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Original Research Article

Influence of Temperature and Time Parameters on Solution Mixing and Drying for Membrane Synthesis of Copolymer (Polyether-Block-Amide)

Seyed Mohammad Faghih, Mahmoud Salimi*, Hossein Mazaheri

Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran

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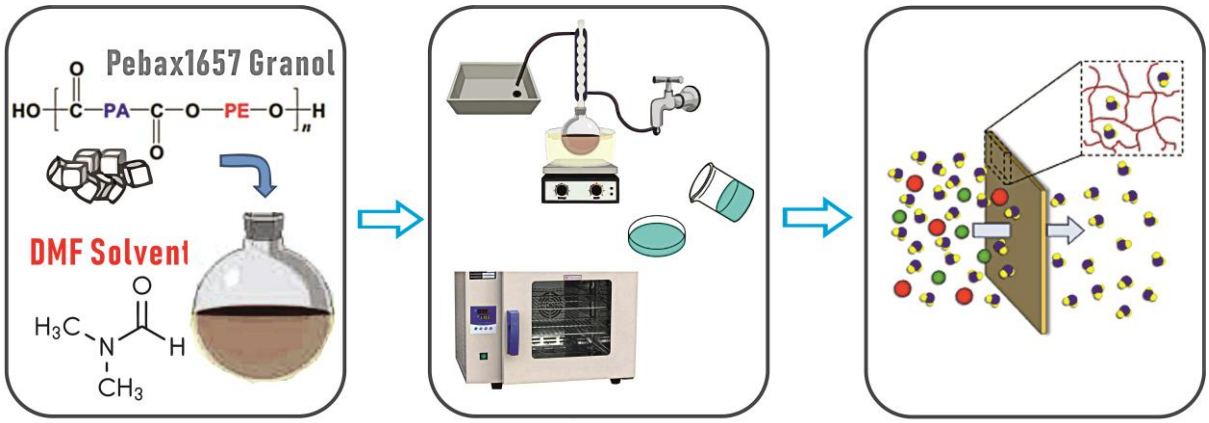
ABSTRACT

Recently, researchers have suggested the use of membranes to separate gases. They found that using Pebax polymer was very suitable for gas separation. This polymer has good properties and good solubility for carbon dioxide absorption. One of the challenges for researchers is how to turn this polymer into a thin layer for usage as a membrane. Therefore, several methods and solvents have been used to make this membrane. Researchers have calculated the carbon dioxide permeability of this polymer and obtained different results. One of the reasons for the non-uniform permeability results for this gas could be the difference in the method of making the thin film. The use of different methods and solvents affects the physical and chemical properties of this polymer. Perhaps the most important parameters during membrane construction are temperature and drying time. In this research, we want to investigate the effect of these two parameters on the final performance. Thus, the membranes were evaluated by XRD, FT-IR, FESEM, and mechanical strength analyses. Finally, the effect of the parameters on the permeability of carbon dioxide and methane was calculated and compared by the Taguchi method.

GRAPHICAL ABSTRACT



* Corresponding author: Mahmoud Salimi
✉ E-mail: Forat. m-salimi@iau-arak.ac.ir

Introduction

Today, the chemical industry is trying to reduce some parts of the air pollution by complying with environmental standards. Carbon dioxide plays a major role in air pollution. Recently, the separation of gases by membranes is considered due to its economic process, especially when high purity is not concerned [1].

Researchers have recently used polyphosphates, polyamides, cellulose acetate, polyurethane, polyurethane urea, polyether-block-amide copolymers, and polyvinylidene fluoride to separate gas [2]. Lane and Freeman concluded that ethylene oxide (EO) has a high selectivity for carbon dioxide. The choice of copolymers containing ethylene oxides, such as polyether-block-amide or PEBA, is suitable to obtain this goal [3]. Polyether-block-amide is an elastomeric thermoplastic whose chemical and physical structure is as displayed in Figure 1.

PA, aliphatic polyamide, and PE polyether are this polymer's hard and soft parts, respectively. The hard part provides mechanical strength and gas penetration through the PE phase. This polymer has good permeability and selectivity for carbon dioxide to methane [5]. Table 1 shows the composition and their melting temperature. PEBA polymers are commercially produced and can also be converted into thin films. Due to their different chemical structure, these polymers have several types of grades, among which grade 1657 had the highest permeability [6].

