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Mixed matrix membranes of Pebax-1657 loaded with 4A zeolite for gaseous separations

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ABSTRACT

Mixed matrix membranes (MMMs) made from selective inorganic fillers and polymers have received extensive attention in the field of gas separation. In this work, poly(ether-*block*-amide), (Pebax)/zeolite 4A MMMs were prepared using ethanol/water as solvent mixture. The concentration of zeolite 4A in membrane was varied from 5 to 30 wt.% of the polymer. The membranes were characterized by SEM, FTIR and XRD to study the morphologies, the effect of zeolite 4A incorporation on intermolecular interactions and degree of crystallinity, respectively. The pure gas permeabilities were recorded at the ambient temperature, using an indigenously built high-pressure gas separation manifold. The permeabilities of Pebax-1657/zeolite 4A membranes were enhanced from 71.4 to 155.7 Barrers for CO_2, 2.2–19.6 Barrers for CH_4, 5.8–17.9 Barrers O_2 and 1.4–12.0 Barrers for N_2. The ideal selectivity of 10 wt.% zeolite 4A MMM enhanced from 54.1 to 94.2 for the CO_2/N_2 gas pair with increase in feed pressure from 5 to 25 kg/cm^2, whereas the corresponding values for CO_2/CH_4 and O_2/N_2 were found to rise from 26.4 to 41.3 and 4.3 to 4.9, respectively. The Pebax/zeolite 4A membranes thus provide a potentially promising means for separation of CO_2/N_2, CO_2/CH_4, and enrichment of O_2 and N_2 from air.

1. Introduction

Polymer membranes play an important role in gas separation due to their superior environmental friendliness, modularity, versatility, simplicity and cost-effectiveness compared to conventional methods such as distillation or absorption [1–3]. Current applications using gas separation membranes include CO_2 and H_2S removal from natural gas, CO_2 and N_2 separation from power plant flue gas, oxygen and nitrogen enrichment, olefin/paraffin separation, hydrogen recovery from refinery, water removal from the air stream and removal of volatile organic compounds from effluent streams [4].

Over the last few decades, many researchers have been working on various polymeric materials such as cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide for the preparation of gas separation membranes. Although polymeric membranes have been successfully developed for gas separation, the well-known permeability and selectivity “trade-off” limits their application in a large industrial scale [5,6]. The concept of MMMs was proposed to overcome the “trade-off” constraints of polymer membranes [7–11]. The MMMs typically consist of organic polymer and inorganic particles such as carbon molecular sieves, zeolites, nanosized particles or conductive polymers. MMMs show much higher gas permeabilities but similar or even improved gas selectivities compared to the corresponding pure polymer membranes [12–14]. The nanocomposite materials may combine the advantages of each component material: for instance, the flexibility and processability of polymers, and the selectivity and thermal stability of the inorganic fillers [15].

Pebax is a thermoplastic elastomer having both polyamide segments, which is hard that gives mechanical strength, and polyether segments, which is flexible and provide high permeability [16,17]. Commercially various grades of Pebax are available by altering ether and amide ratios and have been studied for gas separation applications [16–18]. In the present work, Pebax-1657, which is constituted by 40% amide groups and 60% ether linkages, was selected as the base polymer for modification. As a rubbery polymer material, which has high chain mobility, a good interaction with the filler can be expected. The incorporation of polyhedral oligosilsesquioxane (POSS) nanoparticles into Pebax matrices significantly alters the gas separation performance of the Pebax membrane. Simultaneous enhancement in both CO_2 permeability and CO_2/H_2 ideal selectivity has been achieved by optimizing the POSS loadings [19]. Silica loaded Pebax-1657 exhibited higher permeability coefficients and permselectivities than those of Pebax due

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to additional sorption sites in polyamide block and the organic/inorganic interphase [20]. Pebax-1657 blended with zeolitic imidazolate frameworks (ZIF-7) was successfully fabricated on PAN support and both ideal selectivity and permeability for CO_2/CH_4 and CO_2/N_2 could be increased by inclusion of ZIF-7 filler [21]. In our earlier works, MMMs were fabricated by incorporating activated carbon into Pebax-2533 and multiwalled nanotubes (MWNT) into Pebax-1657 polymer matrix to enhance the performance of membranes [22,23]. Pebax-MWNT membranes showed a significant improvement in permeability.

Zeolites are microporous crystalline aluminosilicates with uniform molecular sized pores and have been used in powder composite form as molecular sieving separation media [24]. Matrimid/Zeolite 4A membranes has enhanced the permeability of H_2, CO_2, O_2 and N_2, and corresponding decrease in the ideal selectivity of gas pairs O_2/N_2, H_2/N_2 and CO_2/N_2 was observed [25]. Huang et al. [26] synthesized polymer–zeolite mixed matrix membranes by incorporating nanosized or microsized zeolite 4A into polyethersulfone. MMMs exhibited decrease in gas permeabilities. Moreover, permselectivity was greatly enhanced for He/N_2, H_2/N_2, He/CO_2 and H_2/CO_2 gas pairs, especially for nanosized zeolite 4A loaded membranes. The addition of zeolite 4A to PVAc increased ideal selectivity for gas pairs CO_2/CH_4, O_2/N_2, H_2/N_2 and CO_2/N_2 with a corresponding decrease in their permeability. At the same time, the thermal stability of membranes was improved [27,28].

