



## Research Paper

Effect of Ethylene Oxide Functional Groups in PEBA-CNT Membranes on CO<sub>2</sub>/CH<sub>4</sub> Mixed Gas SeparationMorteza Asghari <sup>\*,1,2</sup>, Morteza Afsari <sup>1</sup><sup>1</sup> Separation Processes Research Group (SPRG), Department of Engineering, University of Kashan, Kashan, Iran<sup>2</sup> Energy Research Institute, University of Kashan, Ghotb-e-Ravandi Ave., Kashan, Iran

## Article info

Received 2017-03-18  
 Revised 2017-06-09  
 Accepted 2017-06-15  
 Available online 2017-06-15

## Keywords

Mixed Matrix Membranes  
 PEBA  
 Polyethylene glycol  
 Carbon nanotubes  
 Gas mixture

## Highlights

- PEBA/PEG/CNT MMMs have been successfully fabricated via solution casting method
- Good CNT dispersion in PEBA polymer has been achieved
- Presence of ether groups in PEG improved CO<sub>2</sub> permeability and selectivity Mixed Gas test showed the negative effect of plasticization
- Incorporation of both CNT and PEG enhanced separation performance of PEBA membrane

## Abstract

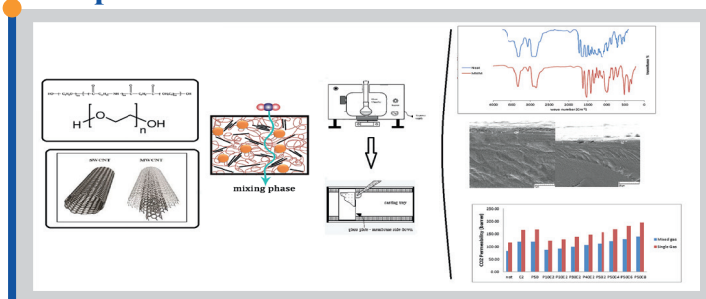
Poly (ether-block-amide) /poly (ethylene glycol)/ carbon nanotubes mixed matrix membranes have been successfully fabricated using solvent evaporation method to determine the effect of ethylene oxide groups on the performance of fabricated membranes. The effects of CNTs (2-8 wt%) and PEG (up to 50 wt%) were investigated in both single and mixed gas test setup in different temperature and pressure. Finally the membranes were structurally characterized using Scanning Electron Microscopy, X-Ray Diffraction, Fourier Transform Infrared Spectroscopy, and Atomic Force Microscopy. Results showed that addition of carbon nanotubes enhanced the gas separation performance of membranes and presence of ether groups in poly ethylene glycol improved the CO<sub>2</sub> permeability. Membrane containing 8 wt % carbon nanotubes and 50 wt% poly ethylene glycol showed the best performance with CO<sub>2</sub>/CH<sub>4</sub> selectivity and CO<sub>2</sub> permeability of 45 and 302, respectively, at 14 bars operating pressure. Moreover, mixed gas permeation experiments were carried out and results showed dramatic decrease in CO<sub>2</sub> selectivity due to membrane plasticizing. The permeability of CO<sub>2</sub> in mixed gas test for membrane containing 50 wt% polyethylene glycol and 8 wt% carbon nanotubes was 193 with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 19 at ambient environment. Furthermore, membranes fabricated by 6 and 8 wt% carbon nanotubes and 50 wt% polyethylene glycol placed above Robeson's trade-off line. The effect of temperature on performance of fabricated membranes was finally investigated. Results showed an increase in permeability and decrease in selectivity for all membranes.

© 2018 MPRL. All rights reserved.

## 1. Introduction

Environment protection, decrease in heat capacity, and increase in corrosion of pipelines are some main reasons for elimination of acidic gasses (CO<sub>2</sub>, H<sub>2</sub>S) from natural gas [1,2]. Recently membrane technology has attracted the attention of many scientists toward gas separation field by using various types of membranes, including organic and inorganic

## Graphical abstract



membranes. Mixed Matrix Membranes (MMMs) are a type of membrane that cover beneficence of both organic and inorganic membranes [3,4]. In general, addition of inorganic fillers to polymer has two opposite effects and the optimum point of nanoparticle loading should be chosen [5,6].

First studies on MMM was carried out by using zeolite as filler in

\* Corresponding author at: Phone: +98 315 591 2427; fax: +98 315 591 2424  
 E-mail address: asghari@kashanu.ac.ir (M. Asghari)

polymeric matrix. Hennepe and co-workers used zeolite based MMM in pervaporation and gas separation experiences. Results showed that addition of NaX and AgX zeolite particles to PDMS increased both selectivity and permeability of ethane/ethylene mixture [7]. Some researchers also used brilliant properties of carbon nanotubes (CNT) like the high aspect ratio, excellent mechanical, thermal and electrical properties to enhance the performance of polymeric membranes [5,8,9].

Line and Freeman investigated the effect of different precursors for fabrication of membranes for CO<sub>2</sub> elimination from gas mixtures. According to this report, polymers which contain ethylene oxide (EO) functions showed good CO<sub>2</sub> separation performance [10]. PEBA is a thermoplastic copolymer comprised of polyamide groups as its hard segments and polyether groups, like PEO, as its soft segments. Presence of ether oxide segments can enhance the efficiency of PEBA-based membranes for separation of high polarity gasses like CO<sub>2</sub> [11,12].

For the same reason, addition of PEG can improve CO<sub>2</sub> permeation through membranes. PEG polymer has ability to solve acidic gasses and have good CO<sub>2</sub> affinity. This property caused recent research goes toward using PEG/polymer membrane for CO<sub>2</sub> separation. literature review have shown good CO<sub>2</sub> permeability and selectivity and sufficient mechanical stability for these membranes [13,14]. Studies on effect of CO<sub>2</sub> on PEG showed that moving chains of PEG polymer enhance the solubility of CO<sub>2</sub> in polymers. Some studies showed that CO<sub>2</sub> has high solubility tendency into low molecular weight PEG due to presence of ether groups which are more polar and attract polar molecules [15,16]. Computer studies of Garzón revealed that difference in electronegativity of C and O atoms causes specific interactions between CO<sub>2</sub> molecules, which has quadric polar moment, by ether links in PEG structure [17]. Studies on membranes composed of poly ethers like poly(ethylene glycol) diacrylate (PEGda) or poly(propylene glycol) diacrylate (PPGda) satisfied this explanation and showed high CO<sub>2</sub> selectivity and permeability [18]. Also Wang et al. studied on the effect of different PEGs on structure and performance of PEBA MMM and revealed that crystallinity of membranes can be improved by using high molecular weight PEG [13].

