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Nano composite PEBAX®/PEG membranes: Effect of MWNT filler on CO$_2$/CH$_4$ separation

ABSTRACT

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The performances of two-phase polymer-liquid PEBAX®/polyethylene glycol (PEG) and three-phase polymer-liquid-solid PEBAX®/PEG/MWNT thin film composite membranes for CO$_2$ and CH$_4$ permeation were studied. The effect of temperature and MWNT/PEBAX® ratio on single gas (CO$_2$ and CH$_4$) permeability was investigated. The permeation of both gases was measured at different temperatures from 303 to 323 ˚K. The results exhibited that the PEBAX®/PEG/MWNT membrane had better permeability for CO$_2$ in comparison to the PEBAX®/PEG membrane, whereas CO$_2$/CH$_4$ selectivities in both membranes were almost the same; i.e. MWNT filler promoted the performance of PEBAX®/PEG membrane in CO$_2$/CH$_4$ Separation. Also, the permeability increases with temperature in all experiments. For the three-phase PEBAX®/PEG/MWNT membrane, CO$_2$ permeability was determined 221 Barrer in 323˚K and the selectivity was obtained as 23 in 303 ˚K.

Keywords: *CO$_2$; Mixed matrix membrane; MWNT; Nanocomposite; PEBAX®.*

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INTRODUCTION

Today's industrial production and infrastructure in the world are based on fossil fuel use, which is related directly with the generation of energy. Thus, it is believed that the combustion of fossil fuels and other human activities are the reasons for the increased concentration of greenhouse gases all over the world, where carbon dioxide (CO$_2$) is one of the largest contributors to global warming. Therefore, its capture from different sources such as power stations, oil refineries and large cement works is very important. Flue gas usually contains low concentration of CO$_2$ (<20%) [1]. Gas separation of exhaust gases, in particular of CO$_2$ is a key task to reduce the so-called greenhouse effect and global warming.

Hence, there is an increasing demand to develop new and more powerful membrane materials for various gas separation applications. However, high throughput, i.e. high permeability and high selectivity are naturally counteracting, and for polymeric membrane materials this is usually expressed as an upper bound proposed by Robeson [2]. Attempts are being made to improve the performance by modifying the polymer both physically and chemically to bring about an increase in both flux and selectivity of the membrane [3].

Recent strategies on materials development are centered in the incorporation of nanoparticles or more generally, a second phase into existing suitable membrane materials [2]. During the last two decades, many new polymers have been developed for gas separation membranes which have been described in literature. Recently, Lin and Freeman have reported an overview about material selection for membrane preparation that removes CO_2 from gas mixtures [4].

In that article, CO_2 solubility and CO_2/gas solubility selectivity in solvents and polymers containing different polar groups were discussed. They have concluded that ethylene oxide (EO) units in the polymer appear to be the most useful groups to achieve high CO_2 permeability and high CO_2/light gas selectivity. Homopoly(ethylene oxide) (PEO) consists of EO monomeric units, but its disadvantage is the strong tendency to crystallize and consequently it presents low gas permeability Block copolymers containing EO units as poly(amide-*b*-ether) has been shown as alternative material for this purpose.

These copolymers were developed in 1972 but in 1981 began to be used for commercial purpose under the trade name PEBAX® produced by ATOCHEM (now ARKEMA). PEBAX® is a thermoplastic elastomer having the following general chemical structure (Figure 1): PA is an aliphatic polyamide "hard" block (e.g., nylon-6, nylon-12) and PE is an amorphous polyether (polyethylene oxide (PEO) or polytetra methylene oxide (PTMO)) "soft" block The PA blocks provide the mechanical strength and gas transport occurs through the PEO phase Block copolymers with immiscible soft and rigid blocks like PEBAX® can form various microphase separated structures.
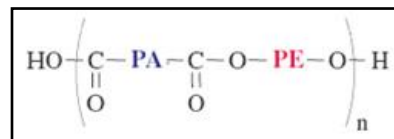