Perhaps the most important parameters during membrane construction are temperature and drying time. In this research, the effect of these two parameters was investigated on the final performance of fabricated membranes. Hence, the first experimental design was performed by hMinitab software, and membranes were made based on this design and their structure was evaluated by XRD, FT-IR, FESEM, and mechanical strength analyses. Finally, the effective coefficient of the research parameters was calculated by the Taguchi method on permeability. Likewise, selectivity, diffusion coefficients, and solubility the membrane density were calculated and compared at 3 bar pressure and 35 °C.

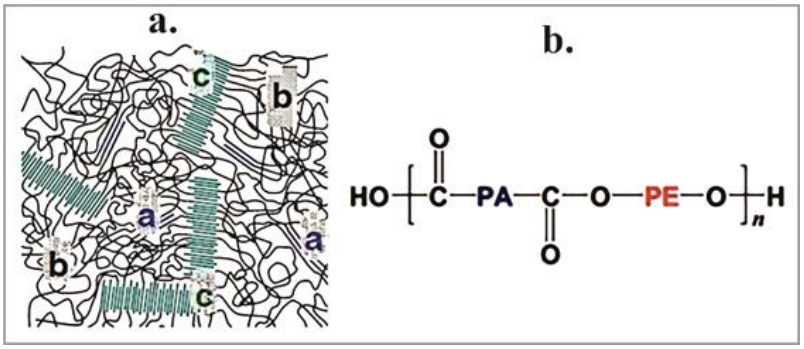


Figure 1: Chemical arrangement of PEBA polymers [3, 4]

Table 1: Composition, structure, and physical properties of Pebax 1657 [3]

Sample Pebax1657	Chemical Structure	Crystallinity%	Melting point (°C)
PE	–(CH_2-CH_2-O)n–	10-14	14-22
PA	–((CH_2)$_5$–CO–NH)–	21-31	200-205

Materials and Methods

Experimental design

The experimental design was performed to study the variables of this study on membrane permeability and selectivity. This design was done by the Taguchi method and by Minitab software. The advantage is that the number of tests is less but effective. Orthogonal array tables and ANOVA analysis were used with this method.

In this research, the effect of four parameters mixing time, mixing temperature, drying time, and

drying temperature was examined. Table 2 represents these parameters and their levels. The orthogonal array L9 consisted of four parameters and each one had three levels. Accordingly, 9 membrane samples with different variables were proposed, named, and listed in Table 3.

Table 2: Variables and their levels

Factor	Unit	Level 1	Level 2	Level 3
Drying time	hr	24	36	48
Drying temp.	°C	30	40	50
Mixing time	min	150	240	300
Mixing temp.	°C	110	140	160

Table 3: Experimental conditions and membranes IDs

Membrane ID	Mixing time	Mixing Temp	Drying time	Drying Temp
PB1	150	110	24	30
PB2	150	140	36	40
PB3	150	160	48	50
PB4	240	110	36	50
PB5	240	140	48	30
PB6	240	160	24	40
PB7	300	110	48	40
PB8	300	140	24	50
PB9	300	160	36	30

Materials

In this research, (polyether-block-amide) grade 1657 with a density of 1.14 g/cc made by the French company Arkema was used. DMF solvent was also purchased from the German company Sigma Aldrich. Methane and carbon dioxide gases with a purity of 99.9% were purchased and used from Khorramshahr Gas Oxygen Company.

Devices

XRD analysis with XRD Philips pw1730 device, FE-SEM analysis with TESCAN MIRA3 device, FT-IR analysis with Thermo device model AVATAR and for mechanical strength test Tensile Zwick device made in England model CAT-350-56 was used, which is equipped with a power supply is connected to two jaws. A digital thickness gauge model GT-313-A1 made in Japan was used to measure the thickness.

Making the membrane

For the membrane with a good mechanical strength, its thickness was selected to be 100 µm (source), and the radius of the casting dish is 3.5 cm. To make a membrane with the sizes mentioned above, 0.438 g of Pebax1657 granules was initially placed at 70 °C for 3 hours to be completely dried [9], and then it was poured into a laboratory balloon with 12.5 g of DMF solvent and it was placed in an oil bath and reflexes were inserted with a certain temperature and duration. To preserve the morphology of the polymer solution, the petri dish was heated to 80 °C in an oven (Figure 2) [10]. The solution was poured into a petri dish, and then it was placed in an oven at a certain temperature and time and it was completely dried. With this method and the variables of this research, 9 membranes were made. The thickness and density of the fabricated membranes were calculated and listed in Table 4.

