



Fabrication of mixed matrix membranes containing TiO₂ nanoparticles in Pebax 1657 as a copolymer on an ultra-porous PVC support



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ABSTRACT

Mixed Matrix Membrane (MMM) recently has shown a great potential for separation of CO₂ from CH₄ as the main part of a gas sweetening process for natural gas treatment. The main objective of this study is to develop novel nanocomposite membranes of TiO₂ as inorganic nano-filler incorporated into poly (ether-*b*-amide) Pebax 1657 as the polymer matrix. Considerable improvement of permeation and selectivity was achieved for synthesized membranes for separation of CO₂ and CH₄ over a range of operating variables. The scanning electron microscopy (SEM) was used to characterize nanocomposite membranes which images showed high degree of agglomeration in high loadings of TiO₂ in polymer matrix. Defect free organic/inorganic membranes showed the best performance at TiO₂ loading concentration of 3% at 30 °C and 15 bar. The CO₂ permeability increased from 129 Barrer for Pebax to 167 Barrer and a remarkable enhancement in the related CO₂/CH₄ selectivity was observed from 37 to 51.

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1. Introduction

Natural gas produced at the wellhead is mainly methane associated with heavier gas components. Besides, it encompasses several impurities such as CO₂, H₂S, N₂, H₂O and heavy hydrocarbons, which must be removed to meet pipeline specifications. The removal of acid gases (CO₂ and H₂S) is essential due to their corrosive nature and reduction effect of CO₂ on the heating value of the gas.

Currently, all the commercial membranes used for CO₂ removal (mostly cellulose acetate and polyamides) are in the glassy state with low selectivity of 12–25 under normal temperature and pressure conditions (Baker, 2002). However, low separation performances (flux and selectivity) are the main challenges in current glassy polymeric membranes. Obtaining both acceptable selectivity and high CO₂ permeability makes membrane separation as a competitive method for CO₂ capture.

Polyamide-*b*-ethylene oxide (Pebax), an elastomer with thermoplastic properties contains rigid polyamide block and flexible

polyether segments which is mostly traded by commercial name of Pebax. Pebax is blend of two monomers including a polyamide (PA) as an impermeable hard crystalline segment which provides stable structure for membrane and a polyether (PE) block as a soft and flexible segment which passes the gasses (Drioli and Barbieri, 2011).

Pebax with resilient chemical interaction with carbon dioxide as a polar molecule and ethylene oxide has captured attention of many researchers for CO₂ application (Rahman et al., 2013; Reijerkerk et al., 2010; Car et al., 2008). Gas passes through the soft amorphous polyether block and rigid polyamide segment which enhances the mechanical stability of the membrane. Different types of Pebax copolymers have been synthesized by altering PA and PE compositions of a block copolymer. Pebax is made of polytetramethyleneoxide (PTMO) or polyethyleneoxide (PEO) and nylon 6 or 12. The proportion of PTMO and PA12 or PA6 specifies the physical property and the grade of Pebax (Kim et al., 2001).

Kim et al. (2001) studied properties of different types of Pebax (2533, 3533, 4033 and 1657) grades, and they figured out that Pebax-1657 has a significant selectivity for polarizable/nonpolar gas. They detected nonpolar gases faces decline in permeability with increasing of the molecular size while, the Pebax permeability is remarkably high for the polarizable and larger gases i.e. CO₂ and

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SO₂. Freeman et al. further examined the effect of PEO block composition in the Pebax copolymers. They confirmed that the solubility of nonpolar gases in Pebax-1074 and Pebax-4011 copolymers increase by rising of the PEO monomers ratio in Pebax copolymer (Freeman et al., 1999). Consequently, Pebax 1657 which constitutes 40% amide groups and 60% ether linkages showed a potential polymer in separation of mixed gas of CH₄/CO₂.

Prior to the present study, Ahmadpour et al. (2014) employed Poly (amide – 6 – b – ethylene oxide) (Pebax MH 1657) copolymer, made of 60 wt% of PEO and 40 wt% of PA6 (nylon-6) to prepare a composite flat sheet membrane of PVC/Pebax 1657 for CO₂ separation showed a remarkable potential for CO₂ separation from CH₄.

Although loads of researches have been performed on Pebax to show its advantages like permeability and selectivity, low cost (because it is a commercial polymer) and sound mechanical and thermal properties (Yave et al., 2011), more efficient membranes were developed by employing the inorganic membrane advantages into the MMMs.