Fig. 1. Chemical structure of PEBAX®

PEBAX® has been shown as promising membrane materials for acid gas treatment. Bondar et al. have studied CO_2/N_2 and CO_2/H_2 separation using different grade of PEBAX® membranes [5]. They have reported high CO_2/N_2 and CO_2/H_2 selectivity, which were attributed to high CO_2 solubility due to the strong affinity of the polar ether linkages for CO_2. Kim et al. have also reported high permeability and high selectivity for CO_2 over N_2 as well as SO_2 over N_2, and these properties were attributed to polarizability of gases due to PEO segments [6]. On the other hand, mesoblends of polyether block copolymers and poly (ethylene glycol) (PEG) were generated by Patel and Spontak, and it was found that CO_2/H_2 selectivity can be improved by incorporation of PEG [7]. The effect of PEG in the polymer chain to CO_2 transport properties in different polymer systems was also described by other researchers and it was proven that EO units influence CO_2 transport in glassy and rubbery polymers [8].

As it is well known, polymeric membranes, which have been traditionally used for water purification and gas separation, have several limitations like low selectivity, permeability, susceptibility to the obstruction or fouling as well as their chemical and thermal resistance. The inherent characteristics of CNTs such as high porosity and surface area have attracted their interest in the preparation of membranes. In fact, they have succeeded to resolve some of these drawbacks. Moreover, CNTs-based membranes not only have been used to discriminate molecules based on their size but also by the use of functionalized CNTs, molecules transport can also be influenced. In this sense, the manufacture of CNTs-based membranes has dramatically increased in recent years, particularly for their use in gas separations and water treatment. Most manuscripts have focused on the use of different types of membranes with CNTs embedded in a polymer matrix, which can improve the selectivity and permeability of the molecules. This new kind of

membranes called CNTs-MMMs offer high stability and efficiency, low cost and ease of operation. However, the fabrication of CNTs-MMMs is still under development in order to prevent aggregation and to ensure that CNTs are homogeneously and individually dispersed throughout the matrix [9]. Cong. et al. reported a CO_2 permeability of 148 Barrers at 5% MWNT concentration [10]. Polycarbonate loaded with single walled (SWNT) and multiwalled (MWNT) carbon nanotubes appeared to have potential for H_2 separation. Hinds et al. reported MWNT loaded membranes to have potential applications in chemical separations and sensors [11]. They also found SWNT to disperse more uniformly in the polymer after functionalization with carboxylic acid [3].

In this work, PEBAX®/PEG/MWNT and PEBAX®/PEG blend membranes were synthesized for single gas (CO_2, CH_4) permeation and their performances were estimated.

EXPERIMENTAL

Materials

Poly(ether-block-amide, PEBA) resin is best known under the trademark PEBAX®, and is a thermoplastic elastomer combining linear chains of rigid polyamide segments interspaced with flexible polyether segments [12,13]. PEBAX-1657 was purchased from Arkema. MWNT of diameter 10-20 nm, length 30 μm, and surface area 200 m^2/g were supplied by Neutrino, Iran. PEG200 and ethanol were supplied by Loba Chemie and Merck, respectively. CO_2 and CH_4 cylinders with the purity of 99.99% were supplied from Roham Gas Co. and deionized water was produced with a lab-scale reverse osmosis system.

Membrane preparation

In order to prepare the membranes, PEBAX® (60 wt% PEO and 40 wt% of PA-6) was dissolved in a mixture of ethanol/water; the polymer solution was stirred under reflux at 75°C for 4 h. After cooling the solution to 30°C, for preparing PEBAX®/PEG membrane, 50 wt% PEG 200 (molecular weight of 200 g/mol), which had individually been stirred in ethanol/water solvent under reflux at 30°C for 2 h, was added to PEBAX®

solution. The solution was then stirred under reflux at 30°C for 20 h. The composite membrane body was prepared by casting the obtained homogeneous dope. Solvent evaporation was controlled by covering it with a glass dish at 30°C for a while. The membrane film was then dried in a vacuum oven to remove residual solvent.