Permeability measurement

A gas permeability measuring system was designed and built as a fixed volume (Figure 3). This system can measure permeability at different pressures. The membrane module was made by using pure stainless steel. Both sides of the rubber ring membrane were used to prevent gas from settling. In addition, a thin metal mesh made of steel was used to prevent the membrane from tearing. The effective surface of the membrane in this system is 17.71 cm^2. Trojan experiments were performed on the required gases at a temperature of 35 °C and a pressure of 3 times, each with three

repetitions. Gas permeability was calculated by using the constant volume method and Equation 1 and it was also reported in the Barrer unit:

$$P(Barrer) = \frac{273.15 \times 10^{10} LV}{760 \times 76(AT\frac{P_0}{14.7})}\frac{dP}{dt} \quad \text{(Eq. 1)}$$

1 Barrer =10^{-10} cm^3 (STP)·cm / (cm^2. s. cmHg)

In this relation, (cm^3) V is the volume of the tank after the cell, L (cm) is the thickness of the membrane, A (cm^2) is the effective surface of the membrane, T (K) is the temperature, (psia) is the absolute pressure of the inlet gas and (bar/s) dP/dt pressure changes over time [11], [12]. The ideal selectivity of gases was calculated by using Equation 2 [13, 14]:

$$\alpha_{CO2/CH4} = \frac{P_{CO2}}{P_{CH4}} \quad \text{(Eq. 2)}$$

CO_2 diffusion coefficient was calculated according to Equation 3 by using the calculation time method [14]:

$$D_{CO2} = \frac{L^2}{6\theta} \quad \text{(Eq. 3)}$$

Where, time θ was obtained by extrapolating the linear part of the pressure diagram in terms of time and its intersection with the time axis. The solubility coefficient of gases was calculated according to Equation 4 [14]:

$$S_A = P_A/D_A \quad \text{(Eq. 4)}$$

Permeability, selectivity, solubility coefficient, and diffusion coefficient of fabricated membranes are reported in Table 5 and Figure 4 and 5 [18, 19].

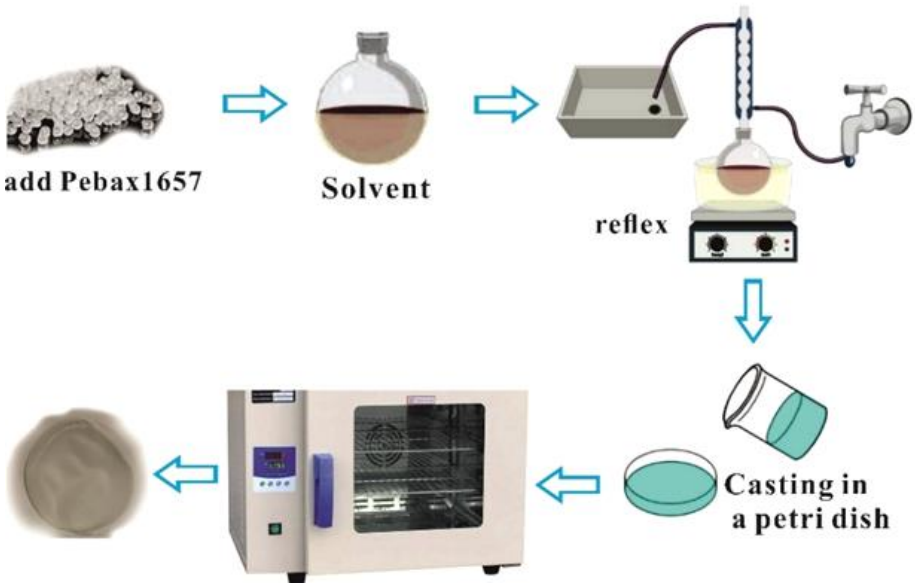


Figure 2: Nanocomposite membrane synthesis steps

Table 4: Mass, thickness, and density of synthesized membranes

Membrane ID	Thickness (μm)	Mass (gr)	Density (cm^3/gr)
PB1	88	110	1.21
PB2	91	140	1.20
PB3	89	160	1.18
PB4	93	110	1.19
PB5	87	140	1.19
PB6	85	160	1.17
PB7	90	110	1.22
PB8	89	140	1.23
PB9	92	160	1.18

