

## ORIGINAL ARTICLE

## Effect of nano Zinc Oxide on gas permeation through mixed matrix Poly (Amide-6-b-Ethylene Oxide)-based membranes

Mahdi Sheikh<sup>1</sup>; Morteza Asghari<sup>1, 2\*</sup>; Morteza Afsari<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran.

<sup>2</sup>Separation Processes Research Group (SPRG), Department of Engineering, University of Kashan, Kashan, Iran.

<sup>3</sup>Energy Research Institute, University of Kashan, Ghotb-e-Ravandi Ave., Kashan, Iran.

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### Abstract

Poly (amide-6-b-ethylene oxide)/zinc oxide (PEBA/ZnO) mixed matrix membranes were fabricated using ethanol/water as solvent by solvent casting method. The concentration of ZnO in membrane was set to 0.1 wt.% and the synthesized membranes were characterized by AFM and FTIR. Effects of ZnO nanoparticle on CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> permeabilities, and CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities of the membranes were investigated at the ambient temperature and pressure range of 4–12 bar. The results revealed that the CO<sub>2</sub> permeability of the nano-composite membrane increased 158 % with pressure, from 54.08 barrer (at 4 bar) to 139.59 barrer (at 12 bar). Furthermore, CO<sub>2</sub> permeability for the nano-composite membrane was higher than neat polymeric membrane. The PEBA/ZnO nano-composite membranes thus provide a promising potential for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation.

**Keywords:** CO<sub>2</sub> permeation; Gas separation; Mixed matrix membrane; PEBA; Nano-composite; ZnO.

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## INTRODUCTION

Membrane gas separation, a dynamic and rapidly growing field, showed excellent operational properties such as high selectivity and permeability, low energy requirements, and ease of the operation. Polymeric membranes are generally considered to be an effective tool for the separation of gaseous mixtures, due to their manufacturability, superior environmental friendliness, modularity, low running costs, robust physical characteristics, and good intrinsic transport properties [1–3] the existing membrane materials, membrane structures and formation processes are inadequate to fully exploit these opportunities. The requirements for viability of membranes vary somewhat with each application. Nevertheless, the key requirements of durability, productivity and separation efficiency must be balanced against cost in all cases. The various 'contender' technologies for large scale gas

separation membrane applications and the gas transport mechanisms are considered. The current spectrum of applications of gas separation membranes include; nitrogen enrichment, oxygen enrichment, hydrogen recovery, acid gas (CO<sub>2</sub>, H<sub>2</sub>S). Although polymeric membranes have been well developed for gas separation processes, but the trade-off between permeability and selectivity limits their application in large industrial scales [4–6]. PEBA have some advantages which made it susceptible for preparation of composite membranes [7–11]. PEBA, a copolymer comprised of hard segments of polyamide (PA) and soft segments of polyether (PE), are known as an excellent material for separation of CO<sub>2</sub> from light gases (e.g. H<sub>2</sub> or N<sub>2</sub>). The polymer structure consists of linear chains of polyamide segments interspaced with polyether segments [12, 13] flexible, or rubbery. The general chemical structure of PEBA is demonstrated in Fig. 1.

\* Corresponding Author Email: [asghari@kashanu.ac.ir](mailto:asghari@kashanu.ac.ir)

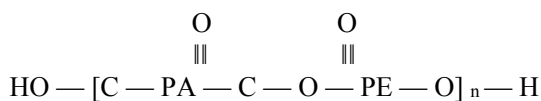


Fig. 1: Chemical structure of PEBA.

