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Research Paper

Preparation and characterization of ultra-thin poly ether block amide/nanoclay nanocomposite membrane for gas separation

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ABSTRACT

Supported Mixed Matrix Membrane (SMMM) Polyether block amide/nanoclay (PEBA/Cloisite 30b), based on Polyacrylonitrile on nonwoven Polyester (PAN/PE), was fabricated by the spin coating method, following optimization of fabrication conditions for Single-Layer Mixed Matrix Membranes (SLMMMs). Cloisite 30b is a type of montmorillonite modified from nanoclays family. The fabricated membranes were examined structurally through The X-ray Diffraction (XRD), The Field Emission Scanning Electron Microscopy (FESEM), The Fourier-transform infrared spectroscopy (FTIR), and The Atomic force microscopy (AFM) analyses, and evaluated operationally by conducting permeability tests of the pure gases of CO_2, CH_4 and N_2. The effect of different Cloisite 30b loadings and the varying pressures on the gas separation performance of the membranes was investigated. Elevation of the loading up to 0.2 wt% Cloisite 30b increased the permeability and the selectivity, whereas further increase up to 1 wt% reduced the permeability and selectivity. After an increase in pressure from 4 to 14 bar, an elevated permeability and selectivity was observed. The membrane with a Cloisite 30b loading of 0.2 wt% had the best performance in the separation of the pure gases of CO_2, CH_4, and N_2 such that the permeability of CO_2, along with the selectivity of CO_2/N_2, and CO_2/CH_4 had increase of about 55.55%, 26.45% and 38% in comparison with the Single Layer Neat Membrane (SLNM). The permeability of CO_2, the selectivity of CO_2/N_2, and the selectivity of CO_2/CH_4 of SMMM with a Cloisite 30b loading of 0.2 wt% also indicated an increase of about 364%, 18% and 47.8% in comparison to the Supported Neat Membrane (SNM). Furthermore, CO_2 permeability through SMMM with cloisite30b loading of 0.2 wt% indicated a growth of about 562.5% in comparison to SLMMM with the same loading.

1. Introduction

Today, industrial productions in the world are based on the usage of fossil fuels, which are directly related to energy production. Combustion of fossil fuels and other human activities have resulted in elevated concentrations of greenhouse gases such as carbon dioxide across the earth, thereby causing global warming and adverse environmental effects. The removal of carbon dioxide from the different output gases of different industries, including power plants, oil refineries, the cement industry as well as the iron and steel industry is important. Moreover, one of the problems that cause the significance of carbon dioxide separation in the natural gas industry is the diminished heat value of natural gas, increased corrosion during transmission and distribution of the gas, and the adverse effects on humans and the environment due to presence of carbon dioxide (Alcheikhhamdon and Hoorfar, 2017). Therefore, separation of carbon dioxide is one of the most effective factors for the storage of energy, environmental protection, and sustainable development. In recent decades, usage of membranes, especially polymeric membranes, has attracted a great deal of attention thanks to their advantages such as their low-cost, low-energy consumption, and fewer environmental and physical effects in comparison to the traditional methods of absorption and adsorption for industrial uses. Development of membranes with a high flux and selectivity is desirable, but one of the major problems of polymeric membranes is that as their permeability increases, their selectivity decreases significantly or vice versa. Various methods have been investigated to overcome this problem thus far; these include: the synthesis of new polymers, mixing common polymers with organic and inorganic nanoparticles, etc. (Kiadehi et al., 2015). Among them, the combination of common polymers with organic and inorganic nanoparticles, known as Mixed Matrix Membranes (MMMs) have attracted the attention of many researchers. MMMs are synthesized in two forms:

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Single-Layer Mixed Matrix Membranes (SLMMMs) and Supported Mixed Matrix Membranes (SMMMs). SLMMMs have been extensively studied due to their simple synthesis process. Recently, the fabrication of SMMMs has attracted the attention of researchers. This type of membrane consists of a porous support coated with a middle microporous layer (Ingole et al., 2017); this layer is coated with a very thin selective layer that has a thickness of below 400 nm. Owing to the application of a porous sublayer, which is selected from inexpensive and available materials, the permeability and mechanical strength of the SMMM increase, while the extent of polymer consumption and expensive nanoparticles is minimized. These membranes are thus more economical and commercial than SLMMMs (Halim et al., 2014). Qiang Fu et al. managed to synthesize a type of SMMMs using amorphous soft nanoparticles mixed in with PEBA 2533[1] as the selective layer. The presence of nanoparticles in the selective layer resulted in an increased membrane free volume, thereby enhancing the separation performance of the membrane (Fu et al., 2014). Shereen Tan et al. also synthesized a type of SMMMs using Supramolecular Soft Nanoparticles (SNPs) mixed with PEBA 2533as the selective layer, where the presence of carbon dioxide absorbent agents in the structure of the nanoparticles led to an improved separation performance of the membrane (Tan et al., 2015). Andri Halim et al. managed to synthesize a type of SMMM with the PEBA 2533 selective layer mixed with soft polymer nanoparticles based on PEG-b-PDMS,[2] whereby they observed the approved separation performance of the membrane (Halim et al., 2014). Jomekian et al. succeeded in synthesizing a type of SMMM using PEBA1657 mixed with ZIF-8[3] nanoparticles as the selective layer with a high separation performance due to the high absorption of carbon dioxide in the pores of the PEBA1657-ZIF-8 matrix (Jomekian et al., 2016). Poly-ether-*block*-amide, known as "PEBAX®", is a copolymer that is obtained from the compressive polymerization of polyamide carboxylic acid and polyether. By altering the level of polyamide and polyether, PEBA, with different degrees of gas separation, is obtained. Among them, PEBA1657, which contains 40% Polyamide6 (PA) as the hard part and 60% polyethylene oxide (PEO) as the soft part, shows a high selectivity for the gas separation of carbon dioxide from other gases due to the powerful interaction between the soft part and carbon dioxide (Estahbanati et al., 2017). The hard part of PEBA1657 provides mechanical strength, whereas its soft part allows for suitable molecular diffusion for gas molecules (Mahmoudi et al., 2015). In recent decades, mineral nanoparticles including ceramics (Ardestani et al., 2010), carbon nanotubes (Murali et al., 2010), silica (Lovineh et al., 2014), zeolite (Mahmoudi et al., 2015), etc. mixed with PEBA1657 have been used for synthesizing SLMMMs. No attention, however, has been paid to nanoclays. As they are well scattered in the polymer matrix, nanoclays have attracted a great deal of attention in the fabrication of polymer nanocomposites (Ghaemi et al., 2011). Clays are natural, fine-grained, inexpensive, and available materials with a wide range of green material structures (Hashemifard et al., 2011) that are divided into five groups: smectites, ilites, kaolinites, chlorites, and sepiolites. The most applicable clays in polymer-clay nanocomposite materials are the clays that belong to the smectite group, in particular, montmorillonites. Montmorillonites are hydrophilic clays, the addition of which, at trace amounts (< 10%), to the polymer matrix increases both the mechanical and the heat resistance of the polymer as well as its hydrophilicity (Ghaemi et al., 2011; Jamil et al., 2017). Cloisite 30b is a type of montmorillonite modified with quaternary ammonium salt (methyl tallow bis-2-hydroxile quaternary ammonium chloride), which has two hydroxyl groups (Fig. 1) (Kotal and Bhowmick, 2015). Considering the aforementioned properties of PEBA1657 and nanoclay, in this research, for the first time we fabricate the SLMMM PEBA1657-Cloisite 30b casting method; after achieving the optimal percentage of nanoclay in terms of the best separation performance, we synthesize the SMMM PEBA1657-Cloisite30 b based on porous polyacrylonitrile/polyester (PAN/PE) support using the spin-coating method. The synthesized membranes are then tested for operational evaluation by the pure gases N_2, CH_4, and CO_2; the membranes are structurally evaluated by the FTIR, the XRD, the AFM, and the FESEM analyses.

[1] Poly Ether Block Amide 2533.
[2] Polyethylene glycol-b-Polydimethylsiloxane.
[3] Zeolitic imidazolate framework-8.

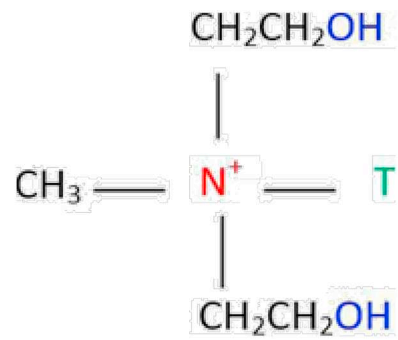

Fig. 1. The structure of modifier in Cloisite30b (T:tallow is carbon chains consist of 65% C18, 30% C16, 5% C14) (Kotal and Bhowmick, 2015).

2. Experimental

2.1. Materials

PEBAX® (Grade: 1657), PAN (Average Mw: 150,000), nonwoven PE (Grade: 85spl CU 42, Basis weight: 83 gsm) and Cloisite 30b (Mineral type: montmorillonite modified, Density: 0.5–0.7 g/cm^3, Particle size: 1–2 nm, Specific surface area: 220–270 m^2/g) were purchased from ARKEMA (France), Polyacrile (Iran), Crane (USA), and Pioneers of Iranian Nanomaterials (Iran), respectively. Ethanol (99.99%) and dimethyl formamide (DMF, 99.99%) were supplied from Merck Co., Germany. CO_2, N_2 and CH_4 gas cylinder (purity 99.99%) were purchased from Roham Gas Company (Iran).

2.2. Membrane synthesis

2.2.1. Synthesis of SLMMM PEBA-Cloisite 30b

To fabricate SLMMM PEBA-Cloisite 30b, first Cloisite 30b was added to a mixture of water and ethanol in the ratio of 30:70%, and then placed inside an ultrasonic probe device such that Cloisite 30b would be well scattered within the solvent. Next, the PEBA 8 wt% solution was fabricated with a mixture of solvent and Cloisite 30b at 80 °C. After 12 h, the prepared polymeric solution was casted on a glass using a casting knife. It was then placed inside an oven at 50 °C for 18 h so that the entire solvent could be extracted from it.

Different Cloisite 30b loadings were performed in the SLMMMs and the optimal loading of Cloisite 30b in terms of the best separation performance was determined. To synthesize a selective layer in the SMMM, optimal loading of Cloisite 30b was used. Table 1 presents the

Table 1
Abbreviation of synthesized membranes.

Samples	Abbreviation
Neat PEBA8%wt	P8
PEBA8%wt + Cloisite30b0.1%wt	P8NP.1
PEBA8%wt + Cloisite30b0.2%wt	P8NP.2
PEBA8%wt + Cloisite30b0.4%wt	P8NP.4
PEBA8% wt + Cloisite30b0.5%wt	P8NP.5
PEBA8%wt + Cloisite30b1% wt	P8NP1
PEBA3%/PAN/PE	SP3
PEBA3% + Cloisite30b0.2%wt/PAN/PE	SP3NP.2