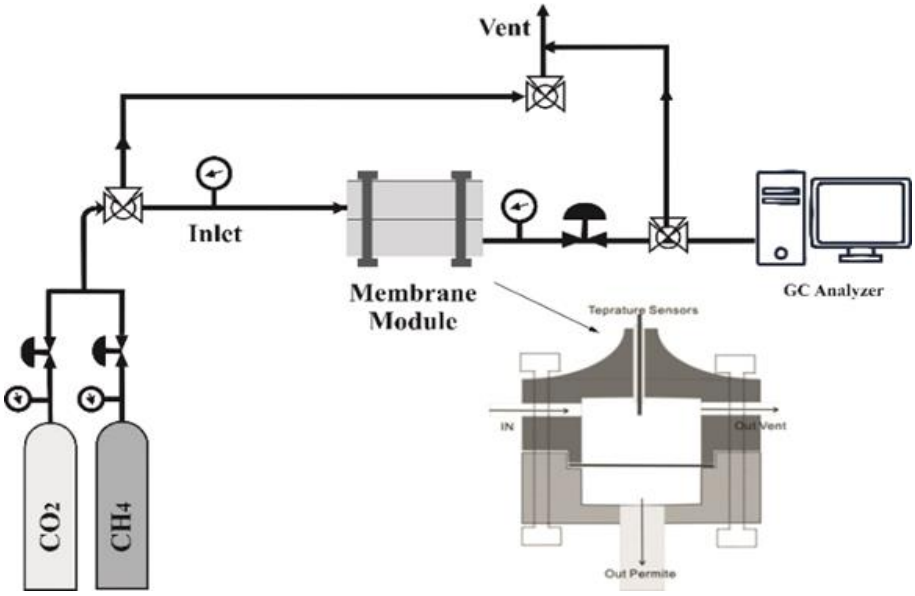


Figure 3: Permeability measurement system

Table 5: Permeability, diffusion coefficient, solubility coefficient, and selectivity

ID	P_{CO2}	P_{CH4}	CO_2/CH_4	D_{CO2}	S_{CO2}
PB1	49.5	3.13	15.81	46.3	1.07
PB2	53.3	3.31	16.1	47.1	1.13
PB3	54.6	3.34	16.34	47.6	1.15
PB4	51.4	3.18	16.16	46.1	1.11
PB5	59.3	3.64	16.29	49.1	1.20
PB6	52.2	3.61	14.6	46.5	1.12
PB7	55.9	3.54	15.79	48.7	1.15
PB8	51.6	3.28	15.7	46.6	1.10
PB9	52.8	3.24	16.3	46.4	1.14