A few researchers have reported incorporation of zeolites into Pebax polymer to enhance performance in gas separation as well as pervaporation applications. Sunitha et al. [29] reported the effect of loading a hydrophilic zeolite 4A in Pebax-2533 matrix for pervaporation of *n*-methyl pyrrolidone (NMP)/water mixtures. The MMMs were further crosslinked with 2% v/v 2, 4-toluylenediisocyanate (TDI) to reduce degree of swelling and improve selective nature with respect to water. Friess et al. [30] examined transport properties of MMMs based on Pebax-4033 containing two different types of ZSM-5 zeolites. Increasing zeolite content in the copolymer resulted in higher values of permeability as well as gas/gas and vapor/gas selectivity when compared to the pristine polymer.

In the present work, preparation of Pebax-1657/zeolite 4A MMMs is proposed as new gas separation membranes. The effect of incorporation on the membrane characteristics and separation performance of the membrane is evaluated. The gas permeation properties of newly fabricated membranes are compared with prisrine Pebax membrane by measuring single gas permeabilities of CO_2, CH_4, O_2 and N_2.

2. Experimental

2.1. Materials

Commercially available Pebax-1657 was procured from Atofina Chemicals, France. Polyethersulfone (PES) powder was purchased from Radel, USA. Zeolite 4A was supplied by Zeolites & Allied Products Pvt. Ltd., Mumbai, India. Ethanol, dimethylformamide (DMF) and propionic acid were purchased from Loba Chemie, Mumbai, India. Pure CO_2, O_2 and N_2 gases were supplied by BOC Gases Ltd., Hyderabad, India, and CH_4 was procured from Bhuruka gases Ltd., Bangalore, India.

2.2. Membrane synthesis

PES ultraporous substrate of roughly 30,000 molecular weight cutoff (MWCO) was synthesized by the procedure described elsewhere [23]. Fig. 1 gives the step wise preparation procedure of the MMM dope solution. Zeolite 4A in proportion of 5, 10, 20 and 30 wt.% of the polymer was first added to a solvent mixture of 70% ethanol and 30% v/v water for better interaction of the polymer matrix and filler and uniform dispersion of the filler. The Zeolite/solvent mixture was kept under constant stirring for 3 h and subsequently subjected to sanction for 3 h. A 4 wt.% Pebax solution was synthesized by adding initially 1/10th of the polymer pellets to the well dispersed zeolite/solvent mixture for wetting of filler. After complete dissolution of the added polymer remaining polymer was added gradually. The polymer dissolved at 90 °C with rigorous stirring while maintaining under constant reflux over a period of 6 h. The bubble free polymer dope solution was cast on top of the PES substrate using a doctor blade. The obtained thin film composite (TFC) membrane was initially kept in air drying at ambient temperature followed by vacuum drying to remove residual solvent. The top layer was cautiously peeled off from the PES substrate to measure the effective thickness of the Pebax layer. Throughout this manuscript zeolite 4A incorporated Pebax is denoted as Pebax/4A.

2.3. Membrane characterization

2.3.1. SEM

The surface and cross-sectional morphology of Pebax and Pebax/4A nanocomposite membranes were examined by scanning electron microscopy (SEM) using a Hitachi S2150 microscope.

2.3.2. FTIR

FTIR spectra of zeolite 4A, Pebax and Pebax/4A nanocomposite membranes were measured using a Perkin–Elmer-283B FTIR spectrometer within the range between 4000 and 400 cm^{-1}.

2.3.3. XRD

A Siemens D 5000 powder X-ray diffractometer was used to obtain the solid state morphology of Pebax, zeolite 4A and Pebax/4A nanocomposite membranes. X-ray of 1.5406 Å wavelength was generated by a Cu Kα source.

2.4. Gas permeability studies

Fig. 2 illustrates the diagram of the laboratory experiment setup and membrane test cell. Indigenously designed and fabricated permeation test cell, having effective area of 42 cm^2, was used for conducting the gas permeation tests. The detailed experimental set-up and procedure was described elsewhere [23]. Nut and ferrule fittings were used to avoid leakage during the transport of gas streams. Needle valves (Swagelok) with ¼ in. SS 316 end connections were used to regulate the flow of inlet and outlet streams.

All the experiments were carried out with pure CO_2, CH_4, O_2 and N_2 gases. Residual air present in the test cell, feed and retentate lines were flushed with the feed gas. The normalized fluxes of the membranes are measured at ambient temperature over a pressure range of 5–25 kg/cm^2. Feed gas was transported steadily into the upper chamber of the test cell with the outlet valve kept partially closed until the gauge specify the required pressure. After attaining the steady state, flow rate of permeate was calculated with the help of a soap bubble meter. The permeability (K) was determined from

$$K = \frac{qt}{a(p_1 - p_2)} \tag{1}$$

where q is the volumetric flowrate of permeated gas (cm^3/s), t is the effective membrane thickness (cm), a is the effective membrane area (cm^2), and p_1 and p_2 are the feed and permeate side pressures (cm Hg), respectively. The unit of permeability is denoted in barrers [1 Barrer = 10^{-10} (cm^3(STP) cm/cm^2 sec cmHg)]. The ideal selectivity