In this segmented block copolymer, two separated micro phase domains are formed: first, the polyamide crystalline domains which provide mechanical strength, and the second the polyether amorphous domains which high chain mobility of its ether linkages offer high gas permeability [14]. Different grades of PEBA polymers are commercially available and they generally have excellent mechanical strength and good chemical resistance [15]. Studies pointed to a hydrophilic grade of PEBA prepared by incorporation of low molecular weight poly ethers, known as PEBA 1657 (60 wt% poly (ethylene oxide) and 40 wt% polyamide) which causes enhancement of permeability without scarifying the selectivity. Higher permeability appears to stem from the increase in poly ether content of the polymer, as well as increase in total free volume [16, 17]. The main purpose for production of mixed matrix membranes (MMMs) is to improve the performance of membranes to exceed the Robeson's upper-bound line [5]. Some recent investigations have been carried out to improve the gas transport properties of polymeric membranes by embedding of nanoparticles. The inorganic fillers which are dispersed in polymeric matrix should be technically capable to improve membrane separation performance. The nanocomposite materials could combine the advantages of both component materials: the flexibility and process-ability of polymers, and the selectivity and thermal stability of the inorganic fillers [18] the existing polymeric membrane materials are inadequate to fully exploit the application opportunities on industrial scale; the improvement in permeability is at the expense of selectivity, and vice versa. A new type of membrane material emerging with the potential for future applications is mixed matrix materials composed of homogeneously interpenetrating polymeric and inorganic particle matrices. Compared to original polymeric membranes, significant improvement in separation properties with trivial loss in membrane flexibility is expected for the resultant mixed matrix membranes (MMMs). There were many inorganic

nanoparticles used to prepare MMMs for gas separation. They are usually organized into two main categories namely porous and nonporous [19]. The inorganic porous filler has got the effect of molecular sieving – separating gases by their size or shape [20, 21]. The resulting membranes revealed higher permeability and selectivity of desired components. Also in the case of pore sizes significantly larger than the size of gaseous molecule, absorption and selective surface flow mechanism is dominated as main mechanism [6].

Nonporous inorganic fillers generally cause decrease in the diffusion of larger molecules and increase in the matrix tortuous pattern. Presence of small size (nanometric) inorganic materials might increase void volume of membranes by disrupting polymer chains, leading to higher gas diffusion [22, 23]. Zinc oxide (ZnO), with its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption, and high photostability is a multifunctional material, fit for using as nano filler in MMMs [24, 25]. Nowadays ZnO is broadly used in nanotechnology science fields to enhance operation of materials and devices through different techniques in nanometer scale. Due to its vast areas of application, various synthetic methods have been deployed to grow a variety of ZnO nanostructures including nanoparticles, nanowires, nanorods, nanotubes, nanobelts, and so on [24, 26, 27]. Some studies surveyed the use of ZnO nanoparticles for fabrication of MMMs, but the role of ZnO in MMMs for gas separation has not been reported, yet.

ZnO is more economical than other nanoparticles used for gas separation, like  $\text{TiO}_2$ . In addition, the supplementation of ZnO could improve mechanical properties of the polymer matrix [25, 27, 28]. Therefore, employment of ZnO nanoparticles in polymeric membranes could be labeled as an innovative and promising technology which may be a key for the development of low cost and high performance gas separation membranes [29-32].

In this work, preparation of PEBA/nano ZnO MMMs was proposed as a novel gas separation membrane. However, we mainly focused on ZnO nanoparticles synthesized by thermal decomposition [26, 33]. The effect of ZnO incorporation on the membrane characteristics and its separation performance was evaluated. Gas permeation properties of these newly

fabricated membranes were compared with neat PEBA membrane using CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> single gas permeation experiments.

## EXPERIMENTAL

### Materials

The copolymer used in this work was supplied by Arkema under the trade name of PEBA~ MX1657. Also, CO<sub>2</sub> and N<sub>2</sub> gas cylinders with purity of 99.99% were supplied from Roham Gas Company, Iran. ZnO nanoparticles was previously produced in University of Kashan (Fig. 2) and the procedure of manufacturing was described elsewhere in detail [26, 33]. According to the transmission electron microscope (TEM) and scanning electron microscopy (SEM) images, the average size of the ZnO nanospheres ranged from 12 to 20 nm.

### MMMs preparation

ZnO nano crystals were firstly added to a solvent mixture of ethanol-water, stirred for 24 h. Then PEBA copolymers were added to solution to obtain 0.1 wt.% solution. In this step nanoparticles are soaked to enhance its dispersion through solution. Afterwards, an 8 wt.% PEBA dope was prepared by gradually addition of the PEBA to the solution. The solution was then sonicated for 15 minutes to obtain a fairly homogeneous solution. Solution casting and solvent evaporation technique were applied to prepare thin films of the membranes. The obtained body of the MMM was dried in a vacuum oven overnight to remove solvent. The MMM preparation procedure is schematically shown in Fig. 3.

