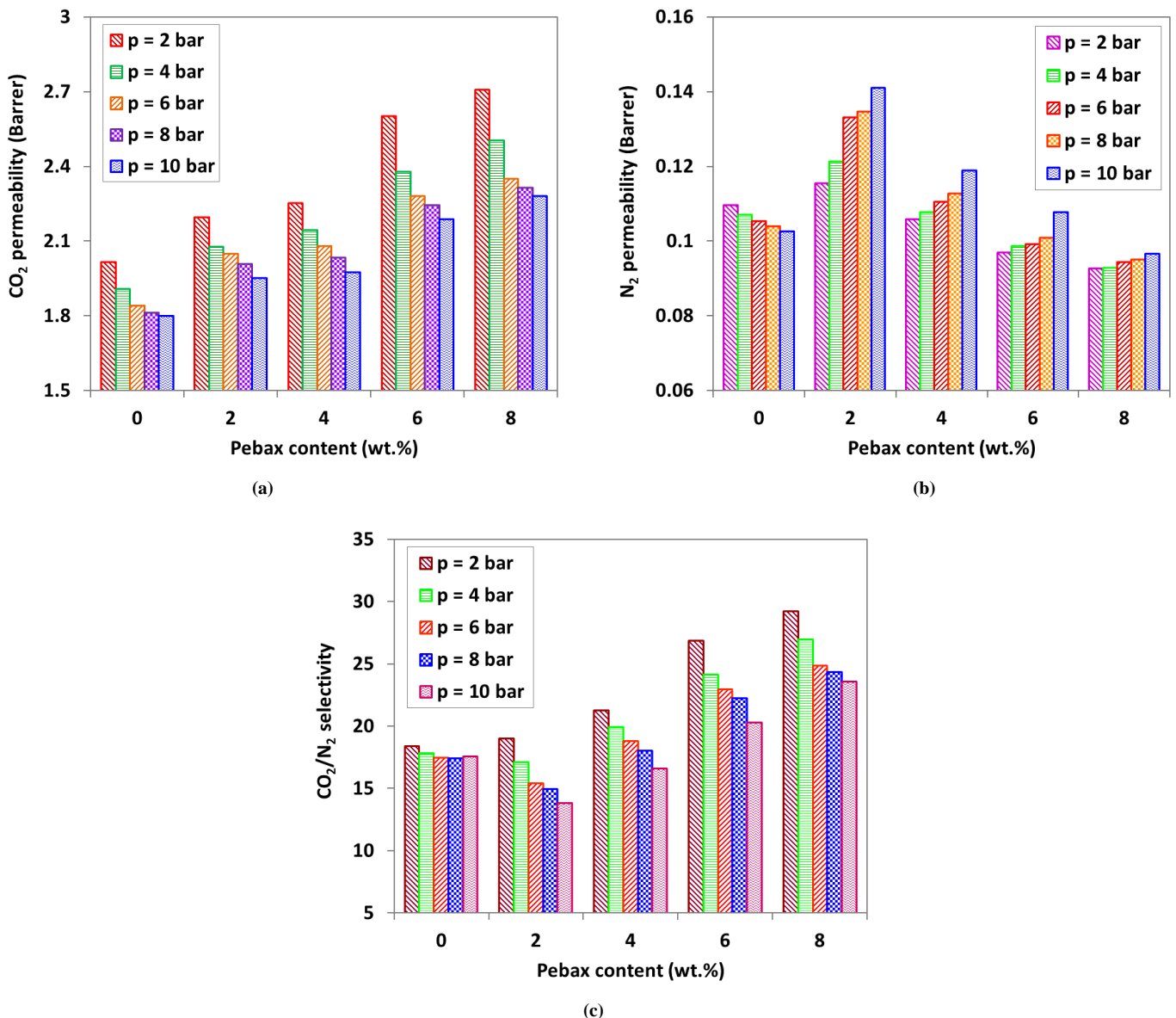


Fig. 7. The effect of Pebax content and feed pressure on (a) CO_2 permeability, (b) N_2 permeability and (c) CO_2/N_2 selectivity.

4. Conclusions

In this work, the cellulose acetate (CA) was used as polymer membrane matrix for physical modification by incorporation of a thermoplastic elastomer, Pebax 1657 copolymer. The blend membranes were successfully prepared by solution casting-solvent evaporation method, and then the performance of the membranes was investigated at 25 °C and 2-10 bar. The SEM images showed uniform formation of CA membrane without any cracks and defects, while the CA/Pebax images showed the bigger clods form, especially in the high amounts of Pebax loading, which are attributed to the relative miscibility of these polymers. In addition, blend membranes had more cavities in comparison with pure CA that can improve the permeability. The FTIR

spectra of membranes showed any chemical interaction between the CA and Pebax. In addition, an increase in d-spacing by the addition of low contents of Pebax was confirmed by XRD analysis. This can enhance the chain mobility and increase the gas permeability. The results of DSC analysis showed a reduction in T_g of the blend membranes in comparison with pure CA membrane, and confirmed the micro-phase separation phenomenon in high contents of Pebax. The gas permeation results revealed an increase about 25% and 59% respectively in CO₂ permeability and CO₂/N₂ selectivity for CA/Pebax (8wt.%) blend membrane as compared to pure CA. This is related to enhanced solubility selectivity with the increase in Pebax content. And finally, it showed that the pressure increase reduces the CO₂ permeability and CO₂/N₂ selectivity that is a common behavior for glassy-based polymers.

Table 4

The effect of Pebax content on diffusion and solution properties (25 °C and 2 bar).

Membrane	Gas	D [cm ² /s]*10 ⁸	S [cm ³ (STP)/(cm ³ .cmHg)]*10 ³	P [Barrer]	D _{CO2} /D _{N2}	S _{CO2} /S _{N2}	P _{CO2} /P _{N2}
CA	CO ₂	4.98	4.00	2.02	4.88	3.77	18.39
	N ₂	1.02	1.07	0.110			
CA/Pebax (2 wt.%)	CO ₂	4.08	5.40	2.19	3.20	5.94	19.00
	N ₂	1.28	0.90	0.115			
CA/Pebax (4 wt.%)	CO ₂	3.78	6.00	2.25	2.19	9.73	21.27
	N ₂	1.73	0.61	0.106			
CA/Pebax (6 wt.%)	CO ₂	2.43	10.70	2.60	1.31	20.50	26.84
	N ₂	1.86	0.52	0.097			
CA/Pebax (8 wt.%)	CO ₂	2.15	12.60	2.71	1.05	27.76	29.22
	N ₂	2.04	0.45	0.093			
Pebax 1657 *	CO ₂	50	10.2	51.02	11.00	7.29	80.2
	N ₂	4.55	1.40	0.637			

* Gas permeation data for Pebax 1657 were obtained from a dense membrane prepared by 1-butanol as the Pebax solvent.

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