For the first time in 1960, James and Barrer (Barrer and James, 1960) reported use of zeolite as the dispersed phase in polymeric binders for ion exchange membrane application. Application of MMM for gas separation has been investigated with different inorganic fillers such as zeolites (Bastani et al., 2013; Casado-Coterillo et al., 2012; Funk and Lloyd, 2008; Gorgojo et al., 2008; Junaidi et al., 2015; Pechar et al., 2006; Şen et al., 2007), carbon molecular sieves (CMSs) (Rafizah and Ismail, 2008; Vu et al., 2003a, 2003b, 2003c), metal oxides (Jiang et al., 2007; Sun et al., 2014; Teow et al., 2012) and carbon nanotubes (CNTs) (Ahmad et al., 2014; Ismail et al., 2011; Khan et al., 2013; Li et al., 2015; Ranjbaran et al.; Sanip et al., 2011; Zhao et al., 2014). Non-permeable nanoscale metal oxides have shown a great potential in their distribution in the polymer chain in a way that polymer free volume increases and voids formation at the interface of the nanoparticles with the polymer are avoided (Ferrari et al., 2010). Therefore, these nanoparticles are not inherently agglomerate together and have potential to be dispersed separately (Goh et al., 2011). Researcher unanimously posit that the inclusion of nanoparticles with optimum ratio would yield a significant improvement in permeability while keeping the selectivity constant, diminishes the overall selectivity of the MMM due to the nanoparticles inability of the porous structure to selectively distinguish the gas molecules based on their size difference (Sanip et al., 2011). Researchers have given special attention to the nanoparticles of titanium oxide (TiO₂) incorporation in polymer matrix for membrane application due to its stable chemical resistance and surface characteristics which make it easy to disperse in solution and modify the morphology of the membrane (Araki et al., 2007).

Moghadam et al. (2011) examined the effect of TiO₂ incorporation nanoparticles on MMMs based on Matrimd5218 which was prepared by solution-casting technique. Their results demonstrated that the presence of TiO₂ nanoparticles increased the gas permeability of MMMs probably because of chain packing distraction, void development at polymer–nanoparticle interface and nanoparticle accumulation. Besides, they revealed that incorporation of TiO₂ nanoparticles improved membrane performance for CO₂/CH₄ separation. Zoppi et al. (2000) detected a substantial growth of selectivity for CO₂/N₂ after incorporation of 20 wt % TiO₂ particles in Pebax matrix. Liang et al. (2012) reported that, CO₂/CH₄ selectivity improved from 24.5 for polyethersulfone based membrane to a maximum of 38.5 in MMMs containing 4 wt% of TiO₂ and then a reduction was observed in higher TiO₂ contents (e.g., 17.3 for 20 wt %). The void formation as well as membrane defects in MMMs contributed to the high gas permeability and low gas selectivity in higher TiO₂ loadings. Moradihamedani et al. (2015) explained the synthesis significance of PSf/TiO₂MMM which enhances

performance of membrane for CO₂/CH₄ separation. They explained that 3 wt% loading of PSf/TiO₂ remarkably enhanced the CO₂ from CH₄ separation at 1 bar pressure and selectivity value of 36.5 at 3 bar feed pressure, however, higher nanoparticle contents (>5 wt %) led to significant reduction in gas selectivity value of CO₂ over CH₄. Nevertheless, the membrane performance improvement is very much influenced by filler type and the level of linkage and dispersion of filler in the polymers matrix (Mahajan and Koros, 2000).

Pebax[®] 1657 features relatively high CO₂ permeability and a moderate selectivity over N₂ and CH₄ which will make it an ideal candidate material for CO₂/CH₄ and CO₂/N₂ separation, if the selectivity increase. Fortunately, Incorporation of porous fillers may achieve this goal (Li et al., 2013).

According to our recent result (Ahmadpour et al., 2014), PVC(Polyvinyl chloride), a glassy polymer, was chosen as the support of the membrane for preparing composite gas separation MMMs because it is commercially available and has shown a good mechanical and thermal stability. The objective of this study was to develop high-performance mixed matrix membranes and investigate the effect of TiO₂ nanoparticles on the morphological and separation performance of the developed nanocomposite membranes over different ranges of temperature (20–30 °C) and pressure (5–20 bar).

2. Experimental

2.1. Materials

Pebax[®] MH 1657 was purchased from ARKEMA (The Netherlands), is a polyether-*block*-amide contains of 60 wt% poly(ethylene glycol) (PEG) and 40 wt% aliphatic polyamide (PA6, nylon6) which is later referred to as 'Pebax 1657'. TiO₂ nanoparticle, purchased from Nanoscale (Manhattan, KS) based on the provider specification sheet, the specific area of nanoparticles was 500 m²/g with density of 3.7 g/cm³. The physical properties of TiO₂ nanoparticles are shown in Table 1 further the TEM image for the nanoparticle was shown in Fig. 1 which was provided by the manufacturer. The PVC was supplied from the Abadan Petrochemical Company, Iran. The solvents ethanol (99.9 wt%) and Dimethylformamide (DMF) were bought from Merck, Germany. Deionized water (conductivity less than 0.1 mS/cm) was obtained from Ramin power plant, Iran. All of these chemicals were used as received. Both CO₂ and CH₄ used in the permeation experiments had purity of 99.999% and were acquired from Persian Industrial Gases, Iran.

2.2. Mixed matrix composite membrane preparation

Ultraporous 15 wt% PVC substrates (MW cut-off 50 kDa) were prepared by phase inversion method (Shamsabadi et al., 2015) the cross section of support is shown in Fig. 2 on nonwoven layers. In

Table 1
Physical properties of TiO₂ nanoparticle.

Specific surface area (BET)	500 m ² /g
Spherical particle diameter	3 nm
Average pore diameter	32 Å
Total pore volume	≥0.4 cc/g
Bulk density	0.6 g/cc
True density	3.7 g/cc
Mean aggregate size, d _{0.5}	5 µm
Moisture content	≤4%
Ti content (based on metal)	≥99.999

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