

Effect of Nano Zeolite 4A Loading on Polymer Membrane to Increase Permeability and Selectivity CO₂/N₂

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ABSTRACT: The separation of CO₂ gas is very important to meet environmental standards, this research aims to prepare a membrane that improves the selectivity of CO₂ over N₂ gas. Polymer (polyether-block amide) has properties that absorb CO₂ well. Nano zeolite 4A has tiny pores proportional to the kinetic diameter of CO₂. This mineral particle can act as a molecular sieve in the membrane and improve thermal and mechanical stability. By these two materials, Pebax/4A membrane was prepared. The structure of the membranes was evaluated by FESEM, BET, FT-IR, and mechanical strength analyses, and the permeability, selectivity, diffusion coefficient, and solubility coefficient of carbon dioxide were calculated in them. Finally, it was found that by adding 10% by weight of 4A, the selectivity of nanocomposite improved by %28 compared to pure polymer.

KEYWORDS: CO₂ Separation; Membrane; Nanocomposite; Pebax; 4A Zeolite.

INTRODUCTION

Today, the chemical industry is trying to reduce some of the air pollution by meeting environmental standards, carbon dioxide plays a key role in air pollution. Recently, the separation of gases by membranes has been considered because of the economics of this process, especially when high purity is not considered [1]. Researchers have recently used polyphosphates, polyamides, cellulose acetate, polyether urethane, polyurethane urethane urea, polyamide-polyester block copolymers, and polyvinylidene fluoride to separate the gas [2]. Lin and Freeman concluded that Ethylene Oxide (EO) has good selectivity for carbon dioxide. the choice of copolymers containing ethylene oxides, such as poly-ether-block-amide or PEBA, is suitable for achieving this goal. [3] polyether-block-amid is an elastomeric thermoplastic whose chemical structure is shown in Fig. 1.

Polyamide aliphatic (PA) and polyether (PE) form the hard and soft parts of this polymer, respectively. The hard part of the mechanical resistance and gas release is done through the PEO phase.

This polymer has good permeability and selectivity for to nitrogen [4] PEBA polymers are commercially produced and can also be converted into thin films. these polymers have several types of grades due to their different chemical structure, of which grade 1657 has the highest permeability [5].

One of the limitations of polymer membranes is the simultaneous increase in permeability and selectivity. Many solutions have been proposed by researchers to solve this problem, the most important of which is the creation of nanocomposite membranes. They are a new generation

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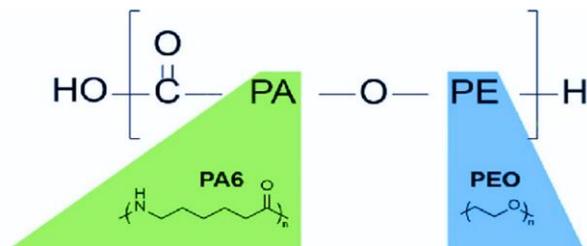


Fig. 1: Chemical arrangement of PEBA polymers [3].

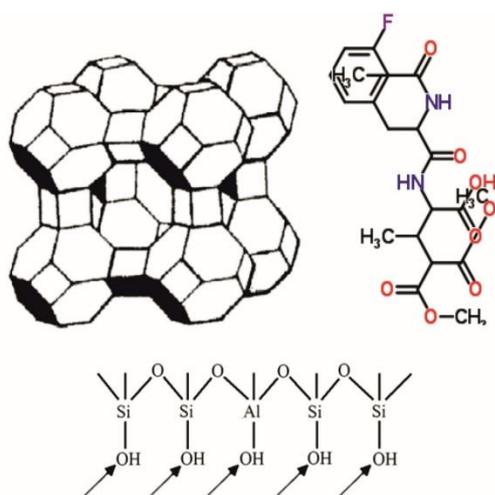


Fig. 2: Three-dimensional and chemical structure of zeolite 4A [9,10].

of membranes that include a polymer phase and filler phase [6]. selectivity of polymer membranes and gas emission from filler pores can create good permeability and solubility in a membrane, simultaneously. One of the most suitable nanoparticles for the filler phase is zeolites. They have regular, fine, and controllable porosity and can act as molecular sieves. [7,8]

Type A zeolite is a known synthetic sample of the common chemical compound $\text{NaAl}_3(\text{Si}_3\text{O}_{12}) \cdot 12\text{H}_2\text{O}$. this type of zeolite has 3 different groups 4A, 3A, and 5A, their difference is in the type of cation in the internal structure. 4A-type zeolite is commonly used to soften water and clean hazardous gases. Due to the pore diameter of this type of zeolite, it can increase gas emissions and play a key role in the selectivity of carbon dioxide. [8]

Pebax1657 and zeolite 4A have physical properties and chemical structures commensurate with the absorption of carbon dioxide. In this study, 1657-grade polyether block amide was selected as the polymer phase and 4A zeolite was selected as the filler phase to modify the membrane structure.