By noticing to superb advantageous of PEBA polymer and PEG and CNT additives, a broad study about the important factors which effect on separation performance of MMMs is necessary [19]. To the best of our knowledge, there is no published result in the open literature that have focused on the optimized percentage of additives and on the behavior of interaction of poly ether groups and gases in different pressure and temperature condition. This research was focused on fabrication of membranes comprised of PEBA, CNT, and PEG in different percentages for separation of CO<sub>2</sub> from natural gas. In this work, effect of different factors such as percentage of CNT and PEG in polymer matrix and also influences of temperature and pressure on CO<sub>2</sub> selectivity and permeability were investigated. Additionally in order to surveying characteristics of membranes, permeation test and structural analysis were carried out in both single and mixed gas setup.

## 2. Experimental

### 2.1. Materials

There are some available grads of PEBA like 1657, 6100 and 1205 but 1657 type showed good efficiency for CO<sub>2</sub>/CH<sub>4</sub> separation [20]. In this work, PEBA 1657 was chosen for continuous phase of MMM and purchased from ARKEMA Company. Ethanol was supplied by Merc. In order to diminish crystallinity of membrane, low molecular weight PEG was used as dispersed phase (PEG200) [13,21]. PEG 200 was bought from LOBA Chemie. CNT used in this study was multi wall carbon nanotubes (MWCNTs) and were bought from Notrino with 10-20 nm diameter, 30 μm length, and 200 m<sup>2</sup>/g surface area. CO<sub>2</sub> and CH<sub>4</sub> cylinders were supplied from Roham Gas Co. with purity of 99.99%.

### 2.2. Membrane preparation

#### 2.2.1 Neat PEBA polymeric membrane

PEBA is a hydrophilic polymer and it should be placed into oven at 60 °C to remove the whole of adsorbed solvent and moisture. Water-ethanol mixture by volumetric proportion of 30/70 was identified as best solvent, so polymer was added to water/ethanol solvent to prepare 8 wt% (polymer based) solution [22–24]. Solution was stirred at temperature of 75 °C for 4 hr and then put in ultrasonic bath for 15 minutes. Solution was cast on the glass plate, using 200 micrometer casting knife, to produce a flat thin membrane. The final thicknesses of membranes are about 60 micrometer, evaluated using precise micrometer.

#### 2.2.2 Mixed Matrix Membranes:

CNTs were added to solvent and placed in to ultrasonic bath for 1 hr to acquire high dispersed CNT. Then polymer was gradually added to it and stirred at 75 °C for 4 hr. Prepared solution was casted on smooth glass plate and then dried in room temperature for 3 hr. Remained solvent has been evaporated overnight in oven at 60 °C.

For manufacturing of PEBA/PEG membrane, PEG was added to solvent and stirred for 2 hr. Then, like previous section, polymer was gradually added to it.

In this study, MMMs by different loading of CNTs and PEG were produced. To produce PEBA/CNT/PEG MMM, desired amount of PEG and CNTs were added to solvent and stirred for 4hr. Then, polymer was added to obtain a homogenous solution. Solution was casted and dried in ambient condition like previous samples.

### 2.3. Membrane characterization

A number of characterization methods have been applied on prepared membranes to determine quality and structure of membranes: XRD analysis was carried out to determine structure of membrane using Ni-filtered Cu Ka radiation by a Philips-X'pertpro, X-ray diffractometer. SEM images were taken to describe morphology of MMMs and dispersion of nano particles. LEO-1455VP which was fitted with an energy dispersive X-ray spectroscopy was used to get SEM images. In order to discovering polymeric bonds and presence of functional groups, Nicolet Magna-550 spectrometer recorded Fourier transform infrared (FTIR) spectra in KBr pellets at room temperature in the range of 400–4000 cm<sup>-1</sup> and resolution of 4 cm<sup>-1</sup> for each spectrum and finally Samples in dimensions of 10 μm × 10 μm were taken for AFM analyzing. AFM analysis was conducted using tapping mode of NT-MDT Solver P47 (The Moscow, Russia) with a spatial resolution of ~2 nm in z direction, and used to find surface morphology of membranes.

### 2.4. Gas separation experiments

Permeation tests were carried out in a stainless steel cylindrical module with effective diameter of 30.86 cm<sup>2</sup>. Figure 1 shows schematic of module and permeation test setup. The permeation tests of gases was carried out in pressure range of 6-14 bar and temperature range of 25 to 40 °C, and data was measured using simple soap flow meter for single gas setup. For mixed gas permeation test, permeability was evaluated by gas chromatography setup (Varian CP-3800, column PORAPAK Q).

CO<sub>2</sub> and CH<sub>4</sub> gases with proportion of 50-50 were entered into a cylinder to prepare homogenous mixed gas.

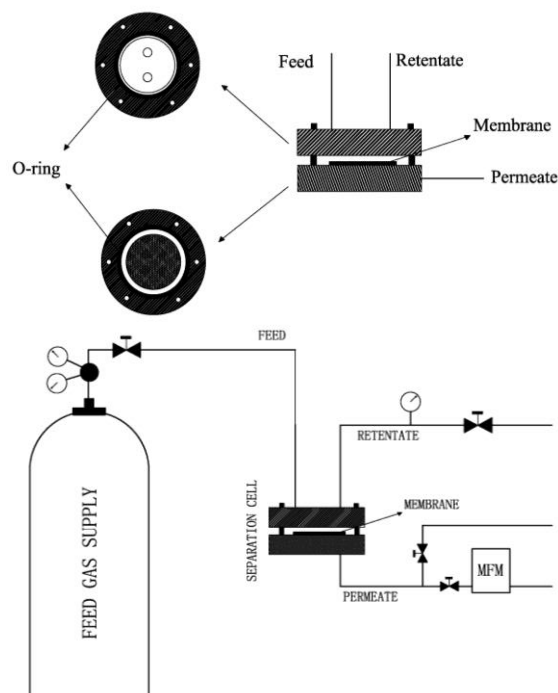


Fig. 1. Schematic of membrane module and permeation test.