### Membrane characterization

In order to characterize the structure and morphology of prepared membranes, Fourier Transform Infrared (FTIR) and Atomic Force Microscopy (AFM) analysis were applied. FT-IR

spectra of all the nanocomposite thin layers were recorded on spectrometer Nicolet-550 in KBr pellets at room temperature and in the range of 400-4000 cm<sup>-1</sup> by resolution of 4 cm<sup>-1</sup> for each spectrum. AFM was conducted with NT-MDT Solver P47 (The Moscow, Russia) to study the surface morphologies of neat PEBA and MMMs. Also SEM images were taken for neat and mixed matrix membranes. The morphology of cross-sectional of membranes was observed using a field emission scanning electron microscopy (FESEM; MIRA3\TESCAN (Czech Republic)) at 15kV.

### Gas permeation experiments

Fig 4 (4a, and 4b) show the schematic of experimental system for gas permeability measurements. It consists of an upstream gas source, a membrane cell, and a downstream device for permeate flux measurement. The membrane's effective area in the module was 20.67 cm<sup>2</sup>. The feed pressure varied in a range of 2 to 12 bar and the permeate side was kept at atmospheric pressure during all the experiments. In stable conditions, the pure gas permeability of the membranes was calculated using the following equation:

$$P = \frac{q(\text{STP})l}{S\Delta P}$$

Where  $P$  is the permeability coefficient in terms of the Barrer, 10<sup>-10</sup> cm<sup>3</sup> (STP) cm/ (cm<sup>2</sup> s cmHg),  $\Delta P$  is the pressure gradient across the membrane expressed in cmHg,  $q$ ,  $l$  and  $S$  are volumetric flow rate (cm<sup>3</sup>/s), membrane thickness (cm), and effective surface area of membranes (cm<sup>2</sup>), respectively. The average thickness of the MMMs thin film was about 15-20  $\mu$ m, estimated by an accurate micrometer.

Ideal separation factor  $\alpha_{A/B}$  is defined as the ratio of the permeabilities of the two pure gases:

$$\alpha_{A/B} = P_A / P_B$$

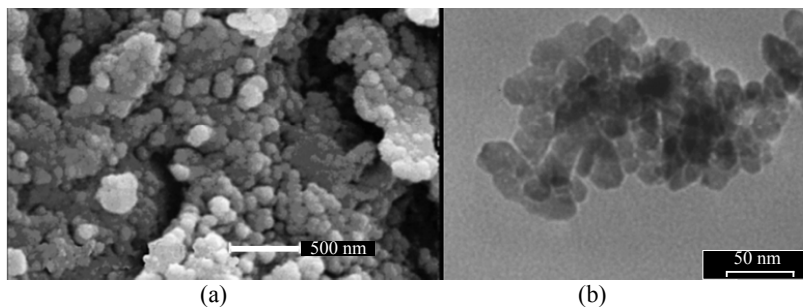


Fig. 2: a and b) SEM image and TEM image of ZnO nanoparticles [27].

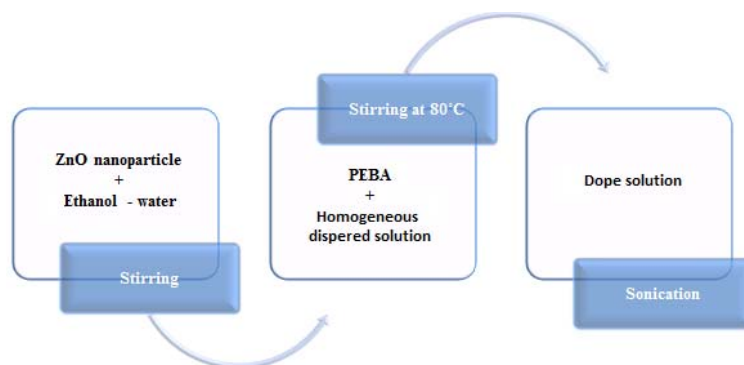


Fig. 3: A schematic procedure for preparation of MMMs of this study.

