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Nano composite PEBAX® membranes: Effect of zeolite X filler on CO₂ permeation

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ABSTRACT

A PEBAX-nano zeolite X mixed matrix membrane was fabricated and operationally characterized using single gas (CO₂) permeation. X-ray diffraction (XRD) analysis was used to study the arrangement of polymer chains of mixed matrix membrane. The membranes were characterized by scanning electron microscopy (SEM) to study cross-sectional morphology. The single gas permeability were carried out for neat PEBAX and PEBAX-nano zeolite X (10 wt. %) membranes. Operating pressures varied from 6 to 14 bars. CO₂ permeability for the nano-composite membrane was higher than the neat polymer membrane and increased with pressure. Adding 10 wt.% of nanozeolite X into the polymeric matrix caused CO₂ permeability to increase. Both structurally and operationally characterizations revealed the defect-free structure of the nano composite membrane.

Keywords: *CO₂; Mixed matrix membrane; Zeolite X; Nanocomposite; PEBAX®.*

INTRODUCTION

The separation of sour gases CO₂, H₂S, and SO₂ from nonpolar gases is of considerable environmental and industrial importance, which is always desirable for global warming reduction, natural gas cleaning, and acid rain formation avoiding. Based on different principles, a wide range of separation technologies such as absorption, adsorption, membranes and cryogenic distillation are being investigated and used for the removal of sour gases. Compared with other separation techniques, polymer-based membranes offer a great potential for low-maintenance operations, low energy requirement, ease of scale-up, and exceptional reliability [1].

Despite the early acceptance of polymeric membranes for gas separation, no large scale applications were introduced until the seventies of last century [2]. Main reason was the lack of polymeric membrane materials and membrane structures, which could combine high selectivity and high flux.

Commercial membrane systems for gas separation were available since the mid 70ies, but the most important innovation for large-scale commercialization of polymeric membranes for gas separation was achieved by Permea (now Air Products) in 1980 [3]. This success of commercialization of polymeric membranes increased the investigations related to the development of new membrane materials and techniques of membrane preparation, and since then, many applications for membrane based gas separation have been developed. Natural gas, with 70 to 90 percent of CH_4, has impurities such as CO_2 and H_2S that produce acid solution in contact with H_2O. This so called sour gas and in combination with water, CO_2 highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. Membrane technology has become an essential alternative for efficient gas separation processes. Polymeric membranes generally undergo a trade-of limitation between permeability and selectivity as shown in the upper bound curves developed by Robeson. 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. Polymeric membranes have received the most attention in this field due to the manufacturability, low material costs, robust physical characteristics and good intrinsic transport properties [4]. Rigid polyamides have attracted much attention as the basic material for preparing gas separation membranes due to their glassy but selective nature. In contrast, polyethers are rubbery polymers containing large free volume owing to their flexible chains and the presence of voids between them. The permeation properties of a polymeric membrane depend on the chemical microstructure, crystallinity and morphology of the polymer [5]. Permeate properties like size, shape and polarity determine transport properties [6]. The permeability depends on the solubility and diffusion coefficient of the permeate species in the polymer. Generally, better selectivities are obtained with glassy polymers because the diffusion coefficients in this type of material are more dependent on molecular size than in rubbery polymers. In this paper, poly (amide-6-b-ethylene oxide) (PEBA 1657) block copolymer, composed of 60 wt% of PEO and 40 wt. % of PA6 (nylon-6), was used to prepare membranes. PEBA 1657 dense film was prepared to investigate the intrinsic permeability of PEBA 1657 copolymer. While PEBA 1657-zeolite X composite membranes were prepared for sour gas separation. The chemical structure of PEBAX-1657 Polymer is given in Figure 1 [4].
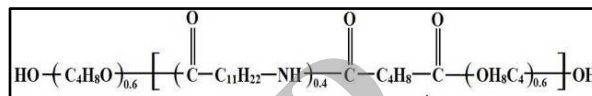

Fig. 1. Chemical structure of PEBAX-1657

This structure creates a blend of properties of thermoplastics and rubbers. The hard amide block provides the mechanical strength, whereas gas transport occurs primarily through the soft ether block [4].

EXPERIMENTAL

Materials

The materials and chemicals used for the membranes were PEBAX® (60 wt% PEO and 40 wt% of PA-6), nano zeolite X (SPRG) and ethanol (Merck). CO_2 gas cylinder purity was 99.999.

