

Mixed Matrix Membranes Prepared from High Impact Polystyrene with Dispersed TiO₂ Nanoparticles for Gas Separation

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ABSTRACT

The current study presents synthesis and characterization of high impact polystyrene - TiO₂ nanoparticles mixed matrix membranes for separation of carbon dioxide from nitrogen. The solution-casting method was used for preparation of membranes. The nano mixed matrix membranes were characterized using scanning electron microscopy to ensure the suitable dispersion of nano particles in high impact polystyrene matrix. The effect of TiO₂ nanoparticles loading on membrane performance was investigated. The separation performance of synthesized membranes was investigated in separation of CO₂ from CO₂/N₂ mixture. Effect of feed pressure and TiO₂ content on separation of CO₂ was studied. The results revealed that increase of feed pressure decreases flux of gases through the mixed matrix membrane. The results also confirmed that the best separation performance can be obtained at TiO₂ nanoparticles loading of 7 wt.%.

INTRODUCTION

Purification of carbon dioxide remains one of the challenging topics because of economical and environmental reasons. Traditionally, CO₂ is removed from flue gas by absorption into amine solvents; however the energy consumption for this process is quite high because of regeneration of CO₂-rich amine solvents. Also, from viewpoint of the global warming and improvements in manufacturing efficiency and organic gas purification under normal temperature and pressure conditions are important issues [1, 2]. Membrane technology for gas and liquid separation has obtained considerable importance in recent years due to its environmental viability; lower energy consumption, capital investment and process safety [3-16]. There has been trade-off restriction between

selectivity and permeability gas separation for polymeric membrane [17, 18]. Several studies have been investigated for development of new membrane material or improvement of the quality of existing polymers to overcome the trade-off restriction, which results in the evolution of organic-inorganic hybrid membranes. This kind of membrane commonly known as mixed matrix membranes (MMMs) and the bulk phase is usually an organic polymer which have superior gas separation properties, whereas the dispersed phase is the inorganic fillers [19, 20]. Polymer-inorganic systems have gained academic and industrial attentions due to their outstanding performance in terms of mechanical resistance, thermal properties and separation of gas and liquid. The advantages of the easy process ability of organic polymers with the superior separation properties of inorganic materials are combined in these systems.

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However, selection of the organic polymer and inorganic filler is very vital for the appropriate interface between filler particles and polymer chains [21-24]. Several materials have been used as the filler in mixed matrix membrane including carbon nanotubes, metal-organic frameworks, carbon molecular sieves, photocatalysts, zeolites and activated carbons [25-27]. Among photocatalysts, titanium dioxide (TiO_2) shows some benefits containing low environmental impact, high stability, low cost and availability. There have two main methods for preparation of mixed matrix membrane using TiO_2 nanoparticles and polymeric materials. The first one is introducing particles in the membrane matrix and the second one is that coating the particles on the surface of the membrane [28, 29]. Typically highly selective polymers can result in MMMs with suitable separation performance. Thus, glassy polymers with appropriate gas selectivity are preferred to highly permeable but poorly selective rubbery polymers. Although, glassy polymers are better than rubbery polymers due to their rigid structure. Adhesion between the polymer phase and the external surface of the inorganic particles is a serious issue when glassy polymers are applied in the fabrication of mixed matrix membranes [30-33]. So, in the selection of polymer materials, gas separation properties and adhesion between polymer and filler must be considered. High impact polystyrene (HIPS) is a low cost and tough plastic material which is not investigated in the literature as polymer material in MMMs for separation of N_2 from CO_2 . The combination of HIPS and TiO_2 as mixed matrix membrane is not reported in the literature. In the current study, high impact polystyrene (HIPS) was used as the polymer matrix and TiO_2 was considered as the filler for synthesis of mixed matrix membranes. The membrane morphology, mechanical property and thermal stability were characterized and the gas separation performance was explored for CO_2/N_2 mixture. The effect of operational parameters such as feed pressure on membrane performance was investigated.