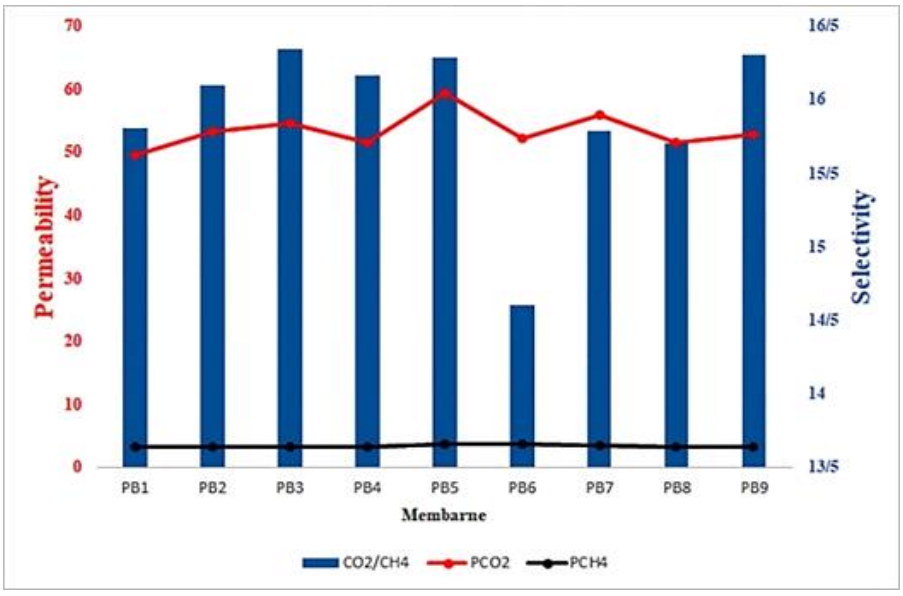


Figure 4: Permeability and selectivity of CO_2 and CH_4

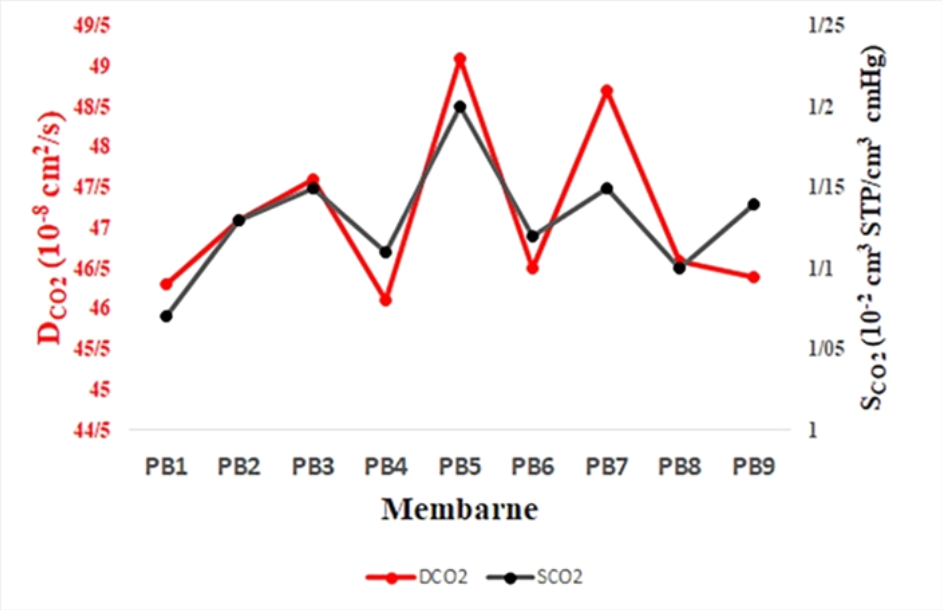


Figure 5: The diffusion coefficient, solubility coefficient of CO_2

Results and discussion

XRD analysis results

The X-ray jump (XRD) test was used to investigate the crystal structure of the synthesized particles. This XRD analysis is from 10 degrees to 80 degrees and the device step is 0.05 degrees per second. At 5.20 and 42.4 degrees, respectively, the X-ray reflections of the crystal structure of the polymer are related [15, 16]. The weaker peaks observed at other angles are related to impurities and unknown phases (Figure 6).