EXPERIMENTAL SECTION

Materials

In this research, Pebax grade 1657 with a density of 1.14 g/cm^3 made by the French company Arkema was used. This polymer contains 40% wt. of polyamide-aliphatic as the hard part and 60 wt. of polyethylene-oxide as the soft part. Zeolite 4A powder with a density of 0.5 g/cm^3 and an average particle size of 250 to 500 nm was prepared from Behdash Iran Chemical Company. Also, ethanol solvent with a purity of 99.5% was purchased from Khorramshahr Alcohol Company of Iran. Nitrogen and carbon dioxide gases with a purity of 99.9% were purchased and used from Khorramshahr Gas Oxygen Company.

Devices used in this research

XRD analysis with XRD Philips pw1730 device, FE-SEM analysis with TESCAN MIRA3 device, FT-IR analysis with Thermo device model AVATAR, BET analysis with a special surface measuring device, Belsorp mini II from Microtrap Bel Corp Japan.

Nanocomposite membrane synthesis

Previous research shows that gas membranes with a thickness of $150 \mu\text{m}$ have good mechanical strength [9]. According to the density of the polymer, the selected thickness ($150 \mu\text{m}$), and the radius of the casting container (3.5 cm), the total mass of the produced membrane was theoretically calculated to be 0.658 g . Based on this, 0.033 g of zeolite powder and 0.625 g of Pebax granules are needed to prepare a membrane with a thickness of $150 \mu\text{m}$ and 5% wt. by of zeolite.

First, the zeolite powder was heated at 70°C for 4 h to dry completely. Dried zeolite and 12.5 g of solvent (70% ethanol, 30% water) were placed on a magnetic stirrer for 3 h. at 45°C [11].

The obtained solution was placed in an ultrasonic device with a temperature of 45°C , a frequency of 42 kHz, and a power of 50 W for 10 min. This was done to de-bubble the solution. Pebax 1657 granules were added to this solution and heated in an oil and water reflux bath for 3 hours. The temperature of this bath was chosen to be 120°C .

The petri dish was heated to 80°C . this action prevented damage to the morphology of the solution before casting [12]. the solution is poured into a Petri dish

Table 1: Percentage by weight of polymer and filler membranes created.

ID	Pebax	4A	Solvent	Thickness
	% Wt.	% Wt.	(gr)	(μm)
PA-0	100	0	12.5	131
PA-5	95	5	12.5	139
PA-10	90	10	12.5	139
PA-18	82	18	12.5	142
PA-35	65	35	12.5	141

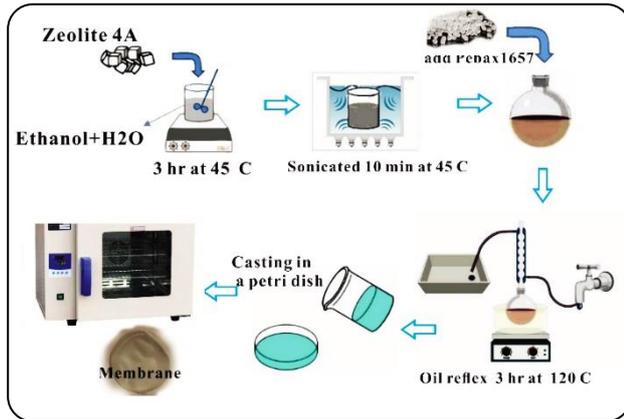


Fig. 3: Nanocomposite membrane synthesis steps.

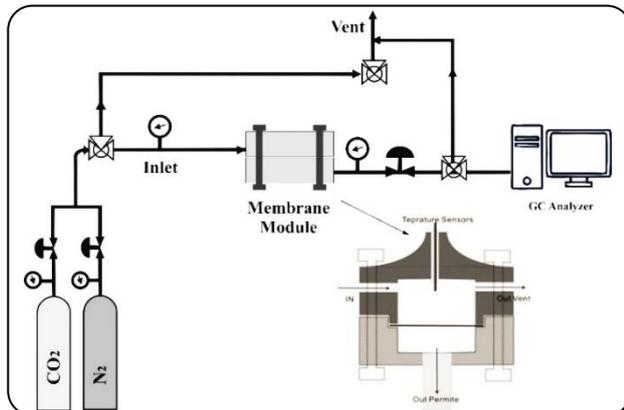


Fig. 4: Permeability measurement system.

and in an oven at 35°C for 30 hours place for dried. to ensure complete evaporation of the solvent, this time the petri dish was heated for 2 hours in a vacuum oven at 35°C and the membrane fabrication operation was completed. Membranes with concentrations of 0, 10, 18, and 35% Wt. of zeolite were made by the same method. the thickness of the membranes was measured by the Japanese digital thickness gauge GT-313-A1 and named according to Table 1.

Permeability measurement

The gas permeability measuring system was constructed

as a fixed volume. this system can measure permeability at different pressures. The membrane module was made using pure stainless steel. rubber rings were used on both sides of the membrane to prevent gas leakage. Also, a thin metal mesh made of steel was used to prevent the membrane from tearing and to withstand pressure. the effective surface area of the membrane in this system is 17.71 cm². permeability tests were performed at 30°C and pressure of 3 bar, each with three replications.

