The influence of fumed silica content and particle size in poly (amide 6-b-ethylene oxide) mixed matrix membranes for gas separation

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ABSTRACT

Mixed-matrix membranes (MMMs) comprised of poly (amide 6-b-ethylene oxide) (PEBAX) as continuous phase and fumed silica (FS) as dispersed phase were prepared to separate CO_2 and CH_4. The influences of FS nanoparticle size and weight percentage on the phase behavior and microstructure of the prepared MMMs were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA), differential scanning calorimeter (DSC) and tensile testing. The performance of the prepared MMMs was characterized by single gas permeation measurement of CO_2, N_2 and CH_4 (at 25 °C). The effects of feed pressure on the gas separation performance of the membranes were also investigated. Generally, PEBAX-FS MMMs showed higher CO_2 permeability and selectivity (α) than the pure PEBAX membrane. Adding 10 wt% of 7 nm FS nanoparticles to the PEBAX matrix led to significant improvement in the CO_2 permeability (~4 times), CO_2/CH_4 and CO_2/N_2 selectivity (~2 times) compared to the pure PEBAX membrane. The CO_2/CH_4 and CO_2/N_2 selectivity for these membranes were also about 64.8% and 45.3% higher than those of MMMs containing 10 wt% of larger FS nanoparticles (16 nm). This was attributed to the higher surface to volume ratio of smaller FS nanoparticles which can provide higher interactions with polymeric matrix and CO_2 gas.

1. Introduction

Carbon dioxide (CO_2) is a major impurity in natural gas that must be removed because of its energy concerning issue and corrosive nature [1–3]. The majority of commercially available polymeric membranes for CO_2 separation are made of glassy polymers such as polysulfone, (PS) cellulose acetate (CA), polyimide (PI), polyamide (PA), polycarbonate (PC) and their derivatives [1,4,5]. The gas separation mechanism in these polymers is based on size sieving by the rigid chain structures of the polymer matrix [6]. A tradeoff relation has been recognized between permeability and selectivity of polymeric membranes. This means that preparing polymeric membrane with high permeability and excellent selectivity is difficult [7]. Different strategies have been proposed to overcome the mentioned problem which can be categorized in four groups as follows; (1) designing new polymers possessing higher gas separation efficiency, (2) improving the properties of the commonly used polymers, (3) blending two polymers with different physical and chemical properties (copolymer membranes), and (4) fabrication of mixed matrix membranes (MMMs) [8–10]. Poly ether-block-amide (PEBAX) has been recognized as a promising polymeric material for separation of gas mixtures like CO_2/N_2 and O_2/N_2. PEBAX is a block copolymer with micro-biphasic structure comprising of soft PEO segments and hard PA segments. PEBAX has received considerable attention in gas separation applications due to its good thermo-mechanical strength, good permeability and selectivity as well as low fabrication cost [6,11]. The gas permeation into the PEBAX-based membranes occurs via the continuous amorphous PEO soft phase, while semi-crystalline hard phase of polymer substrate can cause impermeability [6,12,13]. It has also been established that the amorphous glassy component, the irregularity of the phase architecture and the presence of an interphase structure between the soft and hard phases could affect the overall gas separation performance [6]. The morphology of polymeric membranes can be altered by changing the fabrication conditions such as the concentration of polymer solution and the volatility of applied solvent. MMMs [14,15] comprised of a continuous polymeric phase and dispersed inorganic nanoparticles such as zeolites, carbon molecular sieves (CMS) and metal oxides [15,16] phase have been recognized as an appropriate route to enhance the properties of the membranes for gas separation and to surpass the Robeson upper bound [17]. MMMs show higher

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thermal, chemical and mechanical stability compared to pure polymeric membranes. Porous and nonporous inorganic materials are used in fabrication of MMMs [15]. Porous inorganic nanoparticles such as CMS [18], activated carbon [19] and carbon nanotubes [20] act as molecular sieving agents and separate gas molecules based on their shape or size. In contrast, nonporous nanomaterials such as SiO_2 [21], TiO_2 [22] and MoS_2 [23] can improve the gas separation efficiency by disrupting the polymer chain packing, increasing free volumes between polymer chains and increasing the matrix tortuous pattern. However, dispersing nanoparticles in a polymer is usually challenging because of unfavorable entropic interactions between the polymeric matrix and inorganic nanoparticle, leading to inappropriate distribution of nanoparticles within the polymer matrix. The choice of appropriate polymer is a substantial issue to reach maximum compatibility with the inorganic fillers and to prevent plasticization under aggressive feed steams [1]. SiO_2 has been applied in fabrication of PEBAX-based MMMs and exhibited satisfactory gas permeability and selectivity. Kim et al. [24] has reported the preparation of MMMs based on PEBAX-1657 and silica nanoparticles using a sol–gel process. In this work, a nano-dispersed inorganic network in the PEBAX matrix was produced and the prepared MMMs showed higher gas permeability coefficients and selectivity compared to that of pure PEBAX-1657 membrane. Zoppi et al. [25] has reported fabrication of hybrid organic/inorganic membranes by mixing PEBAX-1657 with SiO_2 nanoparticles, which were separately synthesized through hydrolysis and polycondensation of TEOS. They found that permeability coefficient of different gases decreases by increasing the inorganic phase content. Meanwhile, the results demonstrated that CO_2/CH_4 and CO_2/N_2 selectivity values were enhanced by adding the inorganic phase content, whereas CO_2/H_2 selectivity value indicated an opposite trend. In another work, chemical surface modification of SiO_2 nanoparticles via esterification reaction was employed for preparation of SiO_2/PEBAX nanocomposite membrane [26]. Based on the obtained results, the ideal permeation selectivity values of CO_2/H_2, CO_2/CH_4 and CO_2/N_2 gases were obtained by increasing the loading content of nanoparticles up to 8 wt%.