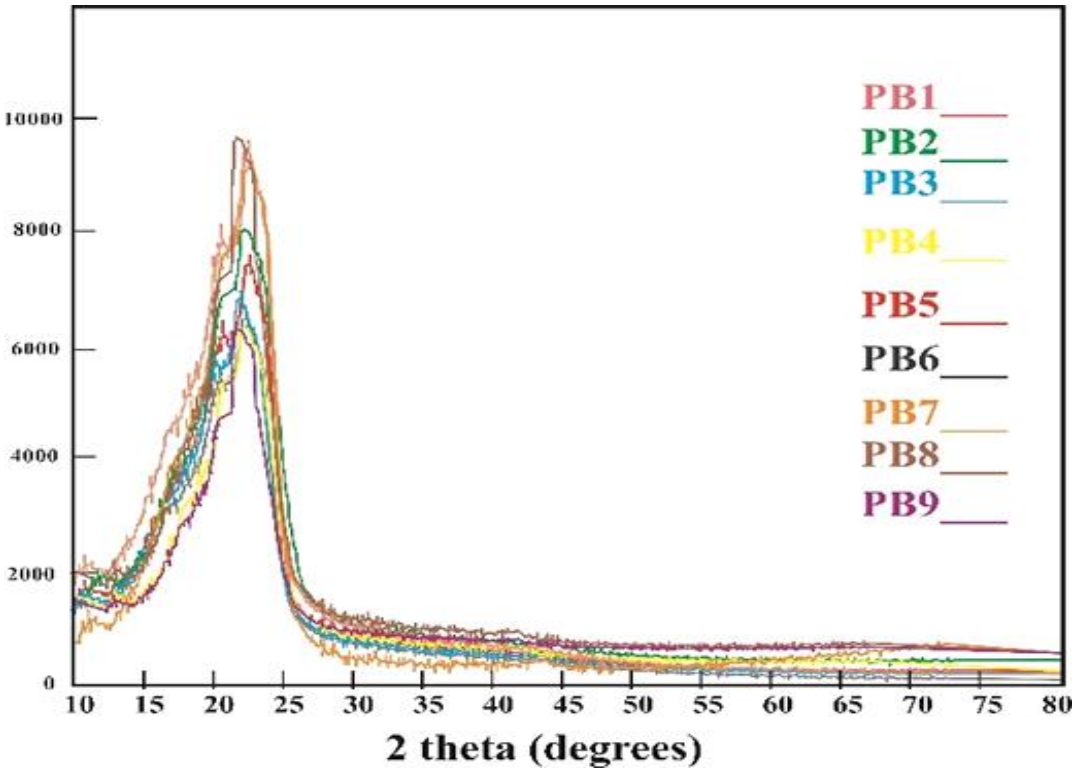


Figure 6: X-ray diffraction (XRD)

FT-IR analysis

This analysis was performed on 600 to 4000 (cm^{-1}) on the desired membranes. As depicted in Figure 7, the peak at 1635 cm^{-1} is the tensile vibrations (C=O) of carbonyl. The peak in wave number 1730 is attributed to another carbonyl group, both of which are in the hard phase. The peak in 1538 is related to the N-H flexural vibration in polyamide parts, and the peak in 3290 cm^{-1} is related to the tensile vibration (N-H) [17]. Peaks 2861 cm^{-1} and peaks 1460 cm^{-1} were further associated with C-H tensile and flexural vibrations, respectively. These results were in good agreement with other studies (Figure 7) [16].

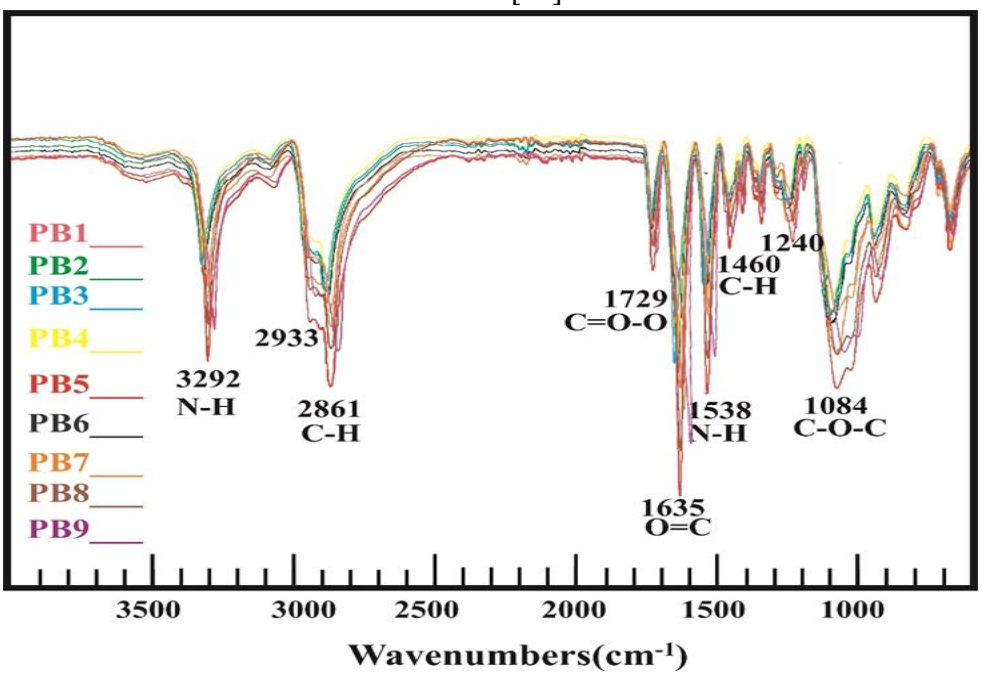


Figure 7: Fourier transform infrared spectroscopy (FT-IR)

FE-SEM analysis

The penetration of gases in polymer membranes depends on their morphology. FESEM imaging was performed to examine the structure of the membranes. Figure 8 displays the images made in this study. The surface of PB-5 and PB-7 membranes is uniform but cracks were observed on PB-4 and PB-9. The accumulated polymer layers were observed in PB-1. Fine particles were also seen on the surface of PB-6 and PB-8. These cases appear to be caused by drying or dissolving the polymer.