In this study both single and mixed gas tests were carried out and permeation of gasses was measured in different pressures. In steady state conditions, permeability and selectivity were calculated from following correlation [25].

$$PA = 10^{10} \times \frac{T_0}{T} \times \frac{P}{P_0} \times \frac{Q \cdot L}{A \cdot \Delta P} \quad (1)$$

$$\alpha = \frac{P_A}{P_B} \quad (2)$$

which  $P_A$  is permeability (barer),  $T_0$  and  $T$  are standard and ambient temperature (K),  $P_0$  and  $P$  are standard and ambient pressures (cm Hg),  $Q$  is volumetric flow rate ( $\text{cm}^3/\text{s}$ ),  $L$  is membrane thickness (cm),  $A$  is effective membrane area ( $\text{cm}^2$ ), and  $\Delta P$  is pressure difference in two sides of membrane (cm Hg).  $\alpha_{AB}$  is ideal selectivity of A respect to B.

Gasses used in this research were  $\text{CO}_2$  and  $\text{CH}_4$  which have kinetic diameter of 3.3 Å and 3.8 Å, respectively. Chemical structure of PEBA compound and PEG200 are depicted in Figure 2.

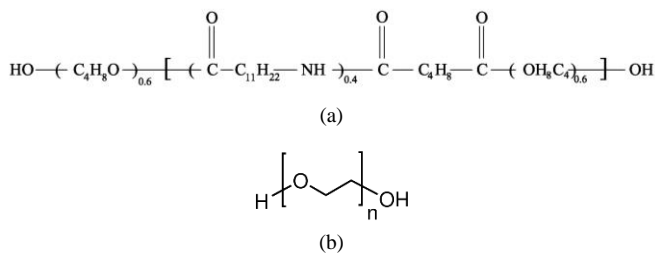


Fig. 2. Chemical structure of (a) PEBA 1657 [26], and (b) PEG 200.

Table 1  
Details of produced membranes.

Membrane composition	Membrane code
PEBA	Neat
PEBA/CNT 2% wt.	C2
PEBA/PEG 50% wt.	P50
PEBA/PEG 10%wt./CNT 2% wt.	P10C2
PEBA/PEG 20%wt./CNT 2% wt.	P20C2
PEBA/PEG 30%wt./CNT 2% wt.	P30C2
PEBA/PEG 40%wt./CNT 2% wt.	P40C2
PEBA/PEG 50%wt./CNT 2% wt.	P50C2
PEBA/PEG 50%wt./CNT 4% wt.	P50C4
PEBA/PEG 50%wt./CNT 6% wt.	P50C6
PEBA/PEG 50%wt./CNT 8% wt.	P50C8

In order to investigate the effect of PEG and CNT, various membranes with different percentage of PEG and CNTs were produced. Details of produced samples are tabulated in Table 1. Additionally some efforts have been done to produce membranes containing more than 50 wt% PEG, but they didn't have adequate strength and mechanical stability, especially in high pressures. All experiments repeated to ensure accuracy and repeatability of membranes.

### 3. Results and discussion

#### 3.1. XRD

XRD results for the neat and MMM membrane with 50% PEG and 2% CNT are shown in Figure 3. A broaden peak can be observed in the range of 15° to 25° degree which shows integration of both hard and soft parts of copolymer [27]. According to this figure, polymer has semi-crystalline structure which shows interconnection of hard part of polymer (polyamides) with soft parts. Neat PEBA polymer has some peaks in  $2\theta = 21^\circ$  and  $23^\circ$  with intensity of 380 and 416, respectively [28]. These peaks describe strong hydrogen bonding between polyamide chains. Therefore additions of CNT and PEG weakened these hydrogen bonds and decreased intensity of peaks in  $21^\circ$ , which means crystallinity of MMM decreased relative to neat PEBA [29].

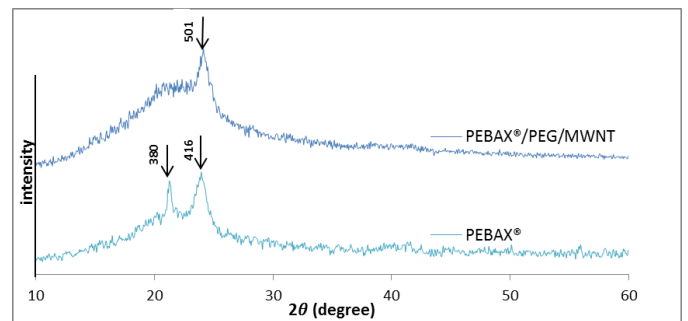


Fig. 3. XRD spectra for neat polymer and MMM.

Additionally, graph showed peak value of  $23^\circ$  reached to value of 501, which this increase could be attributed to elaboration of membrane crystallinity by addition of CNTs [13].

#### 3.2. SEM

In order to prepare samples for SEM image, samples were placed in liquid nitrogen to prepare defect-free cross sections. Figure 4 shows SEM images for neat and MMM membranes with different CNT and PEG loadings. In general, SEM images show absolutely dense morphology without any defect for all neat and MMMs and, therefore, qualify effectiveness of production procedures.

Compatibility between CNT and PEBA are shown in Figure 4 for both 2% and 8% CNT loading (ii-iv). These images specifically show that no CNT aggregations were found in PEBA/PEG/CNT membranes. Figure 4d shows PEBA/PEG MMM which contains 50% PEG.

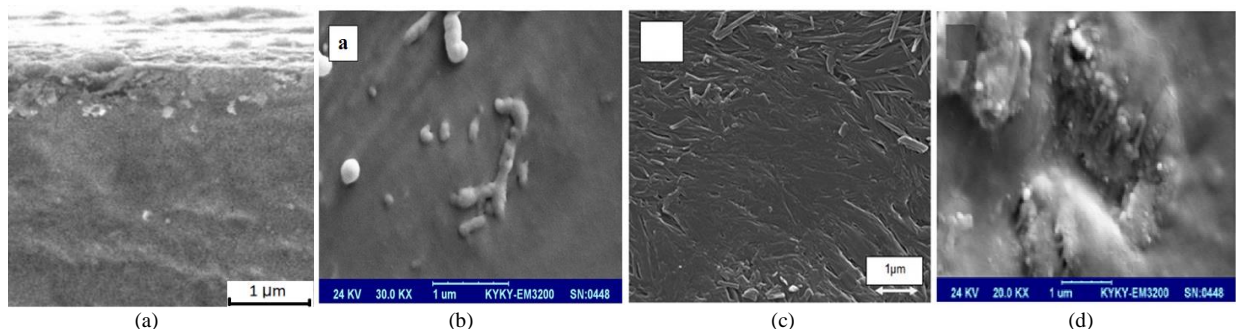


Fig. 4. SEM images of (a) cross sectional of neat PEBA membrane, (b) MMM by 10% PEG and 2% CNT, (c) MMM by 50% PEG and 2% CNT, and (d) MMM by 50% PEG.