Gas permeability was calculated by the constant volume method by Equation 1 and reported in the Barrer unit:

$$P_{(\text{Barrer})} = \frac{273.15 \times 10^{10} L V dP}{760 \times 76 (AT \frac{P_0}{14.7}) dt} \quad (1)$$

$$1 \text{ Barrer} = 10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$$

In this equation, (cm³) V is the volume of the reservoir behind the membrane, L (cm) is the thickness of the membrane, A (cm²) is the effective surface of the membrane, T (K) is the temperature, P₀ (psia) is the inlet gas pressure, and (bar/s) is (dP/dt) is the pressure change over time [13,14].

The ideal selectivity of gases was calculated using Equation (2) [15, 16]:

$$\alpha_{\text{CO}_2/\text{N}_2} = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (2)$$

The CO₂ diffusion coefficient was calculated according to the following equation using the Time-lag method [16]:

$$D_{\text{CO}_2} = \frac{L^2}{6\theta} \quad (10^{-8} \text{ cm}^2/\text{s}) \quad (3)$$

In Eq. (3), time θ was obtained by extrapolating the linear part of the pressure graph in terms of time and its intersection with the time axis.

The solubility coefficient of gases was calculated according to Eq. (4): [16]

$$S_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{D_{\text{CO}_2}} \quad (10^{-2} \text{ cm}^3 \text{ STP}/\text{cm}^3 \text{ cm Hg}) \quad (4)$$

Permeability, selectivity, solubility coefficient, and diffusion coefficient of synthesized membranes are listed in Table 2.

RESULTS AND DISCUSSION

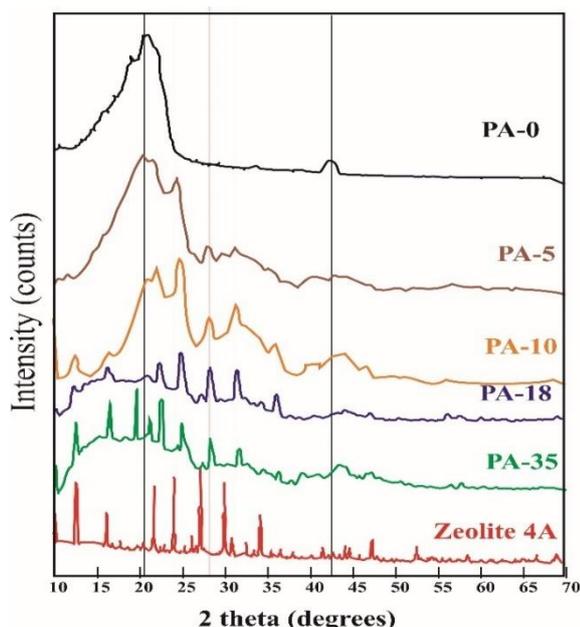
Analysis of X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) test was used to evaluate the crystal structure of the synthesized membranes [17,18]. XRD analysis was performed from 10 to 80 degrees and the device step was 0.05 degrees per second. as can be seen

Table 2: Permeability, diffusion coefficient, solubility coefficient and selectivity.

ID	P _{CO2}	P _{N2}	CO ₂ /N ₂	D _{CO2}	S _{CO2}
PA-0	56	1/4	40/00	48	1/17
PA-5	63/1	1/32	47/80	50/1	1/26
PA-10	69/6	1/36	51/18	52/3	1/33
PA-18	67/8	1/32	51/36	51/5	1/32
PA-35	66/8	1/34	49/85	50/9	1/31

CO₂/N₂: Selectivity of carbon dioxide to nitrogen, D_{CO2} (10⁻⁸ cm²/s): Carbon dioxide diffusion coefficient in the membrane, S_{CO2} (10⁻² cm³ STP/cm³ cmHg) Solubility coefficient of carbon dioxide in the membrane

**Fig. 5: X-ray diffraction (XRD)**

in Fig. 5, the zeolite phase formed by the major peaks of the particles at 20.5 and 42.5° corresponds to the X-ray reflection of the polymer crystal structure and the plates 24, 27, 31, and 43° to the crystal structure of the nanoparticles. [19, 20] The weaker peaks observed at other angles are inevitable, they are related to impurities and unknown phases. In general, surface modification with non-crystalline agents reduces the crystallinity of the base particles. With the presence of zeolite in Pebax substrate, the molecular free volume increases, so the overall hardness of this copolymer decreases, and its softening affects the further penetration of gas.

Analysis of Fourier Transforms InfraRed (FT-IR)

This analysis was performed in the range of 600 to 4000 cm⁻¹ on the membranes. As shown in Fig. 6, the peak at 1635 cm⁻¹ is the tensile vibrations (O = C) of carbonyl.