Mechanical strength analysis

Mechanical strength analysis determines how much tensile strength material can withstand before permanent degradation. It is possible to determine how much pressure the membrane can be exposed to the duration of the gas separation process. The results of this analysis show which membrane has more strength. The band-shaped specimens were placed between the two jaws and lasted at a speed of 5 mm/min.mm/min test, the conditions, and the speed of traction are constant. Table 6 indicates the reaction of the synthesized membranes during the application of tensile force. Studies show the PB-5 membrane is more resistant. The reason for the adhesion and tensile strength of this polymer can be its complete dissolution and drying.

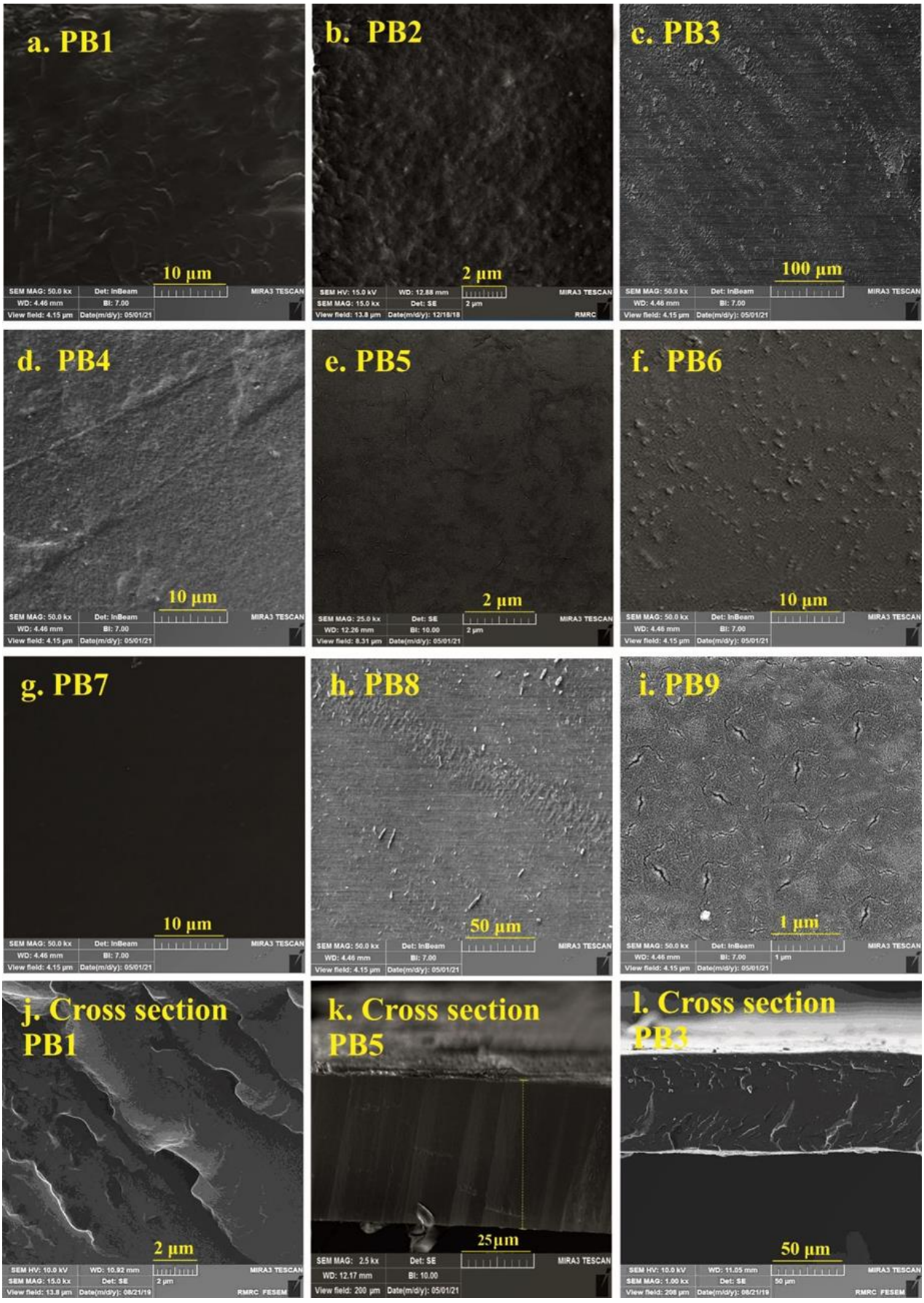


Figure 8: Scanning Electron Microscope (FE-SEM)

