



# Enhancement of the gas separation properties of polyurethane membranes by alumina nanoparticles



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## ABSTRACT

In this work, polyurethane (PU) nanocomposite membranes were prepared using different concentrations of alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles (0, 2.5, 5, 10, 20, and 30 wt%). The main objective of this work is to evaluate the permeability of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> gases in the polyurethane hybrid membranes at various Al<sub>2</sub>O<sub>3</sub> contents and with two different chain extenders. Polyurethane was synthesized by bulk two-step polymerization based on polytetramethylene glycol (PTMG) and hexamethylene diisocyanate (HMDI). 1,4-butanediol (BDO) and 2-methyl-1,3-propanediol (MPD) were used as chain extenders to complete the conversion of the prepolymers to the final polyurethanes. The prepared polyurethane–Al<sub>2</sub>O<sub>3</sub> membranes were characterized using Fourier Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscope (SEM), wide angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC) analyses. The results show a reduction in the gas permeability, but a significant enhancement in the CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> selectivities with alumina content. The separation performances of the membranes were compared with Robeson's upper bound limit. The new modified Higuchi model was applied to predict the permeability of polyurethane–alumina hybrid membranes.

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## 1. Introduction

Incorporation of inorganic fillers into an organic polymer leads to superior performance in gas separation processes, such as separation of oxygen–nitrogen, carbon dioxide–nitrogen, and sweetening of natural gas by removing carbon dioxide. Using the separation properties of inorganic particles along with the low cost and processability of polymers through membrane preparation causes mixed matrix membranes (MMMs) to be more efficient than conventional membranes [1–5].

Inorganic fillers can be classified as porous or nonporous. Nonporous material fillers can enhance the separation properties of prepared MMMs by increasing matrixes' tortuous surfaces and decreasing diffusion of larger gas molecules. These inorganic nonporous particles can also disrupt chain packing and increase free volume between polymer chains, so gas diffusion increases. As the mechanisms of nonporous and porous material fillers in the gas separation process are different, interaction among polymer chain segments and particles as well as functional groups on the surface of the inorganic phase must be considered when these materials are introduced into a polymer matrix [6–8].

Koros and Moaddeb [9] studied the effects of silica particles on the gas separation properties of polyimide. They showed that incorporation of silica particles into the polymer matrix improved gas separation properties, especially in the case of O<sub>2</sub>/N<sub>2</sub> separation. In some silica–polyimide membranes, the improvements in both selectivity and permeability were observed simultaneously. Therefore, the O<sub>2</sub>/N<sub>2</sub> separation characteristics were above Robeson's upper bound limit [10], which is expressed as a line on a log–log plot of selectivity versus permeability. This upper bound limit clarifies that improvement in permeability is often at the expense of selectivity, and vice versa.

Sadeghi et al. [11,12] investigated the effects of silica particles on the gas separation properties of polyurethane (PU) membranes. Incorporation of silica into the polymer matrix decreases the permeability of all gases (e.g., O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>), while enhancement in CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/N<sub>2</sub> selectivity was observed. Clearly, soft segments are permeable domains in polyurethane membranes. Therefore, the presence of impermeable silica particles in soft segment domains decreases gas permeability by increasing the matrix's tortuous network to pass through. The larger gas molecules, N<sub>2</sub> and CH<sub>4</sub> (see Table 2), were also more restricted to pass through the polymer matrix due to the reduction in the free volume of the polymer matrix, so selectivity increased. In polybenzimidazole/silica membranes, the dissolution of CO<sub>2</sub> and CH<sub>4</sub> gases could compensate for the diffusivity reduction of these gases through membranes. Thus,

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the permeability of condensable CO<sub>2</sub> and CH<sub>4</sub> gases is enhanced, whereas the permeability of non-condensable N<sub>2</sub> gas decreased substantially [13].

Metal oxide nanoparticles constitute the specific characteristics to be used in mixed matrix membranes. The primary nanoscale particles and high specific area of these metal oxides induce fine particle distribution and prevent non-selective void formation in the nanoparticles/polymer interface [14]. The polar characteristics of metal oxide nanoparticles introduce sorption selectivity instead of diffusion selectivity, as in the case of polymeric membranes may be a solution to enhance the separation of gases with nearly the same molecular size such as paraffin–olefins, CO<sub>2</sub>/N<sub>2</sub>, etc. [14,15]. In principle, the affinity and interaction between some metal oxide's surface, such as MgO, TiO<sub>2</sub>, ZnO, etc. [14,16–19], and some gases, like CO<sub>2</sub> and SO<sub>2</sub>, lead to a significant enhancement in the transport of these gases in comparison to the almost same molecular size gases such as N<sub>2</sub> and O<sub>2</sub>. This physisorption affinity toward polar gas molecules makes up for small diffusion selectivity and hence improves the overall selectivity. It is however difficult to separate molecules of nearly the same molecular size. It was also reported that contact angle was lower for the metal oxide-mixed matrix membrane than corresponding neat membrane. This indicates that the nanocomposite membrane has higher hydrophilicity which is considered an important property of membranes, as it affects on the flux and anti-fouling properties, especially in the waste water treatment [20–22].

In another work [23], polyimide/TiO<sub>2</sub> nanocomposite membranes were prepared with strong interaction between TiO<sub>2</sub> particles and the polyimide phase. H<sub>2</sub> and O<sub>2</sub> permeabilities, as well as H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> selectivities, improved compared to the pure polyimide membrane. However, the void formation in the TiO<sub>2</sub> nanoparticle–polymer interfaces as well as agglomeration of particles and poor interaction between the two phases at the interface lead to higher permeability than was normally expected. Therefore, a decrement in the selectivity of the mixed matrix membrane relative to the pure polymer matrix was observed [24].