### 3.3. FTIR

Molecular structure of polymers was investigated by FTIR to ensure about structure of polymer and exploring any defects which may be produced during production steps in thermal operations, ultrasonic bath or casting step. Literature revealed that addition of nanoparticles or additives could improve performance of membrane when a powerful interaction between polymer and nanoparticles was formed [30].

FTIR results for neat and blended membrane samples are shown in Figure 5. Peaks located in  $1109\text{ cm}^{-1}$  and  $1733\text{ cm}^{-1}$ , respectively, represent C-O- and  $\text{-C=O}$  stretching vibration bonds. The absorption bands in  $1637$  and  $3302\text{ cm}^{-1}$  show H-N-C=O and N-H bonds of PA structure. Wavenumbers of  $2869$  and  $2930\text{ cm}^{-1}$  belong to symmetric and asymmetric aliphatic groups (C-H) which their intensity attenuated after addition of PEG and CNTs. This change can be attributed to physical interaction between polymer and CNTs [31]. C=O group is detectable in wavenumber of  $1657\text{ cm}^{-1}$ . Ether groups (C-O-C) can be detected at  $1040\text{ cm}^{-1}$ . Obtained results, definitely, show that membrane production made no destruction in structure of polymer.

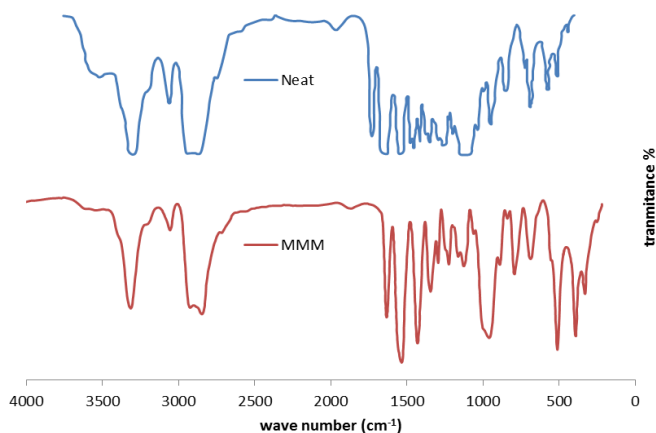


Fig. 5. FTIR results of neat PEBA membrane.

Furthermore C-O-H bonds, relevant to PEG polymer can be observed in  $1544\text{ cm}^{-1}$  and  $1259\text{ cm}^{-1}$ . In  $1540\text{ cm}^{-1}$  peaks of O=C-NH could be also observed, therefore in this area intensity of peaks is stronger. Also peaks at  $1039\text{ cm}^{-1}$  belongs to ether groups of both PEG and PEBA.

Comparison between neat and MMMs revealed that position of peaks for some groups slightly has changed, which suggest existence of some interactions between PEBA polymer and PEG or CNTs. Shifting the peaks of  $\text{-N-H}$  and  $\text{-C=O}$  to lower wave numbers in MMM indicates that addition of PEG enhanced H-bond formation. Also position of C-O-C ether groups shifted to lower wave numbers and could be deduced that H-bond was formed between PEG and PA segments and therefore good interaction between PEG and PEBA has formed [32].

Presence of CNT can shift peaks in  $1100\text{ cm}^{-1}$  to lower frequency. High intensity of peaks in this wavenumber can suggest the good physical blending and chemical stability of matrix and additive polymers. By comparing the graphs, it is also revealed that MWCNT may influence on the C-O and C-H stretching vibration of EO segments through hydrogen bonding interaction [31].

Furthermore peaks of  $1463\text{ cm}^{-1}$  can be attributed to existence of MWCNTs, although CNTs are black bodies and in FTIR test they can adsorb most of IR lights and therefore derived spectrum is not clearly reliable to detect them and FTIR spectrum may have some noise.

### 3.4. AFM

Topography of membrane surface can be significantly explored using AFM technique. Figure 6 shows AFM results for different membranes. Samples in dimensions of  $10\text{ }\mu\text{m}\times 10\text{ }\mu\text{m}$  were taken for AFM analyzing.

As figures show, surface rippling increased with PEG and CNT loading which could be attributed to the formation of bonding between polymer and additives, as previously shown in FTIR spectra results. The formation of H-bonds decreases the fluidity of polymer dope in the stage of solvent evaporation and, as a result, the roughness of surface of MMMs respect to neat ones dramatically increased. Therefore surface area of membranes increased and, consequently, the permeability of membranes increased. Good adhesion between polymer and CNT are revealed in AFM results.

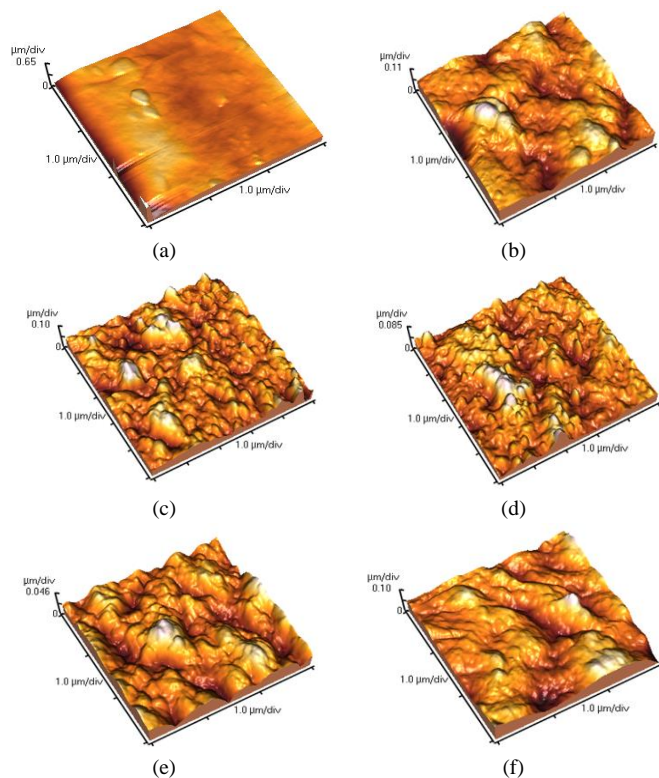


Fig. 6. Surface morphology of membranes obtained by AFM: (a) neat PEBA, (b) MMM with 2% CNT, (c) MMM with 2% CNT and 50% PEG, (d) MMM with 8% CNT and 50% PEG, (e) MMM with 50% PEG, and (f) MMM with 2% CNT.