The peak in wave number 1730 cm⁻¹ is attributed to another carbonyl group, both of which are in the hard phase. The peak in 1538 cm⁻¹ 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) [21]. Peaks 2861 cm⁻¹ and peaks 1460 cm⁻¹ were also associated with C-H tensile and flexural vibrations, respectively. These results were in good agreement with other studies [20].

In the 4A zeolite spectrum, the broad absorption band at 3300 cm⁻¹ to 3600 cm⁻¹ and the absorption band at 1650 cm⁻¹ belong to the hydroxyl (-OH) groups due to the presence of water in the zeolite. The absorptions in 995 wavelengths are related to the bending vibrations of O-Si or O-Al [22]. As the zeolite load increased, the peak intensity increased to 3300 to 3500 cm⁻¹. This change may be due to the increased zeolite load. Zeolite adsorption bands overlap with the corresponding bands in the Pebax spectrum. This issue is more evident in the range of 1000 cm⁻¹, which intensifies with an increasing percentage of zeolite due to the joint effect of Si-O or Al-O bonds on zeolite. Finally, the Pebax and zeolite functional groups did not form a chemical bond, but the crystallinity in the 35% by weight membrane was greatly reduced.

Imaging by method Field Emission Scanning Electron Microscope (FE-SEM)

Permeability depends on the structure and morphology of the membrane. The loading of nano zeolite in the membrane causes a change in its physical structure. It can create more contact surfaces between the gas and the membrane or its regular pores can act as a molecular sieve. FE-SEM imaging was done to examine the morphology of the membranes. Fig. 7 shows the FE-SEM images of the nanocomposite and pure membranes. The pure Pebax membrane has a uniform surface, but very thin cracks are observed on it, which are probably caused by the drying process of the membrane.

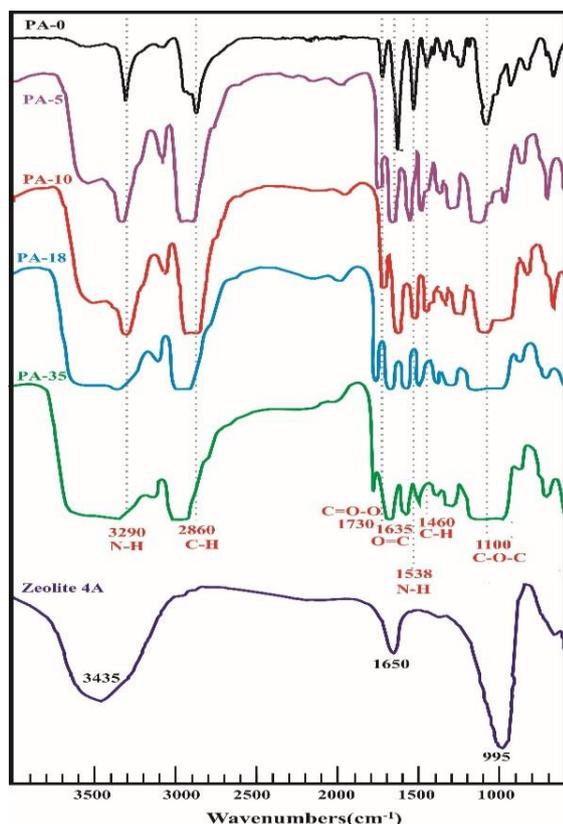
Table 3: Results of BET analysis.

ID	TPV (p/p0=0.990)	$a_{s,BET}$
PA-0	0.0044627	2.596
PA-5	0.013377	3.5192
PA-10	0.0043634	4.8115
PA-18	0.0040921	3.8212
PA-35	0.0039795	1.9897

TPV ($\text{cm}^3 \text{g}^{-1}$) Total pore volume in membrane, $a_{s,BET}$ ($\text{m}^2 \text{g}^{-1}$) Membrane specific surface.

Table 4: The mechanical performance of membranes.

Membrane	Tensile strength (MPa)	Elongation at break (%)
PA-0	19.8	651 ± 6
PA-5	22.3	715 ± 5
PA-10	28.7	761 ± 5
PA-18	22.3	563 ± 3
PA-35	17.9	489 ± 3

**Fig. 6: Fourier Transform InfraRed (FT-IR) spectroscopy.**

FE-SEM images show that by adding zeolite to Pebax, the morphology of the membrane changes. By increasing the weight percentage of zeolite in the membrane, the intensity of these changes has also increased. The loading

of %18 Wt. and especially %35 wt. of the samples indicates the accumulation of zeolite nanoparticles and clumping at several points of the polymer surface. Cross-sectional imaging of a pure Pebax membrane shows a thickness of 138 μm .

Surface measurement specificity and porosity (BET)

BET analysis was performed to determine some physical properties such as surface area, pore volume, and pore surface. nitrogen adsorption and desorption isotherms at 77 °K were calculated for all samples. after loading the filler in membrane number 10, its specific surface area was 85% higher than pure polymer membrane. This parameter is very effective in increasing absorption. The data obtained from this analysis are listed in Table 3.