Recently, informative data on the use of metal oxides nanoparticles in polymeric membranes have been published. Although different strategies using a wide range of nanoparticles have been introduced to enhance the separation of CO<sub>2</sub> from CH<sub>4</sub> and N<sub>2</sub>, there is still a need for investigating different nanocomposite membranes with increased potential applications in the field of CO<sub>2</sub> capturing for energy saving and air pollution, along with long service life of the membrane that is resistant to a CO<sub>2</sub> plasticization effect. Alumina is one of the most common inorganic materials, and thus it is often used to preparation of ultra-filtration membranes. In addition, alumina is inexpensive, accessible, nontoxic, and highly resistant. Also, there are several publications using alumina to enhance the CO<sub>2</sub> sorption capacity of the membranes [20,22,25–28]. Remarkably, the use of alumina nanoparticles in PU membrane has not yet been investigated to a large extent. Therefore, in the present study, the gas separation properties of polyurethane–Al<sub>2</sub>O<sub>3</sub> nanocomposite membranes were explored. We have tested the permeability of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> gases in these membranes at various alumina contents and with two different chain extenders.

## 2. Experimental

### 2.1. Materials

Polytetramethylene glycol (PTMG,  $M_w = 2000 \text{ g mol}^{-1}$ ) was supplied by Arak Petrochemical Company (Tehran, Iran) and dried at 80 °C under vacuum for 24 h to remove residual water. 1,4-butanediol (BDO) and 2-methyl-1,3-propanediol (MPD) were used as chain extenders, provided by Sigma-Aldrich (St. Louis, USA), and dried over 4 Å molecular sieves before use. Hexamethylene diisocyanate (HDI),

N, N-dimethylformamide (DMF), and dibutyltindilaurate (DBTDL) were purchased from Merck (New Jersey, USA). Alumina nanoparticles were obtained from Nano Pars Spadana Co. (Isfahan, Iran).

### 2.2. Polymer synthesis

Polyurethane was synthesized by a bulk two-step polymerization method. First, PTMG was incubated with HMDI for 2 h at 90 °C under nitrogen to obtain a macrodiisocyanate prepolymer. The chain extension was then performed by addition of BDO and MPD at 50–60 °C. In order to obtain a linear polymer, the molar ratio of NCO:OH should be kept at 1:1. The molar ratios of the used components were as follows: PTMG:HMDI:(BDO or MPD)=1:3:2.

### 2.3. Membrane preparation

The PU solution (5 wt%) was prepared by dissolving 0.7 g of the synthesized PUs in 15 g DMF at 60 °C. The mixture was then stirred until a homogeneous solution was obtained. PU–Al<sub>2</sub>O<sub>3</sub> nanocomposite membranes were prepared by the same method following the addition of alumina nanoparticles at different weight fractions into the polymer solution. The bubble-free mixture was cast in clean Petri dishes and incubated at 60 °C for 24 h to allow the solvent to evaporate. Next, the prepared films were placed in a vacuum oven at 60 °C for another day for complete removal of the solvent. The prepared samples containing BDO and MPD as chain extenders were designated as B- $\alpha$  and M- $\alpha$ , respectively, where  $\alpha$  is the weight percent of alumina (ranging from 0 to 30 wt%).

### 2.4. Characterization

The prepared PU and PU–Al<sub>2</sub>O<sub>3</sub> nanocomposite membranes were investigated by an Attenuated Total Reflection-Fourier transfer infrared spectroscopy (ATR-FTIR) spectrometer (Bruker, Tensor 27, Germany) in the range of 4000–600 cm<sup>−1</sup> at room temperature. X-ray diffraction patterns were recorded by monitoring the diffraction angle  $2\theta$  from 5° to 40° on a Philips X'Pert (Netherlands) using Cu radiation under a voltage of 40 kV and a current of 40 mA. The morphological aspects of the prepared membranes in terms of the distribution of Al<sub>2</sub>O<sub>3</sub> nanoparticles and existence of any fracture or void in them were investigated by a scanning electron microscope (KYKY-EM3200 SEM, China). Thermal properties of the membranes were measured by differential scanning calorimetry (DSC, Mettler-Toledo DSC822e, United Kingdom) at a heating rate of 10 °C/min and a temperature range of −120 to 200 °C.

### 2.5. Gas permeation measurements

Prepared membranes were exposed to four different gases, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, and permeation properties were evaluated using the constant pressure method. The feed side pressure of the membrane cell was kept at 760 cmHg, which is the plasticization threshold for the membrane. The permeate side was maintained at atmospheric pressure. Each membrane was tested three times for each gas to determine reproducibility, and the averages of these trials were reported. The gas permeability of the membranes was determined using the following equation:

$$P = \frac{ql}{(p_1 - p_2)A} \quad (1)$$

where  $P$  is the permeability expressed in Barrer (1 barrer =  $10^{-10} \text{ cm}^3(\text{STP})\text{cm}/(\text{cm}^2 \text{ sHg})$ ),  $q$  is the flow rate of the permeate gas passing through the membrane ( $\text{cm}^3/\text{s}$ ),  $l$  is the membrane thickness (cm),  $p_1$  and  $p_2$  are the absolute pressure of the feed side and permeate side (cmHg) and  $A$  is the effective membrane area ( $\text{cm}^2$ ). The ideal separation factor of pure gas A over B ( $\alpha_{AB}$ ) is defined as the

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