### 3.5. Single Gas Permeability and Selectivity experiments

An efficient membrane should have high value of both selectivity and permeability [33]. Figures 7 and 8 show permeability and selectivity trends of prepared membranes versus pressure. Results show that the  $\text{CO}_2$  permeability and the  $\text{CO}_2/\text{CH}_4$  selectivity for all membranes increased with PEG and CNT loading and pressure increment. While permeability of  $\text{CO}_2$  for the neat membrane is less than 105 barrer, addition of CNT or PEG enhanced the permeability to about 200 barrer. This value rises to over 302 barrer when both CNT and PEG were added to the polymer, as shown in Figure 7.

CNT has a good affinity to adsorb  $\text{CO}_2$ , so by increase in CNT loading its permeability and selectivity increases. Also  $\text{CO}_2$  adsorption on CNTs increases by pressure and, therefore, the  $\text{CO}_2$  selectivity increases. By addition of CNT as filler, small accumulations are formed by gathering some CNT particles. Addition of more CNTs leads to reach to critical point of filler loading, which is called Percolation Threshold [21]. For PEBA/CNT MMM, this value estimated to be 8 wt% of CNT. According to Figure 7, the  $\text{CO}_2$  permeability versus pressure increases by lower rate for the neat polymeric membrane and the PEBA/PEG MMM relative to CNT containing membranes. In general, PEBA/CNT/PEG MMMs by 50% loading of PEG and 8% loading of CNT give highest permeability value, equal to 302 barrer, whereas the  $\text{CO}_2$  permeability for neat polymeric membrane reached to 105 barrer. MMM with presence of solo CNT showed the permeability of 211, and membrane with PEG showed permeability of 191 under the best condition.

As observed in Figure 8, the PEBA/PEG membrane showed higher increment rate of selectivity relative to other samples. The highest  $\text{CO}_2/\text{CH}_4$  selectivity belongs to PEBA/PEG/CNT by 50% PEG and 8% CNT loading, with value of more than 43. This value for the neat membrane was 25 and for the CNT containing membrane was 13.

Considering the C2 membrane, which fabricated with only 2 wt% CNT, reveals that it has relatively high  $\text{CO}_2$  permeability and low selectivity. This trait could be attributed to some defects on this membrane. It shows that weak adhesion of polymer-CNT made some cracks in membrane structure and this defect caused increasing the permeability and decreasing the  $\text{CO}_2/\text{CH}_4$  selectivity. Increase in permeability of fabricated MMMs could be explained based on the XRD results, which are shown in Figure 3 and the results of previous works [13,34,35]. In better words, addition of both CNT and low molecular weight PEG can decrease the membrane crystallinity and increase the gas permeability, as well. XRD data in Figure 3 revealed that crystallinity

of membranes decreases with PEG loading and, therefore, the  $\text{CO}_2$  interaction with EO unit increases and the  $\text{CO}_2$  permeability rises. Also, PEG polymer increases free volume of copolymer and, as a result, diffusion coefficients of membrane increases. Experimental results satisfy this description very well.

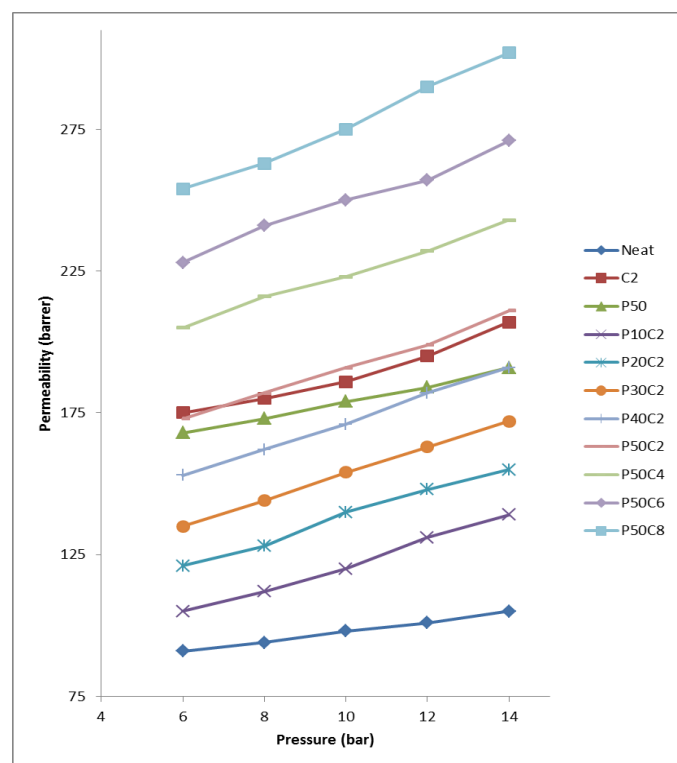


Fig. 7.  $\text{CO}_2$  permeability results of neat and different MMMs.

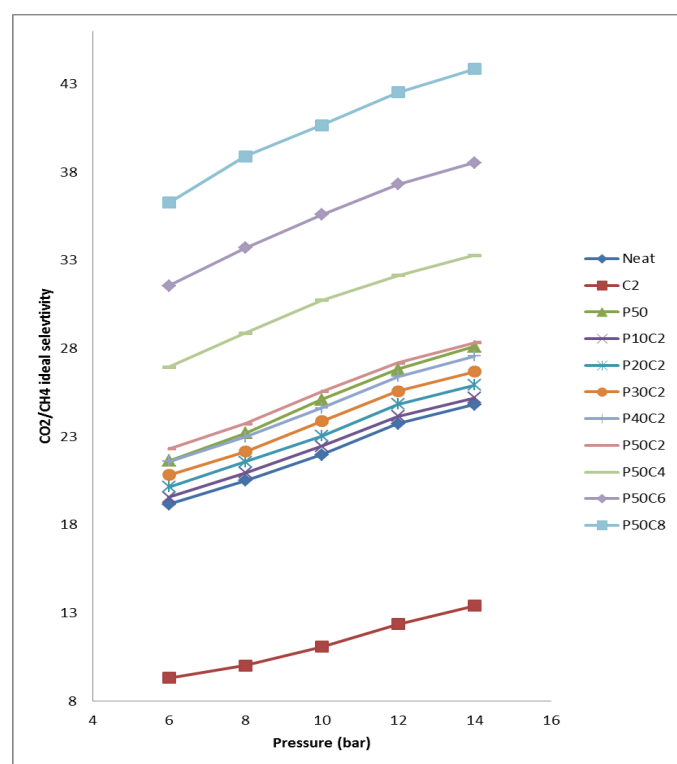


Fig. 8.  $\text{CO}_2/\text{CH}_4$  selectivity for manufactured membranes.