Mechanical strength analysis

Mechanical strength analysis determines how much the membrane can be subjected to pressure during the gas separation process. Strip-shaped samples are placed between the jaws of the machine and are drawn steadily at a speed of 5 mm/min. In this test, the temperature and stretching speed are constant. Table No. 4 shows the reaction of pure membrane and nanocomposite during tensile force.

Table No. 4 shows that by adding particles up to 10% by weight, the mechanical resistance of composite membranes improved, the reason can be the proper interaction of particles and polymer network. Proper distribution and very good adhesion between zeolite and polymer particles have increased tensile strength.

However the mechanical resistance of the membranes decreases after loading more than 10% by weight of zeolite, and they cannot perform as well as the previous membranes. One of the reasons can be the clumping of nanoparticles in some parts of the membrane because the clumping of nanoparticles causes their inability to interact with the polymer matrix and the non-uniform distribution of stress.

The effect of adding nanoparticles

Fig. 8 shows that the permeability of carbon dioxide in membranes with 10 and 18% by weight of zeolite is better than in pure membrane. several factors can increase the permeability of carbon dioxide. the first factor according to the results of the BET test is the increase of penetration

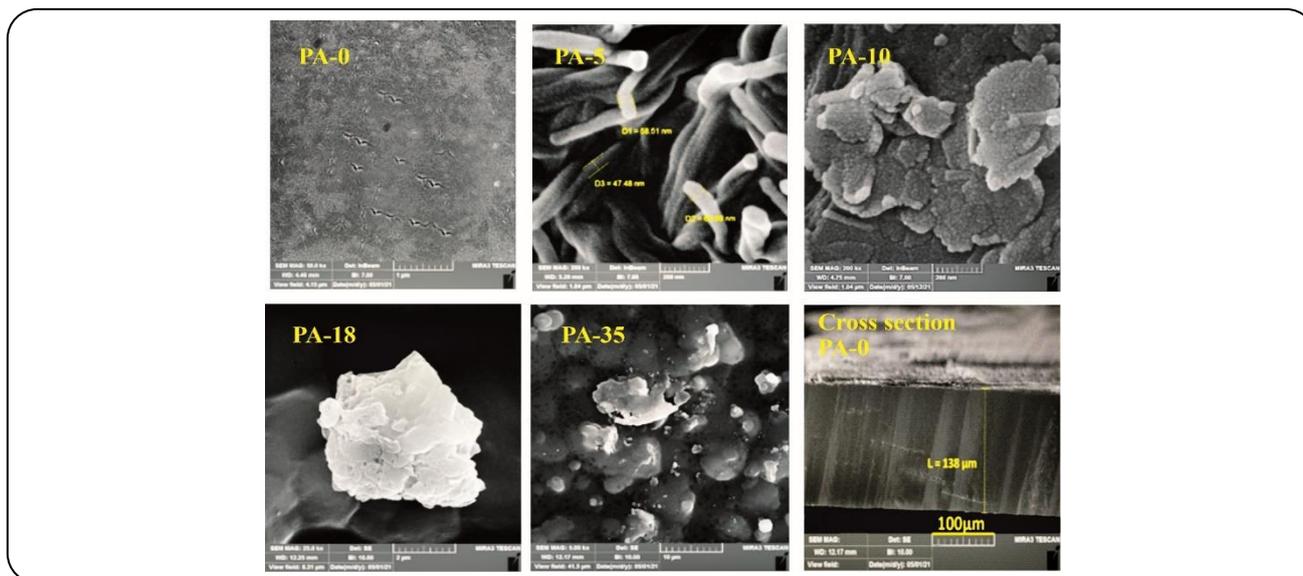


Fig. 7: Field emission scanning electron microscope (FE-SEM).

channels due to the increase in the contact surface, the second factor can be the creation of hydrogen bonds between nanoparticles and polymers, which plays an important role in determining fuzzy separation [11]. loading of nanoparticles reduces the density of polymer chains and weakens the hydrogen bond between them, which leads to an increase in the free volume of the polymer.

The amount of Fractional Free Volume (FFV) within polymers is often calculated according to Equation 5 [23]:

$$FFV = \frac{V_{SP} - V_0}{V_{SP}} \quad (5)$$

V_{SP} is the specific volume of the polymer, and V_0 is the volume occupied by the polymer chains, which is calculated by Equation (6) [23].

$$V_0 = 1.3V_W \quad (6)$$

V_W is the volume of van der Waals calculated by the group correlation method. According to this equation, increasing FFV increases the penetration of gas molecules and ultimately improves permeability.

Much research has been done on the synthesis of Pebax-based membranes with various nanoparticles, the results of them are compared with this research and are listed in Table 5. Robesson reported a comprehensive analysis of the two-component permeability of gases. He proved that high-permeability membranes often have low selectivity for gas pairs. in the permeability selectivity diagram, he set

a limit for polymer membranes called the Robson upper limit. the closer the polymer membrane is to this range, the better its performance and the more suitable it is for industrialization [33]. The performance of the membranes made in this study was compared with the Robeson diagram in Fig. 10. in this diagram, the nanocomposites were placed below the Robson line.