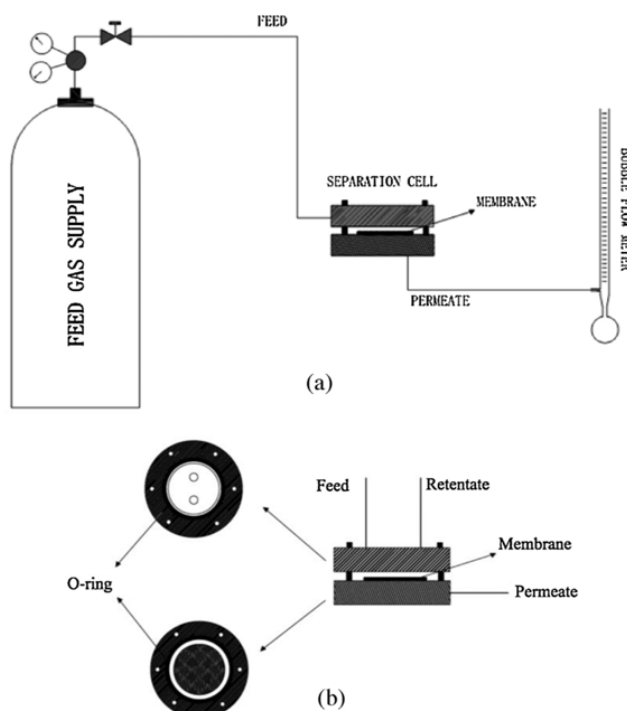


Fig. 4: a and b) Schematic of the experimental setup for gas permeability measurement, and membrane module.

**RESULTS AND DISCUSSION**

*Characterization of the MMMs*

**FTIR:** For better understanding of PEBA and ZnO interaction at the molecular level, FTIR spectroscopy was used in the range of 4000-400  $\text{cm}^{-1}$ . Figs (5a, 5b and 5c) show the FTIR spectra of ZnO nanocrystals, PEBA membrane, and PEBA/ZnO MMM, respectively. As presented in Fig. 5a, the strong peak around 434  $\text{cm}^{-1}$  shows a distinct stretching mode of ZnO crystals. In neat PEBA (Fig. 5b), the characteristic peaks at 1732 and 1102  $\text{cm}^{-1}$  represented  $\text{-C=O}$  and  $\text{-C-O-}$  stretching vibrations, respectively. The peaks at 1641 and

3300  $\text{cm}^{-1}$  indicated the presence of  $\text{H-N-C-O}$  and the  $\text{N-H}$  group, respectively. The stretching vibration at 2940  $\text{cm}^{-1}$  is attributed to the presence of aliphatic  $\text{-C-H}$ . The  $\text{C-O}$  stretching in the amide group of PEBA consist of two types: the free amide  $\text{C-O}$  peak at 1657  $\text{cm}^{-1}$ , and the hydrogen bonded amide peak at 1640  $\text{cm}^{-1}$ . Fig. 5c shows FTIR spectrum of 0.1 wt.% ZnO MMM, where the peaks mostly synchronized with the ones in the neat PEBA membrane. However, a single peak in the range of 400  $\text{cm}^{-1}$  proved the presence of ZnO nanoparticles in prepared PEBA /ZnO MMM.

**AFM:** AFM surface images of neat PEBA and

PEBA/ZnO membranes in Figs (6a and 6b) indicated that the neat membrane surface is very smooth, but the surface roughness increased with loading of 0.1 wt% ZnO. This increase in surface roughness provided a membrane with more effective surface area, proper for better contact of gas molecules with membrane surface and more possibility for gas dissolution onto the polymeric surface [15, 34, 35].

**SEM:** Fig. 7 shows SEM images of neat and MMM. Due to low percentage of nanofillers, addition of ZnO nanoparticle has relatively small effect on structure of membrane matrix. The cross section of both neat and MMM showed a smooth surface and no defect were observed in the images.

#### Gas permeation results

Fig. 8 shows the effect of ZnO nanoparticles on CO<sub>2</sub> permeability of PEBA/ZnO membrane, in comparison to neat PEBA membrane. As shown, the presence of the nanoparticles within the polymeric matrix led to an increase in CO<sub>2</sub> permeability. Zinc oxide is an important type of non-porous inorganic fillers which has good affinity to CO<sub>2</sub>. Unlike porous inorganic fillers, the non-porous ones could alter the chain packing of glassy polymers causing larger free volumes and leading to a significant enhancement in permeability. Additionally Fig. 6 shows that addition of ZnO nanofillers to PEBA increased the surface roughness of the membrane, and subsequently the effective interface of gas-membrane increased, and as a result the gas permeability increased.