Zeolite synthesis

Nano zeolite X used in this work was prepared at SPRG [7]. Specific amount of sodium hydroxide dissolved in water. Sodium aluminate was then added to the solution, stirring at 100°C until dissolved. A solution of sodium silicate and sodium hydroxide in water was prepared in parallel, Afterwards these solutions were mixed and stirred for 30 min. Finally, the obtained gel was hydrothermally heated in an autoclave at 90°C for 14 h. XRD analysis of synthetic zeolite is carried out and showed that zeolite X nano crystals are produced [7].

Membrane preparation

Nano zeolite X was added to a solvent mixture of 70% ethanol and 30% v/v water and stirred at room temperature for 12h. The solution

was then sonicated for 1 h to obtain a fairly homogeneous colloid of zeolite and solvent. PEBAX polymer was dried at 60 °C for 2 h and then added to the zeolite colloid to get a 12 wt% dope with a polymer/zeolite ratio of 90/10. The dope under reflux at 80°C and 12 h stirring to ensure the polymer was completely dissolved. Membrane casting is carried out with solution casting and solvent evaporation technique. After evaporation of solvent for 3 h in room temperature, the film was immersed into a water bath. The obtained body of the mixed matrix membrane was dried overnight at 60°C to remove any residual solvent.

XRD Analysis

X-ray diffractometer was used to measure the solid-state morphology of PEBAX 1657 and NaX-PEBAX. X-rays of 1.5406 Å wavelength was generated by Cu source. The angle (2θ) of diffraction was varied from 0° to 60° to identify the crystal structure and the intermolecular distances between intersegmental chains [8].

SEM Analysis

The morphology of PEBAX and nano composite PEBAX-zeolite X membranes was examined using scanning electron microscopy (SEM) after gold coating of the sample. SEM images of the composite membrane cross section were obtained in a similar way, after fracture in liquid nitrogen.

RESULTS AND DISCUSSION

XRD

XRD analysis of synthetic zeolite showed that zeolite X crystals were produced. A comparison of XRD patterns for NaX in literature and synthetic NaX are illustrated in Figure 2. XRD patterns of PEBAX-zeolite X composite were compared with those of pure nano zeolite X and PEBAX. In general, when a polymer contains a large crystalline region, the peak from XRD is sharp and the intensity is strong. XRD pattern of pure PEBAX showed a profile with strong crystalline peaks at $2\theta = 21$ and 23 with intensity 388 and 424, respectively, resulting mainly from the crystalline region of polyamide block via interchain hydrogen bonding. XRD of the mixed

matrix membrane showed the same pattern. It indicated that the nano zeolite X was distributed to the membrane matrix and there was interaction between zeolite and polymer. PEBAX-nano zeolite showed a profile with intensity of 349 and 313 at $2\theta = 21$ and 23, respectively. It seems reasonable to suggest that the interchain hydrogen bonding between amide blocks was considerably disrupted by incorporation of zeolite (Figure 3).
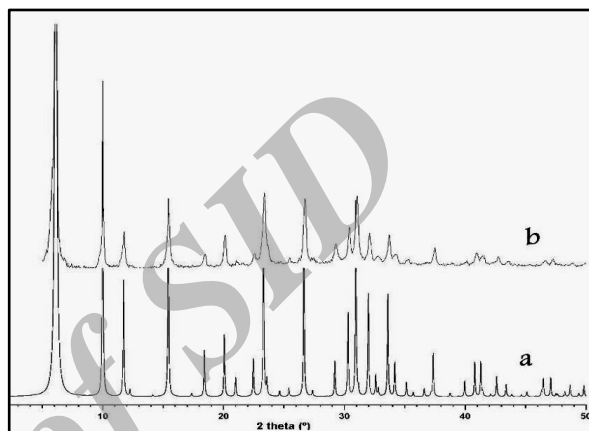

Fig. 2. XRD pattern of NaX (a) in literature, (b) synthetic NaX
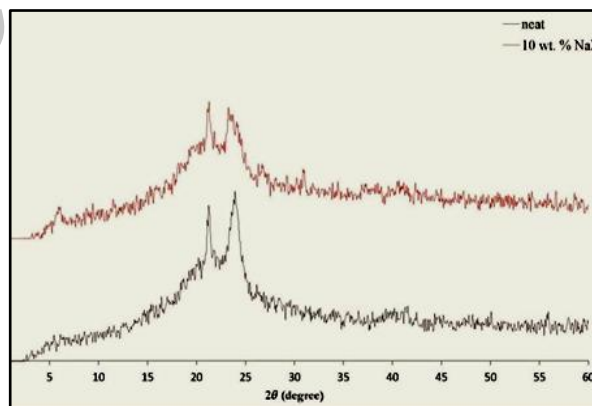

Fig. 3. X-ray patterns of neat PEBAX (down) and PEBAX-nano zeolite X composite (up) membranes.