CONCLUSIONS

In this study, the polymer membrane of Pebax 1657 composite matrix and zeolite 4A particles were fabricated by solvent-evaporation casting method, and its performance in CO_2/N_2 separation at a feed pressure of 3 bar was investigated. the results of the FTIR test ruled out the formation of a new chemical bond between the zeolite and the polymer. but FE-SEM images showed that in membranes amount of more than 18%, the nanoparticles were not well dispersed in the polymer and clumped in some places, a problem that negatively affected permeability. BET analysis shows that increasing nanoparticles by up to 10% by weight can have a good effect on increasing the gas-membrane contact surface. Figs 8 and 9 of the permeability test data show that by increasing the nanoparticle to 10% by weight, we can have a higher permeability than the pure membrane in the nanocomposite. also, its penetration coefficient and solubility coefficient were higher, but compared to similar studies, a lower penetration coefficient was obtained [23, 34].

Table 5: Results of some previous research.

Ref.	Filler phase	Polymer	Temperature(°C)	Pressure (Bar)	Permeability (CO ₂)	Selectivity CO ₂ /N ₂
[24]	Zeolite 13X	Pebax1657	25	14	168.59	45
[25]	ZIF-8	Pebax1657/PE	60	25	758	16.1
[26]	DD3R	Pebax1074	55	20	188	38.5
[27]	ZIF-7	Pebax1657	35	30	150	40
[28]	NH ₂ -CuBTC	Pebax1657	30	20	163	26.2
[29]	ZIF-7	Pebax1657	25	22	145	23
[30]	Zeolite NaY	Pebax1657	40	30	131.8	130.8
[31]	Zeolite NaX	Pebax1657/PES	25	2	45	121.5
[32]	ZIF-8	Pebax2533	35	-	1293	9
This work	4A	Pebax1657	35	3	69.6	51.8

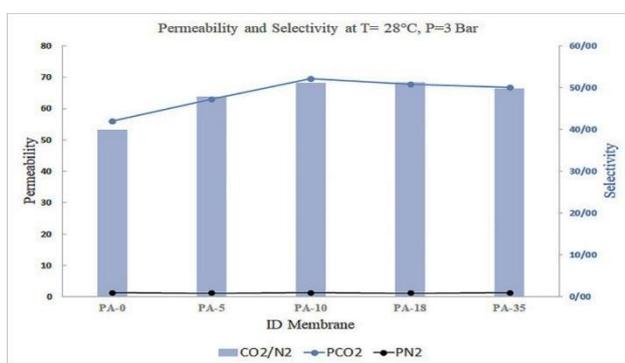
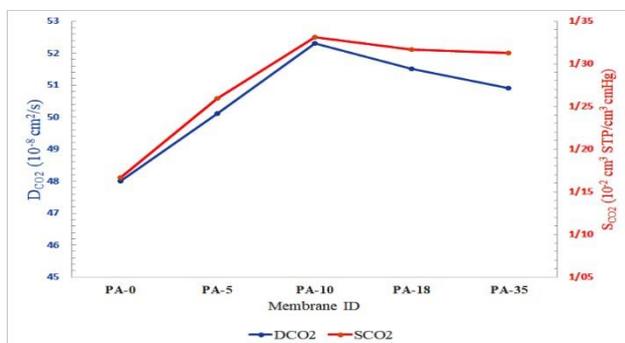
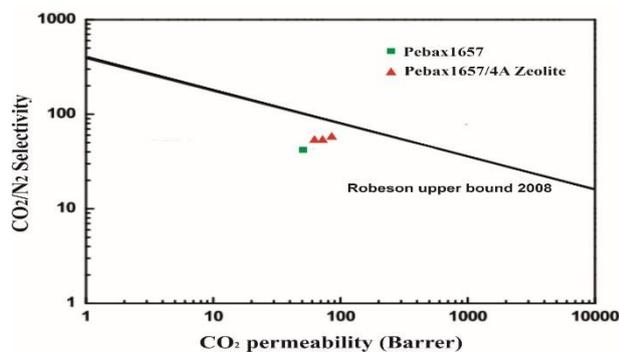
Fig. 8: Permeability and selectivity of CO₂ and N₂.Fig. 9: Diffusion coefficient, solubility coefficient of CO₂.

Fig.10: Robeson upper limit chart.

The most important parameter affecting the gas penetration is the thickness of the membrane, it seems that due to the thickness of the membrane has increased the mass transfer resistance. The reduction of diffusion coefficients and solubility at 18 and 35% by weight can be due to particle aggregation, clumping, and the formation of a common level between the particles and the polymer. also, a small amount of solvent in the polymer may clog some pores and reduce permeability.

According to the successful research that has been done in this field, parameters such as the type and amount of solvent, as well as the dissolution temperature and drying time, may not have been selected correctly in the synthesis method of this membrane. the correct choice of these variables seems to be very effective in making membranes with uniform morphology.