MATERIALS AND METHODS

High impact polystyrene (HIPS) (which contains 93% polystyrene (PS) and 7% poly butadiene rubber (PBR)) was purchased from Tabriz Petrochemical Corporation. The chemical structure of high impact polystyrene is depicted in Fig. 1. The solvents, methyl

ethyl keton (MEK) and toluene with purity >99% were supplied by Merck and Titanium dioxide (TiO_2) nanoparticles was purchased from Nanopars Lima Corporation. Based on provider specification sheet, the specific area of nanoparticles is 180-600 (m^2/g), with density of 2.4 g/cm^3 . The equivalent spherical particle diameter was approximately 10-15 nm, which is calculated as $6/(\text{surface area} \times \text{density})$.

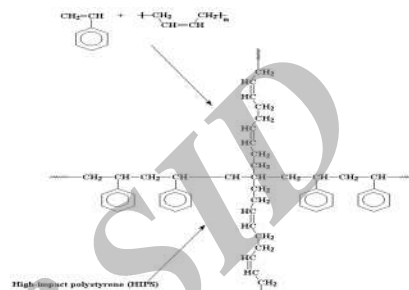


Fig. 1. Chemical structure of high impact polystyrene

Membrane fabrication

Pure high impact polystyrene and mixed matrix membrane filled with TiO_2 nanoparticles were fabricated by solution-casting method [34, 35]. Before membrane synthesis, TiO_2 nanoparticles and high impact polystyrene were dried under vacuum oven for 12 h in order to remove the whole water content. TiO_2 nanoparticles were dispersed in methyl ethyl keton. In order to improve interaction between polymer and TiO_2 nanoparticles, HIPS was gradually dissolved in nanoparticles/ solvent solution and stirred for 30 min. After that the solution sonicated (5 min) for fine dispersion of TiO_2 nanoparticles in polymer matrix. The resulting solution was then casted on a glass plate by using casting knife. The membrane was then dried for 24 h at ambient pressure and temperature. The 7 wt.% nanoparticles concentration was selected in order to prevent TiO_2 nanoparticles sedimentation at lower concentration. Furthermore, it was observed that dispersion of TiO_2 nanoparticles at higher concentration (more than 7 wt.%) leads to aggregate formation on the top surface of the membrane film. The thickness of the fabricated membranes was 200 μm .

Characterization

Scanning electron microscopy

In order to investigate the membrane morphology, pure high impact polystyrene and HIPS/TiO₂ mixed matrix membranes were analyzed by Scanning Electron Microscopy (SEM). The samples were fractured in liquid nitrogen, then were coated with gold and tested by Philips-XL30 Scanning Electron Microscopy.

Permeation test

The pure-gas permeation tests were conducted at ambient temperature, with the permeation apparatus depicted in Fig. 2. The variable feed pressure and the constant permeation volume system were used at ambient temperature. Before the feed side exposing to the selected gas at a certain pressure, the membranes were kept under vacuum for about 6 min to reach a steady state. A circular sample with 29.2 cm² effective area was cut from mixed matrix membrane samples and placed in the cross-flow stainless steel membrane module. The gas permeability of mixed matrix membranes was determined by solution-diffusion mechanism [36, 37]. The gas permeation is estimated using the following equation:

$$P_i = \frac{Q \times L}{A \times \Delta p} \tag{1}$$

Where P_i is the gas permeation through the mixed matrix membrane, which is expressed customarily in GPU (1 GPU = 10⁻⁶ cm³ (STP)/cm².s.cm.Hg); Q the gas permeation rate (cm³/s); A the effective membrane area for permeation (cm²); Δp the pressure difference across the membrane (cmHg), and L the membrane thickness (cm). The ideal selectivity for two gases is calculated as:

$$\alpha = \frac{P_{N_2}}{P_{CO_2}} \tag{2}$$

Where P_{CO₂} and P_{N₂} are the permeation of pure gases CO₂ and N₂ (Barrer) respectively. It should be pointed out that the permeation experiments were repeated, and average deviation of less than 10% was observed.