In order to prepare PEBAX®/PEG/MWNT mixed matrix membrane, a given amount of PEBAX® was added to a sonicated MWNT-water/ethanol colloid. The obtained mixture was stirred for 4 hours. PEG was then introduced to the mixture stirred for 2 hours at 30°C. Preparation of the nano-composite membrane body and solvent evaporation was done as before.

Membrane characterization

The resulting morphologies of the synthesized membranes were characterized using scanning electron microscopy (SEM). The SEM analyses were carried out with the apparatus of FESEM Hitachi S4160**.**

Permeability of pure CO_2 and CH_4 through the membranes was measured at different temperature from 303 to 323 k and constant pressure of 4 bar using a lab-scale dead-end sheet membrane module.

A constant pressure apparatus was applied for gas permeation tests. When the steady-state conditions were achieved, the gas permeability and the intrinsic selectivity could be determined by Eqs. (1) and (2):

$$P = (Q \cdot l)/(A \cdot \Delta p) \ \times \ T_0/T \qquad (1)$$

$$\alpha_{A/B} = \ P_A/P_B \qquad\qquad (2)$$

Where *P* is permeability in Barrer (1 Barrer = 10^{-10} cm^3(STP) cm/ (cm^2·s·cmHg), or 3.35×10^{-16} mol/(m·s·Pa) in SI unit), *Q* the permeation rate measured by bubble flow meters (cm^3/s), *l* and *A* the thickness (cm) and the effective area (cm^2) of the membranes, respectively, Δp the transmembrane pressure difference (cmHg), *T* the absolute temperature (K), and T_0 represents 273.15 K. The permeances and selectivities of the nano-composite membranes were determined by the following equation:

$$J = Q/(A \cdot \Delta p) \times T_0/\text{T} \qquad (3)$$

$$\alpha_{A/B} = J_A/J_B \qquad (4)$$

Where *J* is the pure gas permeance in GPU (1GPU=10^{-6} cm^3(STP)/(cm$^2 \cdot$s$\cdot$cmHg), or 3.35×10^{-10} mol/(m$^2 \cdot$s$\cdot$Pa) in SI unit) [14].

RESULTS AND DISCUSSION

Variables tailoring MMMs performance

Among all the studies on MMMs, a number share the view that the performance of MMMs is not a simple addition of the intrinsic properties of individual phase. Many variables may seriously affect MMM performance, making it difficult to understand. Currently, the major concerns in research on MMM are a suitable combination of polymers and particles, the physical properties of the inorganic fillers (e.g., particle size and particle agglomerations), and the polymer/particle interface morphologies.

- ### *Solvent preparation*

Addition of PEG into the PEBAX® matrix improved the permeability and selectivity of the membranes, especially when a condensable gas is present in a mixture of gases (i.e. condensable and permanent gas mixture). This improvement of CO$_2$ permeation was mainly attributed to the presence of EO units (polar ether oxygen) in the polymer matrix due to the favorably interaction with CO$_2$ molecules [2]. PEBAX® copolymers are hydrophilic and show excellent chemical resistance towards solvents. The solubility of these copolymers in different solvents is determined by

the ratio of PA and PEO blocks. Higher content of PEO makes the polymer more hydrophilic and thus, it leads to different solubility property. The solubility parameter (*δ*) for PEBAX® MH 1657 estimated by Small method was found as 22 MPa$^{0.5}$ approximately. Thus solvents or mixtures of two or more solvents which have a solubility parameter similar to PEBAX® can dissolve to it. The mixtures of ethanol/water have a solubility parameter between 26 MPa$^{0.5}$ (ethanol) and 48 MPa$^{0.5}$ (water). The mixture used here has an estimated solubility parameter of 33 MPa$^{0.5}$, which is not very close to the PEBAX® solubility parameter. In this case, the gelation problems can be explained better by the polarity of solvents. The hydrophilic compound needs solvents with high polarity (high dielectric constant), and thus, values of dielectric constants give information about the gelation of a polymer solution; *n*-butanol and formic acid have a dielectric constant of 17.6 and 58.5, respectively, and formic acid dissolves PEBAX® (hydrophilic) at room temperature due to its high dielectric constant. The mixture ethanol/water has an estimated dielectric constant of 45, which helps to explain the good solubility of PEBAX® MH 1657 in this mixture [8].