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REFERENCE

- [1] Brunettia A.,Scura F., Barbieria G., Driolia E., Membrane Technologies for CO₂ Separation, *Journal of Membrane Science*, **359**(1-2): 115-125 (2010).
- [2] Ehsani A., Pakizeh M., Synthesis, Characterization and Gas Permeation Study of Zif-11/Pebax@2533 Mixed Matrix Membranes, *Journal of the Taiwan Institute of Chemical Engineers*, **66**: 414-423 (2016).

- [3] Lin H., Freeman B.D., Kalakkunnath S., Kalika D.S., Effect of Copolymer Composition, Temperature, and Carbon Dioxide Fugacity on Pure-and Mixed-Gas Permeability in Poly (Ethylene Glycol)-Based Materials: Free Volume Interpretation, *Journal of membrane science*, **291(1-2)**: 131-139 (2007).
- [4] Zanetti M., Camino G., Thomann R., Mülhaupt R., Synthesis and Thermal Behaviour of Layered Silicate-Eva Nanocomposites, *Polymer*, **42(10)**: 4501-4507 (2001).
- [5] Budd P.M., McKeown N.B., Fritsch D., Yampolskii Y., Shantarovich V., Gas Permeation Parameters and Other Physicochemical Properties of a Polymer of Intrinsic Microporosity (Pim-1), *Journal of the Taiwan Institute of Chemical Engineers*, 29-42 (2010).
- [6] Omrani H., Naser I., Rafiezadeh M., Preparation and Characterization of a Novel Polysulfone (Ps) Mixed Matrix Membrane Modified with a Sap0-34 Nanofiller for CO₂/CH₄ Gaseous Mixture Separation, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **41(3)**: 902-912 (2022).
- [7] Suhas D.P., Aminabhavi T.M., Raghu A.V., Para-Toluene Sulfonic Acid Treated Clay Loaded Sodium Alginate Membranes for Enhanced Pervaporative Dehydration of Isopropanol, *Applied Clay Science*, **101**:419-429 (2014).
- [8] Jyothi M., Reddy, K. R., Soontarapa, K., Naveen, S., Raghu, A. V., Kulkarni, R. V., . . . Aminabhavi, T. M., Membranes for Dehydration of Alcohols via Pervaporation, *Journal of Environmental Management*, **242**: 415-429 (2019).
- [9] Xie F.G., Recent Progress on Fabrication Methods of Polymeric thin Film Gas Separation Membranes for CO₂ Capture, *Journal of Membrane Science*, **572**: 38-60 (2019)
- [10] Ahmad J., Hägg M.-B., Preparation and Characterization of Polyvinyl Acetate/Zeolite 4a Mixed Matrix Membrane for Gas Separation, *Journal of Membrane Science*, **427**: 73-84 (2013).
- [11] Dehaghani A.H.S., Rashidian S., Pirouzfard V., Su C.-H., The Novel Composite Membranes Containing Chloride and Acid Functionalized Multiwall Carbon Nanotube Fillers for Gas Separation, *Colloid and Polymer Science*, **299(12)**: 1933-1944 (2021).
- [12] Raghu A.V., Gadaginamath G.S., Mathew N.T., Halligudi S.B., Aminabhavi T.M., Synthesis and Characterization of Novel Polyurethanes Based on 4,4'-[1,4-Phenylenedi-Diazene-2,1-Diyl] Bis(2-Carboxyphenol) and 4,4'- [1,4-Phenylenedi-Diazene-2,1-Diyl] Bis (2-Chlorophenol) Hard Segments, *Reactive and Functional Polymers*, **67(6)**: 503-514 (2007).
- [13] Azizi N., Isanejad M., Mohammadi T., Behbahani R.M., Effect of TiO₂ Loading on the Morphology and CO₂/CH₄ Separation Performance of Pebax-Based Membranes, *Frontiers of Chemical Science and Engineering*, **13(3)**: 517-530 (2019).
- [14] Hosseinzadeh Beiragh H., Omidkhah M., Abedini R., Khosrav, T., Pakseresht S., Synthesis and Characterization of Poly (Ether-Block-Amide) Mixed Matrix Membranes Incorporated by Nanoporous Zsm-5 Particles for CO₂/CH₄ Separation, *Asia-Pacific Journal of Chemical Engineering*, **11(4)**: 522-532 (2016).
- [15] Jamshidi M., Pirouzfard V., Abedini R., Pedram M.Z., The Influence of Nanoparticles on Gas Transport Properties of Mixed Matrix Membranes: An Experimental Investigation and Modeling, *Korean Journal of Chemical Engineering*, **34(3)**: 829-843 (2017).
- [16] Fraga S.C., Monteleone M., Lanč M., Esposito E., Fuoco A., Giorno L., . . . Jansen J.C., A Novel Time Lag Method for the Analysis of Mixed Gas Diffusion in Polymeric Membranes by on-Line Mass Spectrometry: Method Development and Validation, *Journal of Membrane Science*, **561**: 39-58 (2018).
- [17] Myneni V.R., Kanidarapu N.R., Shaik F., Vangalapati M., Response Surface Modeling of the Removal of Methyl Orange Dye from an Aqueous Solution Using Magnesium Oxide Nanoparticles Immobilized on Chitosan, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **41(5)**: 1602-1618 (2022).
- [18] Sobhanipour A.R., Khodabakhshi M.R., Karimian R., Alizadeh M., Removal of Nitrate from Water Using TiO₂/PVDF Membrane Photobioreactor, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **40(1)**: 167-183 (2021).
- [19] Khoramzadeh E., Mofarahi M., Lee C.-H., Equilibrium Adsorption Study of CO₂ and N₂ on Synthesized Zeolites 13x, 4a, 5a, and Beta, *Journal of Chemical & Engineering Data*, **64(12)**: 5648-5664 (2019).
- [20] Surya Murali R., Ismail A.F., Rahman M.A., Sridhar S., Mixed Matrix Membranes of Pebax-1657 Loaded with 4a Zeolite for Gaseous Separations, *Separation and Purification Technology*, **129**: 1-8 (2014).