Table 6: Mechanical strength and stress-strain analysis data

Membrane ID	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
PB1	17.3	113.1	697 ± 2
PB2	19.2	118.3	792± 5
PB3	18.95	151.3	641 ± 5
PB4	20.6	130.5	736 ± 3
PB5	21.8	148.4	791 ± 2
PB6	20.8	119.9	751± 5
PB7	17.9	99.3	741 ± 5
PB8	18.87	108.3	636 ± 3
PB9	19.3	138.3	691 ± 2

Analysis of variance (ANOVA)

This analysis is to examine the involvement degree of experimental factors in the outcome. If one of them has less than a 5% effect, it may be ignored. Carbon dioxide permeability is analyzed in Table 7 and the methane gas permeability is indicated in Table 8. According to these data, the drying time parameter has played a greater role in the permeability of these two gases.

Finally, according to the obtained data by the Taguchi method, the optimized value for effective factors was suggested by Minitab software and listed in Table 9.

Table 7: Analysis of variance for the maximum CO_2 permeability

Factor	Degrees of Freedom	Sum of Squares	Variance	Total net squares	Percentage of participation
Mixing time	2	124.168	62.084	124.168	5.941
Mixing Temp	2	65.214	32.607	65.214	3.12
Drying time	2	1556.43	778.215	1556.43	74.47
Drying Temp	2	344.049	172.24	344.049	16.462
Error	0	0	-	-	-
Sum total	8	2089.886	-	-	-

Table 8: Analysis of variance for the maximum CH_4 permeability

Factor	Degrees of Freedom	Sum of Squares	Variance	Total net squares	Percentage of participation
Mixing time	2	0.354	0.177	0.342	8.73
Mixing Temp	2	0.335	0.167	0.323	8.248
Drying time	2	0.961	0.48	0.949	24.193
Drying Temp	2	2.22	1.11	2.208	56.283
Error	9	0.052	0.005	-	2.546
Sum total	17	10.854	-	-	-

Table 9: Optimized amount of research factors by Minitab software

Mixing Time (min)	Mixing temp. (°C)	Drying Time (hr)	Drying temp (°C)
220	143	38	42

Conclusion

In this study, the polymer membrane was produced through the molding and evaporation of solvents. Its performance in CO_2/CH_4 separation was investigated at feed pressure 3 times and a temperature of 35 °C. The results of the FT-IR test ruled out the formation of a new chemical bond between the zeolite and the polymer. FESEM images of the membranes revealed that the search parameters had a significant impact on their morphology. Permeability, selectivity, solubility

coefficient, and diffusion coefficient of fabricated membranes have the best selectivity performance. The diffusion coefficient and the solubility coefficient obtained are in good agreement with similar research. Research variables are very important in membrane construction. If not selected correctly, they can cause the following problems:

1- Lack of perfect evaporation of solvent causes blockage of the existing pores and reduces solubility and permeability.

2- The thickness of the membrane is the most important parameter to estimate the coefficient of gas penetration into the membrane. Improper drying or incomplete dissolution of the polymer in the solvent affects the thickness. The value of this parameter mass transfer and mechanical strength at the same time.

3- Mechanical strength and membrane density are further affected by research variables. The XRD analysis shows that the amount of hard phase crystallization of the membranes is significantly different.

A small amount of solvent or impurities in the membrane can clog some pores and reduce solubility and permeability. Finally, it can be concluded that the correct choice of research variables, especially drying time, is an important factor for Pebax membrane synthesis and has a great impact on achieving the highest permeability and selectivity.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

There are no conflicts of interest in this study.

ORCID:

Seyed Mohammad Faghih
https://www.orcid.org/0000-0002-1552-8591
Hossein Mazaheri
https://www.orcid.org/0000-0003-4461-5018

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