- ### *Particle sedimentation and agglomeration*

The schematic for the formation of a pattern at the surface is shown in Figure 2. During the fabrication of an MMM, one factor of great importance is particle agglomeration due to sedimentation or migration to the surface. Second factor is due to the totally different physical properties and difference in density between MWNT and polymers.
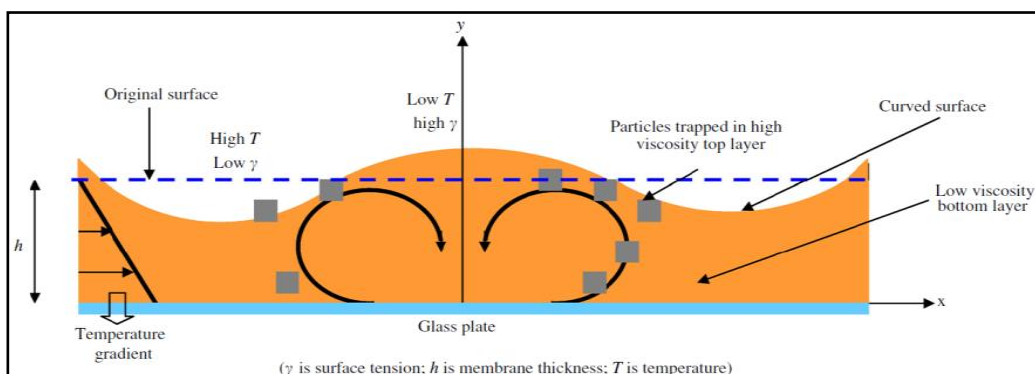

Fig. 2. Development of the instability in films cast at elevated temperature

In contrast to sedimentation, particles may move to the membrane surface and agglomerate. This phenomenon often occurs when the membranes are formed at high temperatures. It is believed that agglomeration at the surface is the result of convection cells that form during casting of films. The formation of convection cells in liquids that are heated or cooled can be due to instabilities driven by buoyancy or surface tension. Increasing casting solution viscosity, decreasing the membrane thickness, and heating the membrane from the top side may efficiently prevent the surface pattern from propagating.

- *Interface morphologies*

The transport properties of organic/inorganic MMMs are strongly dependent on the nanoscale morphology of the membranes. The morphology of the interface is a critical determinant of the overall transport property. Figure 3 shows a schematic diagram of various nano-scale structures at the polymer/particle interface.
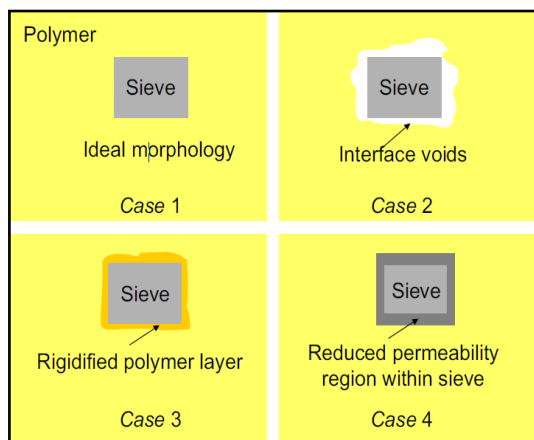

Fig. 3. The schematic diagram of various nanoscale morphology of the mixed matrix structure

Case 1 represents an ideal morphology, corresponding to the ideal Maxwell model. Case 2 shows the detachment of polymer chains from the inorganic filler surface, causing the interface voids. Case 3 indicates that the polymer chains in direct contact with the filler surface can be rigidified compared to the bulk polymer chains. Case 4 displays a situation in which the surface pores of the filler has been partially sealed by the rigidified polymer chains.