The rubbery characteristic of PEBA provides the quadrupolar nature and cause more permeation of CO<sub>2</sub> relative to N<sub>2</sub> and CH<sub>4</sub>. On the other hand, kinetic diameter of CO<sub>2</sub> (3.3 Å) is also smaller than those of N<sub>2</sub> (3.64 Å) and CH<sub>4</sub> (3.8 Å), which may also led to greater diffusivity of CO<sub>2</sub>, compare

to N<sub>2</sub> and CH<sub>4</sub>. For polymeric membranes the solution-diffusion mechanism has gained widespread acceptance in describing the gas permeation results. After ZnO loading, PEBA/ZnO membrane showed significant improvement in CO<sub>2</sub> permeability, from 74.34 barrer for neat membrane to 139.59 barrer for MMM with 88% increase, in 12 bar, while ZnO loading had little effect on N<sub>2</sub> and CH<sub>4</sub> permeabilities and remained almost constant in about 4.2 and 8.9 for N<sub>2</sub> and CH<sub>4</sub>, respectively. As a consequence, ideal selectivities of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> increased, from 17.2 to 33.16 for CO<sub>2</sub>/N<sub>2</sub> and from 8.2 to 15.77 for CO<sub>2</sub>/CH<sub>4</sub>.

For neat PEBA, CO<sub>2</sub> permeability increased from 61.18 to 74.34 barrer with pressure, whereas for PEBA/ZnO MMM it enhanced from 58.56 to 139.59 barrer.

CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> permeabilities through PEBA/ZnO MMM at different operating pressures are shown in Fig. 9. As seen, the CO<sub>2</sub> permeability increased from 54.08 to 139.59 barrers in pressure range of 4 to 12 bar, while the CH<sub>4</sub> and N<sub>2</sub> permeations were almost remained constant by pressure. Gradual increase in the permeability with pressure is attributed to increase in the sorption of the polar CO<sub>2</sub> gas into the polymer membrane, which has a preferential affinity for this gas. These membranes revealed a suitable permeability for CO<sub>2</sub>, as a gas by high polarity characteristic, and low permeation for CH<sub>4</sub> and N<sub>2</sub>, as gases by lower polarity characteristic. Fig. 10 illustrates the CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> ideal selectivities of the synthesized MMM. The ideal selectivity also enhanced by pressure from 6.67 to 15.77 for CO<sub>2</sub>/CH<sub>4</sub>, and from 10.97 to 33.16 for CO<sub>2</sub>/N<sub>2</sub>, respectively. The rise in CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> ideal selectivities of the membranes could be attributed to the plasticization effect of the PEBA polymer matrix.

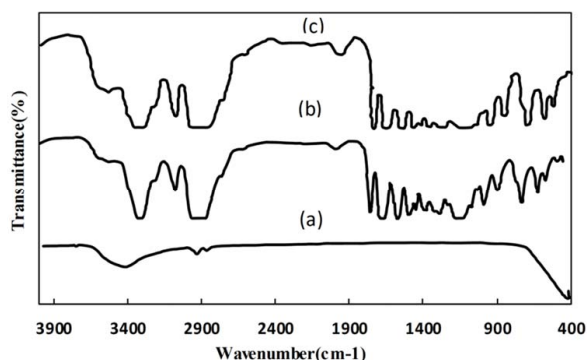


Fig. 5: a, b and c) - FTIR of ZnO nanocrystals, neat PEBA, and PEBA/0.1 wt.% ZnO MMM.