As mentioned earlier, AFM results showed that addition of additives increases the surface area of the membranes and consequently enhance the gas permeability. Also, FTIR results in Figure 5 revealed that by addition of PEG and CNTs, interaction between the polymer and additives increased and this result demonstrates that no voids were formed between PEBA, PEG, and CNTs during blending. This description was experimentally verified as are shown in Figures 7 and 8.

Figure 9 shows the position of fabricated membranes in upper bound curve drawn by Robeson in 2008 and 1991 and comparison of the best prepared membranes by previous studies. Membranes fabricated by addition of CNTs from 2 to 8% with loading of 50% PEG gave points above Robeson's trade off curve (2008) and it can be concluded that they can be applied in commercial scale. As could be observed in Figure 9, the neat membrane has very low selectivity due to its rubbery characteristics and is not suitable for industrial usage. However, incorporation of PEG or CNT enhanced the selectivity of fabricated membranes: MMM uses the beneficence of high permeability of polymeric matrix and high selectivity of nanofillers and therefore membranes could place above the Robeson line.

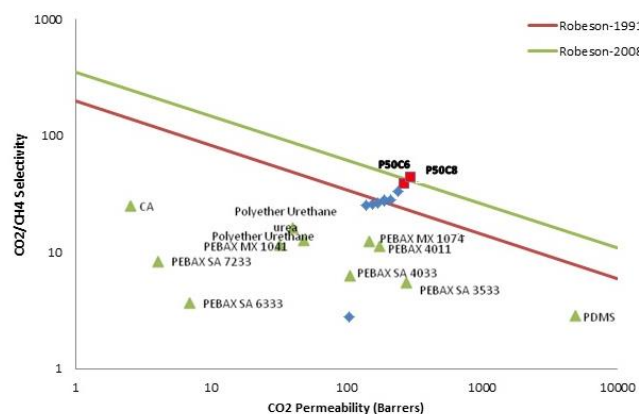


Fig. 9. Position of produced MMM in Robeson's trade off curve.

### 3.6. Mixed gas tests

Lots of studies have carried out about gas separation processes in single gas test mode. Although single gas tests gain adequate data to evaluate the performance and efficiency of fabricated membranes, but real gas separations are performed in mixed conditions. To obtain more accurate results and discovering the effect of different parameters like gas interactions and plasticization, mixed gas test have been carried out in this study.

A gas mixture was prepared by mixing 50%  $\text{CO}_2$  and 50%  $\text{CH}_4$  in pressure of 12 bar. To determine the effect of temperature on the membranes performance, mixed gas experiments were carried out at the temperature range of 298-313 K. Gas fluxes for this mixture in different membranes are shown in Figure 10.

Fluxes for all samples increased with temperature, although membranes which contain both CNT and PEG showed more rapid increment rate. These results have coincidence with loosens of polymer chains in upper temperatures. Like single gas test data, the PEBA/PEG/CNT membrane sample with 50% PEG and 8% CNT showed greatest permeation value, which was about 193 barrer. This value for the neat membrane was 131 under the best conditions. Also, the permeability values for PEBA/CNT (C2) and PEBA/PEG (P50) membranes were 16 and 158, respectively.

Selectivity values of different membranes in mixed gas feed are shown in Figure 11. Selectivity for all samples decreased versus the temperature and PEBA/PEG MMM with 50% PEG showed the most rapid rate. Also, PEBA/PEG/CNT by 50% PEG and 8% CNT showed greatest selectivities in the mixed gas test mode. This change could be attributed to the  $\text{CO}_2$  interactions by the MMM segments. Temperature increment causes the weakness of  $\text{CO}_2$  interactions by the EO groups and carbon parts of membrane, but it does not have such a powerful impact on the  $\text{CH}_4$  interaction. Therefore, temperature increments can diminish the  $\text{CO}_2/\text{CH}_4$  selectivity.

Figure 12 shows the comparison of  $\text{CO}_2$  permeability in two studied conditions: Mixed gas and single gas test modes. It is obvious that the  $\text{CO}_2$  permeability in the mixed gas is lower than that of the single gas results. Relative to single gas results, the  $\text{CO}_2$  permeation in mixed gas condition have dramatically decreased and the  $\text{CH}_4$  permeation showed a significant

increment. This change could be attributed to the plasticization effect, which causes polymer swelling and increase in membrane free volume and the CO<sub>2</sub> permeability.

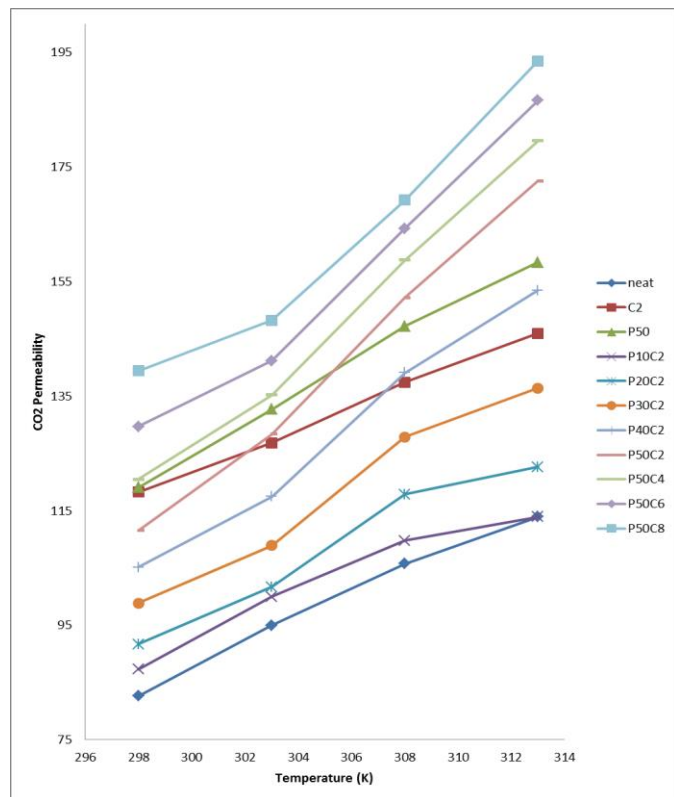


Fig. 10. CO<sub>2</sub> Permeability in mixed gasses for all manufactured membrane.