SEM

The morphologies of the cross-sectional membrane areas are investigated using SEM and shown in Figure 4. Dense matrix and no voids are formed. As SEM micrographs indicate (figure 4), there are no voids around the dispersed fillers. SEM images also showed a homogeneous distribution of good-dispersed fillers in polymer matrix.
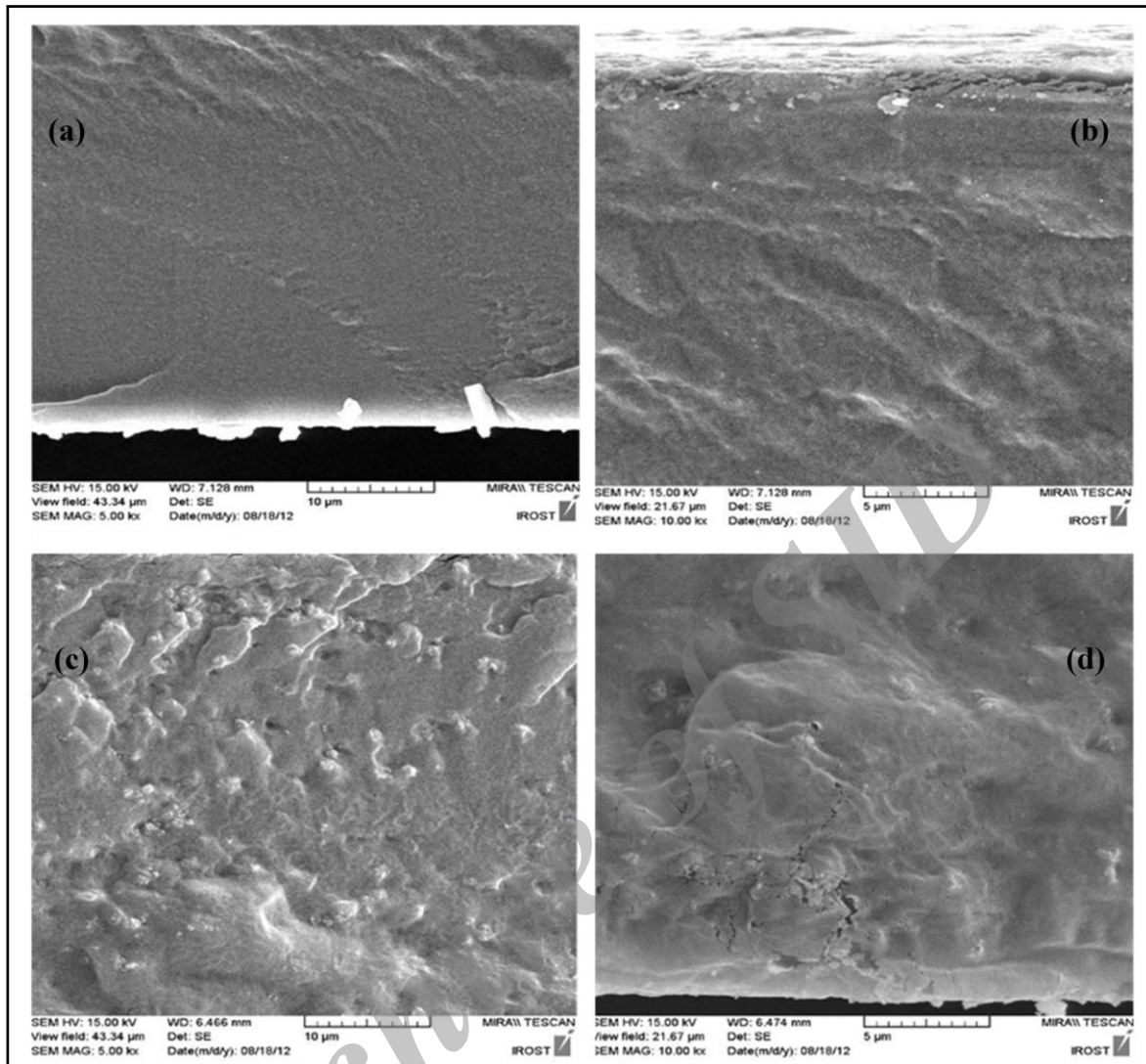
Fig. 4. SEM pictures representing the cross-sectional morphologies of (a) neat PEBAX (5kx), (b) neat PEBAX(10kx), (c) PEBAX-nano zeolite X (10 wt.%)(5 kx), (d) PEBAX-nano zeolite X (10 wt.%)(10 kx).