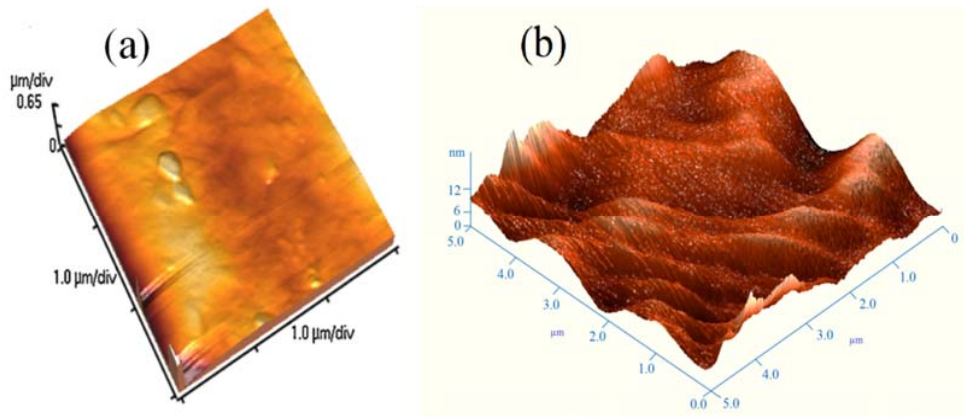


Fig. 6: a and b) Surface morphology of membranes obtained by AFM for neat PEBA, and PEBA/0.1 wt. % ZnO 0.1 MMM.

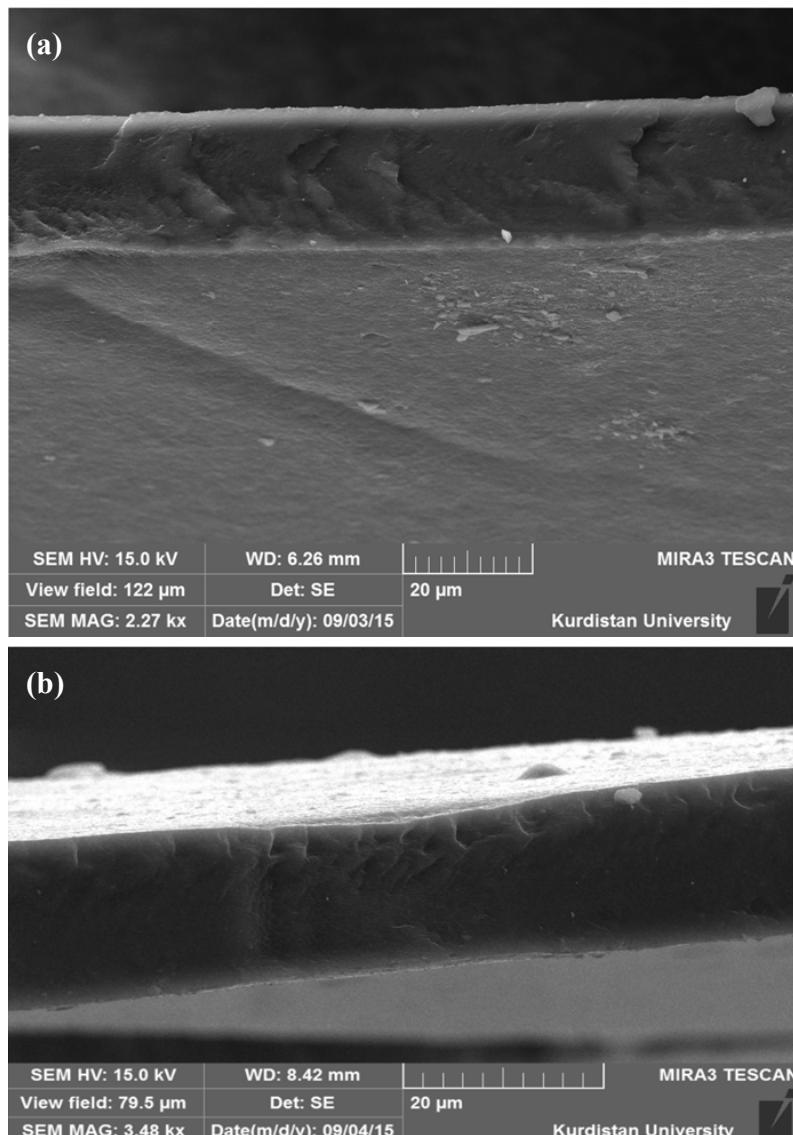


Fig. 7: a and b) SEM images of mixed matrix membranes and neat membrane.