Fumed SiO_2 (FS) is a synthetic amorphous SiO_2, also known as pyrogenic silica, which is produced by hydrolysis of chlorosilanes in a flame of oxygen–hydrogen gas based on the following reaction: [27]

$$SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl$$
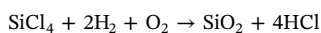
In contrast to crystalline silica which is carcinogenic, FS is non-toxic and non-irritating. FS nanoparticles exhibit higher hydrophilicity and higher surface energy due to their extremely large surface area and the presence of numerous silanol groups on their surfaces. [27,28] silanol groups can provide high reactivity with gases such as CO_2 or SO_2 and consequently improve the permeability of the resultant MMMs [21,27,29,30]. The aim of the present work is to study the effects of FS size and wt% on the phase behavior and microstructure of the PEBAX-based MMMs through scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction spectroscopy (XRD) and stress – strain measurements. Furthermore, the influence of FS content and particle size on the gas permeability and selectivity of PEBAX-based MMMs was evaluated for CO_2/CH_4 gas separation process.

2. Experimental

2.1. Materials

PEBAX MH (1657) was obtained from Arkema Inc. (France) in the form of elliptic pellets.

The hydrophilic FS nanoparticles with particle size of 7 nm and 16 nm were supplied by Degussa. These nanoparticles were named as FS-7 and FS-16 in this text to indicate their particle size. Dimethyl acetamide (DMAc) was used as solvent for preparation of PEBAX solution and purchased from Merck (Germany). The CO_2 and N_2 gases (purity 99.99) were purchased from Roham Gas Co., (Tehran, Iran). The

Table 1
Naming system of the prepared MMMs.

FS-7 filled MMMs	FS-16 filled MMMS	Weight percent of FS
PEBAX-FS7-2	PEBAX-FS16-2	2
PEBAX-FS7-5	PEBAX-FS16-5	5
PEBAX-FS7-7	PEBAX-FS16-7	7
PEBAX-FS7-10	PEBAX-FS16-10	10
PEBAX-FS7-12	PEBAX-FS16-12	12

purchased polymer, FS and DMAc were used as received.

2.2. Preparation of PEBAX membrane

The pure PEBAX membrane and FS-filled PEBAX-based MMMs were prepared by solution-casting. PEBAX was dried in a vacuum oven, dissolved (3 wt%) in DMAc under vigorous stirring for 2 h at 90 °C. The prepared solution was cast on Teflon-coated plate and placed in an oven at 60 °C for 16 h. The prepared PEBAX membrane was further dried in a vacuum oven at 50 °C for 4 h to remove residual solvent.

To prepare MMMs, the FS nanoparticles were dispersed in DMAc by stirring for 1 h and probe sonicating for 50 min before adding PEBAX polymer. To improve PEBAX/FS interaction, the prepared PEBAX solution (3 wt%) were gradually added to the FS/DMAc solution, stirred for 2 h at 75 °C and then further sonicated for 10 min. The prepared solution was cast on the Teflon-coated plate and dried in an oven at 60 °C for 16 h. The FS content of MMMs were varied from 0 to 12 wt% and the thickness of the fabricated membranes was measured by a micrometer. The naming system of the prepared membranes is shown in Table 1. Adding higher amount of FS nanoparticles to PEBAX resulted in no membrane formation. A schematic representation of pure PEBAX membrane and FS-filled PEBAX-based MMMs is shown in Fig. 1.

2.3. Membrane characterization

The morphology of the fabricated membranes was investigated using a HITACHI S-4160 scanning electron microscopy (SEM). Samples were prepared by breaking membranes in liquid nitrogen followed by Au coating. Thermal stabilities of the PEBAX membrane and MMMs were evaluated using a Mettler-Toledo (model 1600, Swiss) thermogravimetric analysis (TGA) and Mettler Toledo DSC 822 (Switzerland). For TGA measurements, samples were heated from 30 to 700 °C under nitrogen environment using a heating rate of 10 °C/min. The DSC tests were carried out in the range of −80 °C to 300 °C under nitrogen atmosphere and heating rate was adjusted at 10 °C/min. Stress–strain measurements of the prepared membranes were conducted on 10×40 mm specimen using a Tensile Zwick (CAT-350-56, England) equipment with cross-head speed of 5 mm/min. XRD patterns were acquired using EQUINOX3000 Intel with Cu/Kα source ($\lambda = 0.15418$ nm) operated at a voltage of 40 kV and a current of 30 mA. Samples were scanned with rate of 10° per minute between 2θ of 10°–90°. The *d* spacing, that is, the distance between the diffracting planes, was calculated using Bragg equation.

2.3.1. Gas permeability measurement

The pure gas permeation properties of the prepared membranes were studied at three different pressures of 4, 8 and 12 bar at 25 °C using the set-up demonstrated in Fig. 2. The circular membrane with an effective surface area of 12.56 cm^2 was mounted within a steel diffusion cell. The gas permeability of membranes was determined using Eq. (1):

$$P_A = \frac{Vl}{At\Delta p} \tag{1}$$

where *P* is permeability expressed in Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)), *V* is the volume of permeate gas passing through the membrane (cm^3 (STP)), *l* is the membrane thickness (cm), *t*