The poor polymer/inorganic filler contact could result in interface voids, presumed to be the major cause for the more or less deteriorated performance as gas molecules take this non-selective and less resistant by-pass instead passing through pores in the particle. Other possible causes for the interface voids formation include repulsive force between polymer and filler and different thermal expansion coefficients for polymer and particle. Upon the formation of intimate contact between polymer and particles, other situations including polymer chain rigidification (Case 3) and pore blockage (Case 4) might occur. The mobility of polymer chains in the region directly contacting the particles can be inhibited relative to that for the bulk polymer, an effect called rigidification [15].

Membrane Morphology

- *SEM*

The SEM images of PEBAX®/PEG/MWNT and PEBAX®/PEG membranes are represented in Figure 4. The morphology of the PEBAX®/PEG/MWNT (Figure 4a) shows a homogeneous distribution of good-dispersed fillers in polymer matrix. Figure 4b exhibits the surface morphology of PEBAX®/PEG membrane. As seen, PEBAX®/PEG has a smooth and homogeneous surface. The mmembranes thickness, measured by a digital micrometer, was about 90 μm.
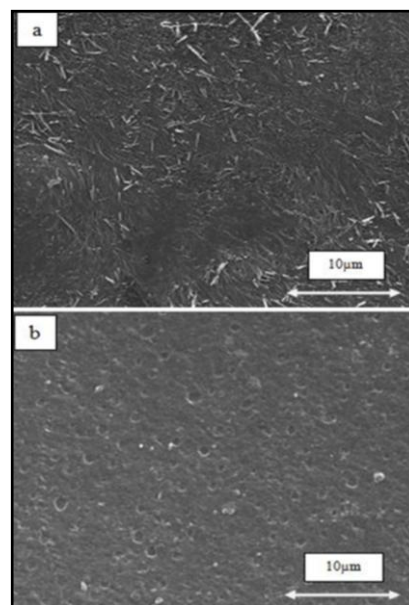

Fig. 4. SEM pictures representing the (a) surface of PEBAX®/PEG/MWNT, (b) surface of PEBAX®/PEG

Gas permeability

In the case of measuring gas permeability, two kinds of membrane (PEBAX®/PEG, PEBAX®/PEG/MWNT) were examined to determine their performances. Figure 5 shows the permeation trend for the membranes versus feed temperature. As seen, gas permeability has increased with temperature in the range of 303 to 323 K. It is found that after MWNT loading, the three–phase PEBAX®/PEG/MWNT membrane showed a substantial enhancement in permeability for CO_2. CO_2 molecules appeared to experience greater diffusivity and exhibited a more substantial increase from 191 Barrers at 0% MWNT to 221 Barrers at 2% loading under the pressure of 4 bars and temperature of 323 K. The obtained data for permeation and selectivity at 4 bar pressure are presented in Table 1.
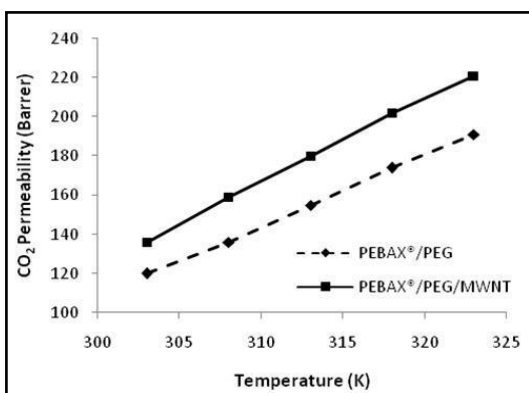

Fig. 5. Effect of temperature on CO_2 permeation through PEBAX®/PEG/MWNT and PEBAX®/PEG Membranes

Polymeric membranes are generally nonporous, and gas permeation is governed by the solution–diffusion mechanism, which, as the name implies, is determined by solubility and diffusivity of gases within the polymer matrix. Gas molecules diffuse from the feed side to the gas-membrane interface where they dissolve and permeate across the membrane by random molecular diffusion, followed by desorption and diffusion into the permeate bulk stream. Diffusion occurs in free-volume elements (0.2 and 0.5 nm in size) between the polymer chains that appear and disappear continuously due to thermal motion. Gas diffusion through the nonporous polymeric structures is inherently slow; thus, polymeric membranes exhibit low CO_2 permeance with moderate CO_2/CH_4 selectivity [16].