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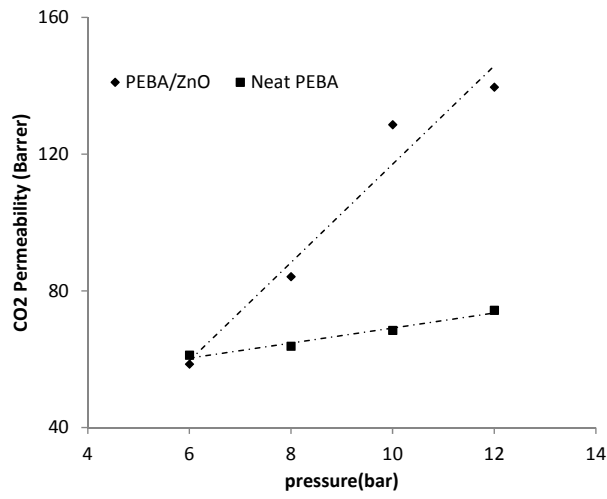


Fig. 8: CO<sub>2</sub> permeation through PEBA and PEBA/ZnO membrane versus pressure.

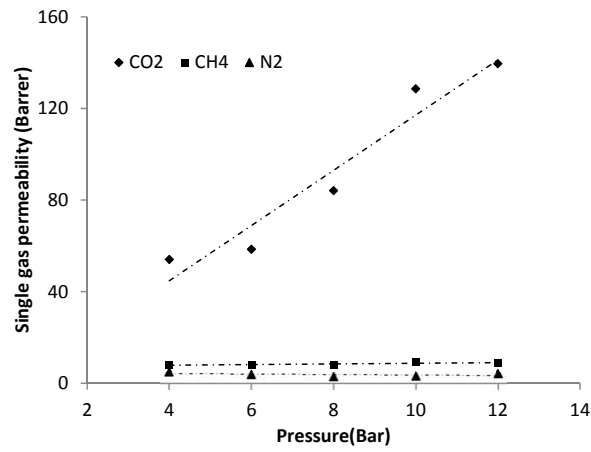


Fig. 9: CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> permeability versus feed pressure for PEBA/ZnO MMMs.

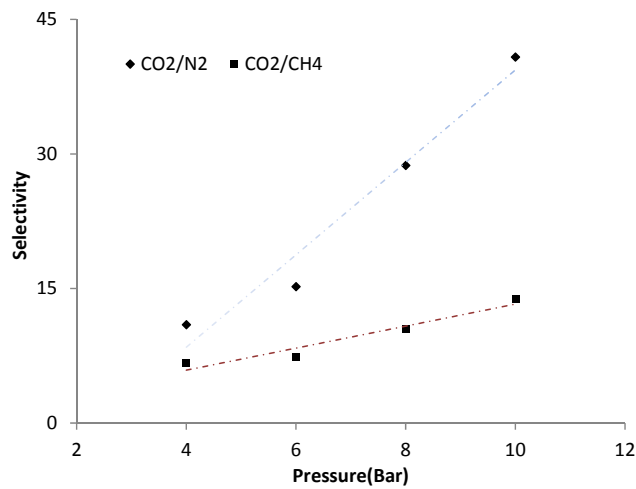


Fig. 10: Effect of feed pressure on ideal selectivity.

## CONCLUSIONS

The nanocomposites membrane, based on PEBA and ZnO were fabricated for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation. The effects of incorporation of ZnO nanoparticles into the polymer matrix were investigated. The FTIR of nanocomposite revealed that ZnO nanoparticles induced physical interactions with the polymer matrix. AFM images showed that the neat membrane surface was very smooth and its roughness increased with ZnO loading. The gas permeability experiment showed that the permeation of CO<sub>2</sub> increased with feed pressure for PEBA-ZnO 0.1 wt.%, while the permeation of CH<sub>4</sub> and N<sub>2</sub> was fairly independent to pressure. PEBA-ZnO 0.1 wt.% membrane exhibited higher CO<sub>2</sub> permeability relative to the neat PEBA membrane under the same conditions. Incorporation of ZnO nanoparticles into PEBA-1657 polymer matrix showed high potential for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation processes. Therefore, the ZnO filled PEBA membrane has shown enough potential for further research.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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