- [21] Suhas D.P., Aminabhavi T.M., Jeong H.M., Raghu A.V., Hydrogen Peroxide Treated Graphene as an Effective Nanosheet Filler for Separation Application, *RSC Advances*, **5(122)**: 100984-100995 (2015).
- [22] Zou W., Bai H., Zhao L., Li K., Han R., Characterization and Properties of Zeolite as Adsorbent for Removal of Uranium(VI) from Solution in Fixed Bed Column, *Journal of Radioanalytical and Nuclear Chemistry*, **288(3)**: 779-788 (2011).
- [23] Habib N., Shamair Z., Tara N., Nizami A.-S., Akhtar F. H., Ahmad N. M., . . . Khan A.L., Development of Highly Permeable and Selective Mixed Matrix Membranes Based on Pebax®1657 and Nott-300 for CO₂ Capture, *Separation and Purification Technology*, **234**: 101-116 (2020).
- [24] Asghari M., Mosadegh M., Harami H. R., Supported Peba-Zeolite 13x Nano-Composite Membranes for Gas Separation: Preparation, Characterization and Molecular Dynamics Simulation, *Chemical Engineering Science*, **187**: 67-78 (2018).
- [25] Jomekian A., Behbahani R. M., Mohammadi T., Kargari A., CO₂/CH₄ Separation by High Performance Co-Casted Zif-8/Pebax 1657/Pes Mixed Matrix Membrane, *Journal of Natural Gas Science and Engineering*, **31**: 562-574 (2016).
- [26] Karamouz, F., Maghsoudi, H. and Yegani, R., Synthesis of High-Performance Pebax®-1074/Dd3r Mixed-Matrix Membranes for CO₂/CH₄ Separation, *Chemical Engineering & Technology*, **41(9)**: 1767-1775 (2018).
- [27] Khoshkham A., Azizi N., Behbahani, R.M., Ghayyem M.A., Separation of CO₂ from CH₄ Using a Synthesized Pebax-1657/Zif-7 Mixed Matrix Membrane, *Petroleum Science and Technology*, **35(7)**: 667-673 (2017).
- [28] Khosravi T., Omidkhah M., Kaliaguine S., Rodrigue D., Amine-Functionalized Cubtc/Poly (Ether-B-Amide-6)(Pebax® Mh 1657) Mixed Matrix Membranes for CO₂/CH₄ Separation, *The Canadian Journal of Chemical Engineering*, **95(10)**: 2024-2033 (2017).
- [29] Li T., Pan Y., Peinemann K.-V., Lai Z., Carbon Dioxide Selective Mixed Matrix Composite Membrane Containing Zif-7 Nano-Fillers, *Journal of Membrane Science*, **425**: 235-242 (2013).
- [30] Zheng Y., Wu Y., Zhang B., Wang Z., Preparation and Characterization of CO₂-Selective Pebax/Nay Mixed Matrix Membranes, *Journal of Applied Polymer Science*, **137(9)**: 48398 (2020).
- [31] Zarshenas K., Raisi A., Aroujalian A., Mixed Matrix Membrane of Nano-Zeolite Na_x/Poly (Ether-Block-Amide) for Gas Separation Applications, *Journal of Membrane Science*, **510**: 270-283 (2016).
- [32] Nafisi, V., Hägg M.-B., Development of Dual Layer of Zif-8/Pebax-2533 Mixed Matrix Membrane for CO₂ Capture, *Journal of Membrane Science*, **459**: 244-255 (2014).
- [33] Robeson L.M., The Upper Bound Revisited, *Journal of Membrane Science*, **320(1-2)**: 390-400 (2008).
- [34] Rahman M.M., Shishatskiy S., Abetz C., Georgopoulos P., Neumann S., Khan M.M., . . . Abetz V., Influence of Temperature Upon Properties of Tailor-Made Pebax®MH 1657 Nanocomposite Membranes for Post-Combustion CO₂ Capture, *Journal of Membrane Science*, **469**: 344-354 (2014).