RESULTS AND DISCUSSION

Morphology

In mixed matrix membranes, morphology of dispersed phase strongly affects the gas transport properties. Fig. 3 shows the SEM images of the top surface of pure high impact polystyrene with different TiO₂

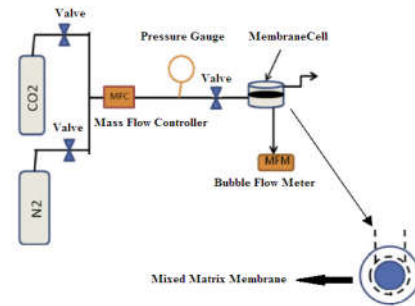


Fig. 2. The diagram of the set-up for the permeation measurement

nanoparticles loadings ranging from 5 to 8 wt.% respectively.

According to Fig. 3, the mixed matrix membrane with 7 wt.% TiO₂ loading shows the best TiO₂ dispersion. Increasing TiO₂ loading leads to the coagulation of nanoparticles in polymer matrix which in turn leads to reduction of the separation performance.

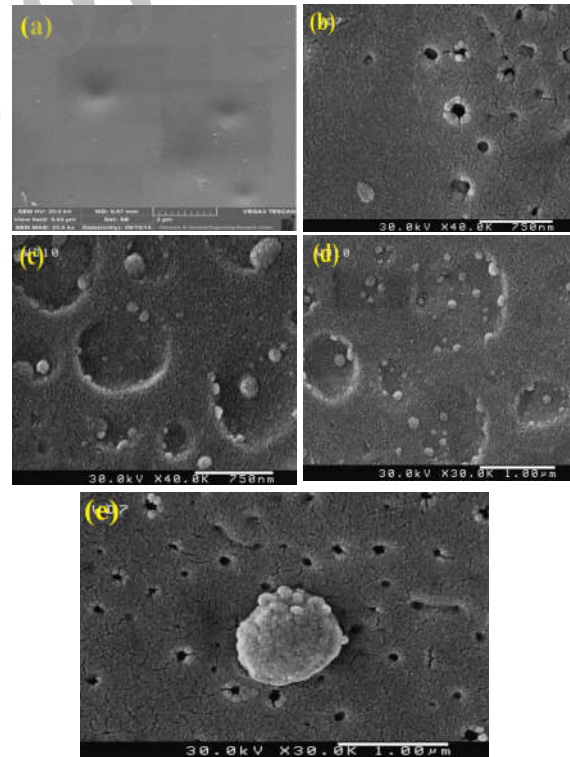


Fig. 3. SEM images of synthesized membranes at different TiO₂ loadings: (a) pure high impact polystyrene; (b) 5 wt.%; (c) 6 wt.%; (d) 7 wt.%; (e) 8 wt.%

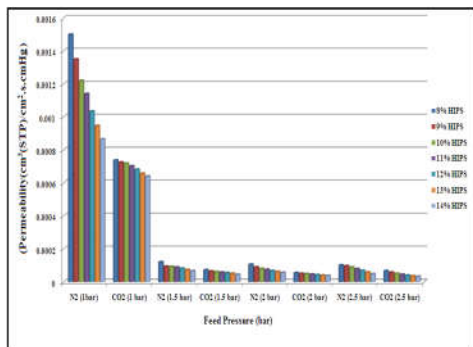


Fig. 4. Effect of feed pressure and HIPS concentration on permeability of N₂ and CO₂ (Pure HIPS)

Influence of feed pressure and HIPS concentration on permeability and selectivity