If solution-diffusion is assumed as the mode of transport of the compounds through the membrane, the permeability of a single gas (P_i) [cm^3 standard temperature and pressure (STP) cm/cm²·s·cmHg] can be described as the product of its solubility (S_i) [cm^3 gas/cm^3 Polymer cmHg] and diffusivity (D_i) [cm^2/s] through the material [17]:

$$P_i = D_i \cdot S_i \qquad (5)$$

The experiments showed that at all temperatures, the PEBAX®/PEG/MWNT membrane has exhibited higher CO_2 permeability in comparison to PEBAX®/PEG membrane. As shown in Figure 5, higher temperatures enhance the gas flux through the membranes. It could be due to the increased motion of polymer chains, and thus the increase of CO_2 diffusivity within the membrane matrix. High porosity and surface area of MWNT resulted in a higher permeability of CO_2 through the PEBAX®/PEG/MWNT membrane in comparison to the PEBAX®/PEG membrane. Afterward, CH_4 permeation was measured at different temperatures for both membranes in order to determining CO_2/CH_4, selectivity. As seen in Figure 6, the selectivity decreased with temperature, due to the increased CH_4 permeation as the temperature increase.
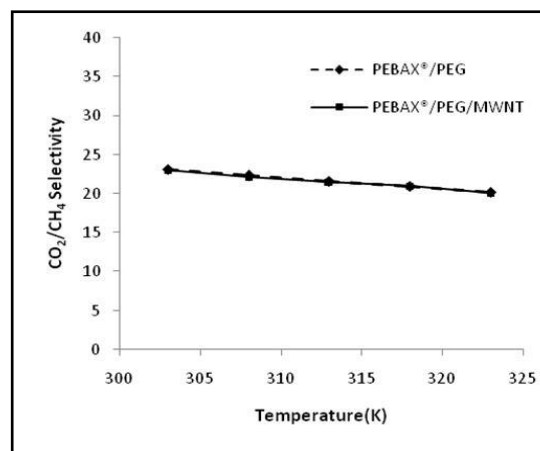

Fig. 6. Effect of temperature on CO_2/CH_4 selectivity in PEBAX®/PEG/MWNT and PEBAX®/PEG Membranes

We think there are still more ways for increasing the permeation of CO_2 and we hope that present better results in future, in order to have a more efficient sweetening of natural gas.

Table 1. Effect of temperature and MWNT Concentration on CO_2 Permeability and CO_2/CH_4 selectivity

Temperature (K)	CO_2 Permeability (Barrer)		CO_2/CH_4 Selectivity	
	PEBAX®/PEG	PEBAX®/PEG/MWNT	PEBAX®/PEG	PEBAX®/PEG/MWNT
303	120	136	23.1	23.0
308	136	159	22.3	22.1
313	155	180	21.6	21.5
318	174	202	21.0	21.0
323	191	221	20.2	20.1

CONCLUSIONS

Effect of MWNT filler presence in the matrix of composite PEBAX®/PEG membranes on their CO_2/CH_4 separation performances in different temperatures has been studied. As operationally characterization of the fabricated membranes, gas temperatures varied from 303 to 323 ˚K in a lab-scale dead-end sheet membrane module. The morphological study on the fabricated membranes using SEM as well as the reasonable trend of CO_2 permeation through the membranes indicated the defect-free structure of PEBAX®/PEG/MWNT membrane. CO_2 Permeation increased gently with temperature for both PEBAX®/PEG membranes (with or without MWNT), whereas their CO_2/CH_4 selectivities decreased. Additionally, results showed that the three-phase PEBAX®/PEG/MWNT membrane had a higher permeability in comparison to the two-phase PEBAX®/PEG membrane, while the selectivities were the same. For the three-phase PEBAX®/PEG/MWNT membrane, CO_2 permeability was determined 221 Barrer in 323 ˚K and the selectivity was obtained as 23 in 303 ˚K.

ACKNOWLEDGEMENTS

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