Solution-diffusion mechanism in polymeric membrane

The membranes operate on the principle of solution-diffusion through a nonporous membrane. CO_2 first dissolves into the membrane and then diffuses through it. Because the membrane does not have pores, it does not separate on the basis of molecular size (as a molecular sieve). Rather, it separates based on how well different compounds dissolve into the membrane and then diffuse through it. Because carbon dioxide, hydrogen, helium, hydrogen sulfide, and water vapor, for example, permeate quickly, they are called "fast" gases. On the other hand, carbon monoxide, nitrogen, methane, ethane and other hydrocarbons permeate less quickly and so are called "slow" gases [9].

The membranes allow selective removal of fast gases from slow gases. For example, as CO_2 is removed from a natural gas stream, water and H_2S are removed at the same time; but methane, ethane, and higher hydrocarbons are removed at a much lower rate. Fick's law, shown below, is widely used to approximate the solution-diffusion process:

$$J = \frac{k \times D \times \Delta\rho}{\ell} \qquad (1)$$

where, J is flux of gas that is, molar flow of gas through the membrane per unit area; k is solubility of gas in the membrane; D is diffusion coefficient of gas through the membrane; $\Delta\rho$ is partial pressure difference of gas between feed and permeate sides of the membrane; and ℓ is the membrane thickness [9].

In solution-diffusion model, it is assumed that each permeating molecule dissolves in and diffuses through the membrane phase in response to a concentration gradient. There is no pressure gradient inside the membrane. In general, gas transport phenomenon in polymer membranes progresses through five successive steps as follows (illustrated in Figure 5).

1. Diffusion through the boundary layer at the upstream side.
2. Relative sorption of the gases by the polymer membrane.
3. Diffusion of the gases inside the polymer membrane. The diffusion step is the slowest and becomes the rate-determining step in gas permeation.
4. Desorption of gases at the permeate side (lower partial pressure).
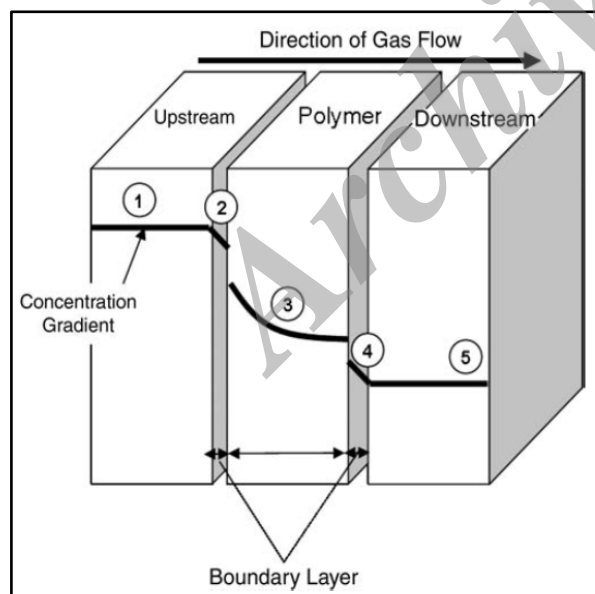5. Diffusion out of the boundary layer of the downstream side.

Fig. 5. Schematic representation of gas permeation step across polymer membrane according to the solution-diffusion mechanism.

As said, gas permeation through a dense polymer membrane is described using a solution–diffusion model (Equation 2) in which permeability coefficient (PA) [cm^3 standard temperature and pressure (STP) $cm/cm^2.s.cmHg$] of gas molecule A is the product of a diffusion coefficient (DA)(cm^2/s) and a solubility coefficient (S_A) (cm^3 gas/cm^3.cmHg):

$$P_A = D_A.S_A \qquad (2)$$

Equation 2, first postulated by Graham (1866), is a basic expression representing the solution–diffusion mechanism of gases through homogeneous dense polymer membranes.

Selectivity ($\alpha_{A/B}$) of gas A to gas B is either due to differences in the solubility coefficient (solubility selectivity, S_A/S_B) or to differences in the diffusion coefficient (diffusivity selectivity, D_A/D_B):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right]\left[\frac{S_A}{S_B}\right]$$

$$(3)$$

Here, separation occurs because of the difference in solubilities and mobilities of different penetrants in the membrane [11].