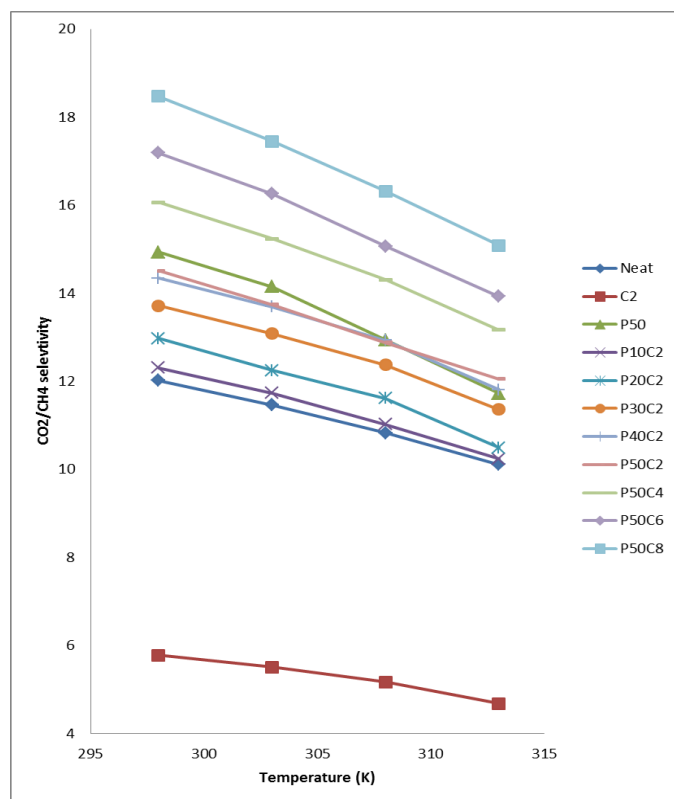


Fig. 11. CO<sub>2</sub>/CH<sub>4</sub> selectivity vs. temperature for all samples in mixed gas feed.

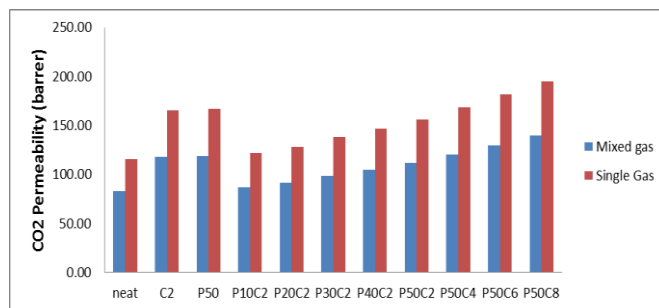


Fig. 12. CO<sub>2</sub> permeability comparison for both mixed and single gas test.

#### 4. Conclusions

By noticing to the remarkable properties of PEBA, which recognized in previous studies (e.g., good permeability and selectivity, chemical resistivity and its price) it was chosen as an adequate polymer for membrane production. This type of membrane could be used for removal of acidic gases from natural gas or flue gas streams. MWCNT and PEG200 were selected to improve efficiency of membrane. Results revealed that CNT loading in the range of 2 to 8 wt.% could have positive effect and PEG percentages between 10-50% shows superb results in gas separation. Best results have gained in MMM with 8wt% loading of CNT and 50wt% loading of PEG. Selectivity increased by addition of both CNT and PEG. Mixed gas test showed that plasticization affected on the MMM performance and decreased the CO<sub>2</sub> selectivity. Temperature increased the permeability for all membranes but decreased the CO<sub>2</sub> selectivity.

#### 5. Acknowledgments

The authors are grateful to Energy Research Institute at University of Kashan for supporting this work.

#### References

- [1] S. Alexander Stern, Polymers for gas separations: the next decade, *J. Membr. Sci.* 94 (1994) 1–65
- [2] P.D. Sutrisna, J. Hou, H. Li, Y. Zhang, V. Chen, Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fiber membranes, *J. Membr. Sci.* 524 (2017) 266–279.
- [3] M.N. Nejad, M. Asghari, M. Afsari, Investigation of carbon nanotubes in mixed matrix membranes for gas separation: a review, *ChemBioEng Rev.* 3 (2016) 276–298.
- [4] K. Li, H. Liang, F. Qu, S. Shao, H. Yu, Z. shuang Han, X. Du, G. Li, Control of natural organic matter fouling of ultrafiltration membrane by adsorption pretreatment: Comparison of mesoporous adsorbent resin and powdered activated carbon, *J. Membr. Sci.* 471 (2014) 94–102.
- [5] D. Zhao, J. Ren, Y. Wang, Y. Qiu, H. Li, K. Hua, X. Li, J. Ji, M. Deng, High CO<sub>2</sub> separation performance of Pebax®/CNTs/GTA mixed matrix membranes, *J. Membr. Sci.* 521 (2017) 104–113.
- [6] B. Freeman, Y. Yampolskii, *Membrane gas separation*, John Wiley and Sons, Ltd., West Sussex, UK, 2010.
- [7] H.J.C. te Hennepe, D. Bargeman, M.H.V. Mulder, C.A. Smolders, Zeolite-filled silicone rubber membranes, *J. Membr. Sci.* 35 (1987) 39–55
- [8] S.M. Fatemi, M. Foroutan, Review on carbon nanotubes and carbon nanotube bundles for gas/ion separation and water purification studied by molecular dynamics simulation, *Int. J. Environ. Sci. Technol.* 13 (2015) 457–470.
- [9] H. Susanto, A.M. Samsudin, N. Rokhati, I.N. Widiasta, Immobilization of glucose oxidase on chitosan-based porous composite membranes and their potential use in biosensors, *Enzyme Microb. Technol.* 52 (2013) 386–392.
- [10] H. Lin, B.D. Freeman, Materials selection guidelines for membranes that remove CO<sub>2</sub> from gas mixtures, *J. Mol. Struct.* 739 (2005) 57–74.
- [11] E.I. Unuabonah, B.I. Olu-Owolabi, K.O. Adebowale, Competitive adsorption of metal ions onto goethite–humic acid-modified kaolinite clay, *Int. J. Environ. Sci. Technol.* 13 (2016) 1043–1054
- [12] I. Khalilnejad, H. Sanaeepur, A. Kargari, Preparation of poly(ether-6-block amide)/PVC thin film composite membrane for CO<sub>2</sub> separation: effect of top layer thickness and operating parameters, *J. Membr. Sci. Res.* 1 (2015) 124–129.