In this research, permeability of nitrogen and carbon dioxide in pure high impact polystyrene and HIPS–TiO₂ mixed matrix membranes have been investigated at 1–2.5 bars at 25 °C. The permeability coefficients of the two gases in prepared membranes at different feed pressure and HIPS concentration are demonstrated in Fig. 4. According to Fig. 4, the permeabilities of N₂ and CO₂ decrease with increasing of feed pressure. This phenomenon is related to the effect of pressure on the interactions between dispersed phase and rigidified interfacial matrix chain layer in mixed matrix membranes which cause the reduction of the permeability of gas through MMMs. It is also seen that the enhancement of HIPS concentration in solvent results in an decrease in gas permeability, however, the membrane with 10 wt.% HIPS was selected as the best one due to suitable mechanical resistance. The separation performance of pure HIPS was investigated by ideal selectivity calculation of gas pairs. Selectivity results of CO₂/N₂ are shown in Table 1. As can be seen, these data exhibit a general reduction in pure HIPS selectivity with increasing of feed pressure and HIPS concentration due to the enhancement of polymer chains strength.

Table 1. Effect of feed pressure and HIPS concentration on selectivity α (N₂/CO₂)

HIPS (wt.%)	Feed pressure (bar)	Selectivity α (N ₂ /CO ₂)
8	1	2.04
	1.5	1.18
	2	1.93
	2.5	1.91
9	1	1.86
	1.5	1.40
	2	1.37
	2.5	1.80
10	1	1.70
	1.5	1.54
	2	1.67
	2.5	1.74
11	1	1.62
	1.5	1.54
	2	1.66
	2.5	1.79
12	1	1.52
	1.5	1.51
	2	1.59
	2.5	1.73
13	1	1.44
	1.5	1.45
	2	1.56
	2.5	1.67
14	1	1.35
	1.5	1.49
	2	1.51
	2.5	1.51

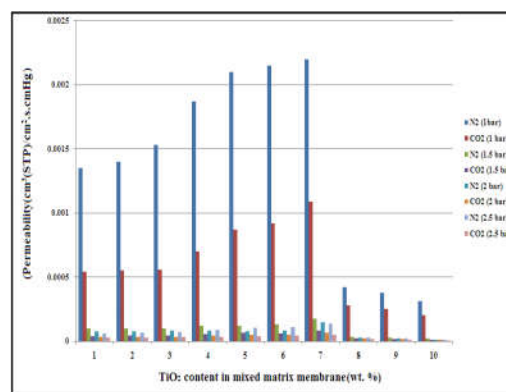


Fig. 5. Effect of TiO₂ content at various feed pressures on CO₂ and N₂ permeability

Table 2. Effect of TiO₂ content at different feed pressure on selectivity

TiO ₂ (wt%)	Feed pressure (bar)	Selectivity α (N ₂ /CO ₂)
1	1	2.50
	1.5	2.44
	2	2.51
	2.5	2.09
2	1	2.55
	1.5	2.32
	2	2.32
2.5	1	2.28
	1.5	2.60
	2	2.35
3	2	2.41
	2.5	2.26
	1	2.17
4	1.5	2.27
	2	2.02
	2.5	2.54
5	1	2.16
	1.5	1.97
	2	1.79
2.5	2.5	2.80
	1	2.00
	1.5	1.98
6	2	1.56
	2.5	2.63
	1	2.01
7	1.5	2.09
	2	2.28
	2.5	2.77
8	1	1.51
	1.5	1.36
	2	1.31
	2.5	1.43
9	1	1.49
	1.5	1.58
	2	1.39
	2.5	1.43
10	1	1.49
	1.5	1.49
	2	1.33
2.5	1.31	

CONCLUSION

In this study, high impact polystyrene mixed matrix membranes containing TiO₂ nanoparticles were prepared by solution blending and casting method. The membranes were characterized by scanning electron microscopy. The influence of TiO₂ nanoparticles content on the structure and gas separation properties of mixed matrix membranes were investigated. The results showed that the permeability of N₂ and CO₂ decreases with increase of feed pressure and in all pressure range the permeability of N₂ was higher than CO₂ due to small Leonard John's diameter.

The best performance was obtained at 10 wt.% of HIPS, 7 wt.% TiO₂ loading, feed pressure=1 bar and ambient temperature.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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