Mixed matrix membrane

Mixed matrix membrane properties can be estimated to a first approximation through use of the so-called Maxwell model. This model is well understood and accepted as a simple, but effective, tool for estimating mixed-matrix membrane properties. The Maxwell model equation is as follows:

$$P_{MM} = P_M \left[\frac{P_D + 2P_M - 2\phi_D(P_M - P_D)}{P_D + 2P_M + \phi_D(P_M - P_D)}\right]$$

$$(4)$$

Table 1 exhibits a summary of important models established for gas permeation in mixed matrix membranes.

Table 1. Summery of important models established for gas permeation in mixed matrix membranes [10]

Authors	Model
Maxwell	$P_r = \dfrac{P}{P_M}\left[\dfrac{2(1-\phi)+(1+2\phi)\,\lambda_{dm}}{(2+\phi)+(1-\phi)\,\lambda_{dm}}\right]$
Bruggeman	$\left(P_r\right)^{1/3}\left[\dfrac{\lambda_{dm}-1}{\lambda_{dm}-P_r}\right]=\left(1-\phi\right)^{-1}$
Lewis-Nielson	$P_r = \dfrac{P}{P_M}\left[\dfrac{1+2\left((\lambda_{dm}-1)/(\lambda_{dm}+2)\right)\phi}{1-\left((\lambda_{dm}-1)/(\lambda_{dm}+2)\right)\phi\psi}\right]$ where $\quad \psi = 1+\left(\dfrac{1-\phi_m}{\phi_m^{\,2}}\right)\phi$
Pal	$\left(P_r\right)^{1/3}\left[\dfrac{\lambda_{dm}-1}{\lambda_{dm}-P_r}\right]=\left(1-\dfrac{\phi}{\phi_m}\right)^{-\phi_m}$

Permeation results

Pure gas permeability measurements was carried out using neat PEBAX and PEBAX-nano zeolite X (10 wt.%) membranes, which had considerable different loading of zeolite. Table 2 exhibits the effect of nano zeolite presence in polymer matrix on the gas permeation through PEBAX and PEBAX-NaX membranes for pressure variation from 6 to 14 bars.

Table 2. Effect of nano zeolite presence in polymer matrix

Pressure	CO₂ Permeability (barrer)	
	Neat PEBAX	**CO₂ Permeability (barrer)**
6	56	60.78
8	61.06	64.64
10	65.68	68.85
12	69.75	73.03
14	74.19	76.79

Figure 6 display the effect of varying pressure (6-14 bars) of pure CO_2 gas on the performance of the neat and composite membranes in flat-sheet form. The 10% wt. NaX loading was chosen to further investigate the effect of feed pressure, which was varied from 6 to 14 bars in intervals of 2 bar each. The results are compared with neat PEBAX membrane. The permeability CO_2 increased with pressure for all the membranes as shown in Figure 6 due to increasing solubility

and the driving force for mass transfer. For neat PEBAX, CO_2 permeability increased from 56 to 74.19 barrers whereas For PEBAX-NaX was enhanced from 60.78 to 76.79 barrers. A gradual increase in permeability for both membranes occurred. This could be attributed to the increased sorption of CO_2 in the membranes.

Significant increase after incorporation of zeolite observed.
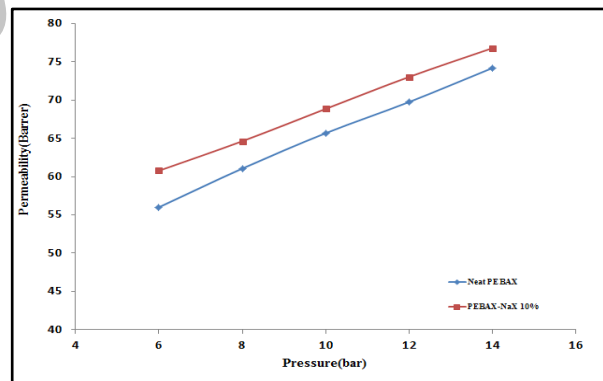
Fig. 6. Influence of pressure difference on gas permeation through PEBAX and PEBAX-zeolite X Membrane.

CONCLUSIONS

The present study demonstrated the feasibility of fabricating PEBAX-NaX nano composite membranes for CO_2 permeation studies. The effect of incorporation of zeolite into the polymer matrix was also investigated. XRD patterns showed that synthetic zeolite X nano crystals were produced and the nano crystaline

powder distributed to the membrane polymeric matrix and there possibly also was interaction between zeolite and polymer. CO_2 permeation was enhanced with increasing feed pressure. Also, CO_2 transport through the membrane increased with adding nano zeolite to the polymeric matrix of the membrane.

ACKNOWLEDGEMENTS

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