- [13] S. Wang, Y. Liu, S. Huang, H. Wu, Y. Li, Z. Tian, Z. Jiang, Pebax-PEG-MWCNT hybrid membranes with enhanced CO<sub>2</sub> capture properties, *J. Membr. Sci.* 460 (2014) 62–70.
- [14] N. Azizi, T. Mohammadi, R.M. Behbahani, Synthesis of a new nanocomposite membrane (PEBAX-1074/PEG-400/TiO<sub>2</sub>) in order to separate CO<sub>2</sub> from CH<sub>4</sub>, *J. Nat. Gas Sci. Eng.* 37 (2017) 39–51.
- [15] V.I. Bondar, B.D. Freeman, I. Pinnau, Gas transport properties of poly(ether-b-amide) segmented block copolymers, *J. Polym. Sci. Part B Polym. Phys.* 38 (2000) 2051–2062.
- [16] K. Okamoto, M. Fujii, S. Okamoto, H. Suzuki, K. Tanaka, H. Kita, Gas permeation properties of poly(ether imide) segmented copolymers, *Macromolecules* 28 (1995) 6950–6956.
- [17] B. Garzo, L.F. Rull, Computer simulation of vapor-liquid equilibria of linear dipolar fluids: Departures from the principle of corresponding states, *J. Chem. Phys.* 102 (1995) 7204–7215.
- [18] N.P. Patel, M.A. Hunt, S. Lin-Gibson, S. Bencherif, R.J. Spontak, Tunable CO<sub>2</sub> transport through mixed polyether membranes, *J. Membr. Sci.* 251 (2005) 51–57.
- [19] Y. Labreche, Functionalized polymeric membranes for CO<sub>2</sub> capture, *J. Membr. Sci. Res.* 2 (2016) 59–65.
- [20] S. Sridhar, T.M. Aminabhavi, S.J. Mayor, M. Ramakrishna, Permeation of carbon dioxide and methane gases through novel silver-incorporated thin film composite pebax membranes, *Ind. Eng. Chem. Res.* 46 (2007) 8144–8151.
- [21] A. Car, C. Stropnik, W. Yave, K. V. Peinemann, PEG modified poly(amide-b-ethylene oxide) membranes for CO<sub>2</sub> separation, *J. Membr. Sci.* 307 (2008) 88–95.
- [22] H.W. Yen, Z.H. Chen, I.K. Yang, Use of the composite membrane of poly(ether-block-amide) and carbon nanotubes (CNTs) in a pervaporation system incorporated with fermentation for butanol production by *Clostridium acetobutylicum*, *Bioresour. Technol.* 109 (2012) 105–109.
- [23] T. Wu, N. Wang, J. Li, L. Wang, W. Zhang, G. Zhang, S. Ji, Tubular thermal crosslinked-PEBA/ceramic membrane for aromatic/aliphatic pervaporation, *J. Membr. Sci.* 486 (2015) 1–9.
- [24] S. Liu, G. Liu, X. Zhao, W. Jin, Hydrophobic-ZIF-71 filled PEBA mixed matrix membranes for recovery of biobutanol via pervaporation, *J. Membr. Sci.* 446 (2013) 181–188.
- [25] H. Cong, J. Zhang, M. Radosz, Y. Shen, Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4-phenylene oxide) for gas separation, *J. Membr. Sci.* 294 (2007) 178–185.
- [26] J.P. Sheth, J. Xu, G.L. Wilkes, Solid state structure-property behavior of semicrystalline poly(ether-block-amide) PEBAX<sup>®</sup> thermoplastic elastomers, *Polymer* 44 (2002) 743–756.
- [27] S. Wang, Y. Liu, S. Huang, H. Wu, Y. Li, Z. Tian, Pebax-PEG-MWCNT hybrid membranes with enhanced CO<sub>2</sub> capture properties, *J. Membr. Sci.* 460 (2014) 62–70.
- [28] S.G. Lovineh, M. Asghari, G. Khanbabaei, CO<sub>2</sub> permeation through poly(amide-6-b-ethylene oxide)-nanosilica membranes, *Appl. Surf. Sci.* 318 (2014) 176–179.
- [29] S. Liu, G. Liu, J. Shen, W. Jin, Fabrication of MOFs/PEBA mixed matrix membranes and their application in bio-butanol production, *Sep. Purif. Technol.* 133 (2014) 40–47.
- [30] K. Nath, Z.B. Maroulis, D.S. George, Membrane separation processes, *Food Process Des.* 8 (2008) 336–338.
- [31] X. Zheng, Q. Xu, Comparison study of morphology and crystallization behavior of polyethylene and poly(ethylene oxide) on single-walled carbon nanotubes, *J. Phys. Chem. B.* 114 (2010) 9435–9444.
- [32] M. Asghari, A. Mahmudi, V. Zargar, G. Khanbabaei, Effect of polyethyleneglycol on CH<sub>4</sub> permeation through poly(amide-b-ethylene oxide)-based nanocomposite membranes, *Appl. Surf. Sci.* (2014) 218–222.
- [33] N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, *Advanced membrane technology and applications*, John Wiley and Sons, Ltd., West Sussex, UK, 2008.
- [34] Y. Li, T.-S. Chung, Molecular-level mixed matrix membranes comprising Pebax<sup>®</sup> and POSS for hydrogen purification via preferential CO<sub>2</sub> removal, *Int. J. Hydrogen Energ.* 35 (2010) 10560–10568.
- [35] V.I. Bondar, B.D. Freeman, I. Pinnau, Gas sorption and characterization of poly(ether-b-amide) segmented block copolymers, *J. Polym. Sci. Part B Polym. Phys.* 37 (1999) 2463–2475.