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Characterization of polyethersulfone/polyimide blend membranes prepared by a dry/wet phase inversion: Precipitation kinetics, morphology and gas separation

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ABSTRACT

Flat sheet gas separation membranes of polyethersulfone (PES), polyimide (Matrimid, MI) and their blends were fabricated by a spin casting method followed by a dry/wet induced phase inversion process. The mixing compatibility and thermal stability of the blend membrane were studied by Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA) respectively. The forming behavior was investigated by the ternary phase diagram and an optical microscope with PES, MI and PES/MI blend (5:5). In this ternary system, the average of diffusion coefficient, D_e, of PES, MI and EM5050 were respectively 8.35×10^{-5}, 10.22×10^{-5} and 3.09×10^{-5} cm^2/s. The morphology of membranes was studied by a scanning electron microscope (SEM). All prepared membranes had an ultrathin dense skin layer (<1 μm) on the top of the membrane. The blend membrane with MI composition from 40 to 80 wt.% showed sponge-like sub-layer whereas pristine membrane as well as the rest of the composition showed the finger-like sub-layer (macrovoids). Gas permeance of N_2, increased with increase in feed pressure irrespective of blend composition. The permselectivity of PES/MI (30/70 wt.%) decreased from 5.4 to 4.9 with increase in the feed pressure.

1. Introduction

Membrane technology for gas separation and purification process has been attracting enormous attention [1]. This is mainly due to relatively higher reliability, energy efficiency and lower capital cost than other conventional gas separation processes [2,3]. Organic polymeric membrane has advantage over its inorganic counterpart because of the ease of processing and appropriate robustness. However, individual polymer materials, used for gas separation, do not have all the required properties. Polymers with higher gas permeability possess lower selectivity and materials having chemical and plasticizing resistance are very expensive and difficult to process [4,5]. This is the driving force for looking towards polymer blending methods to combine the properties of different materials into binary or ternary blends [6,7]. By this way, the already available commercial polymers can be easily used instead of going for whole new polymer synthesis or modification [8–12].

The thick skins (>2 μm) in such cases limit their applicability. The present study describes a process that produces equally thin or thinner selective layers without the need of such undesirable additional post-treatments. The dry/wet phase inversion process has been used to form ultrathin and defect-free membranes from a variety of polymers [13].

The most commonly used commercial polymers for gas separation are the phenyl groups based polysulfone (PSf), polyethersulfone (PES) and aromatic polyimide (PI). PSf and PES are high performance engineering polymer which has good stability, permeability, selectivity, high critical pressure of plasticization and low cost. PI, such as Matrimid® 5218 (MI), is thermally stable, has good mechanical properties along with gas permeabilities and selectivities. These materials have been prepared in several membranes and characterized [14–21].

PES/PI blend system has not been studied as much as PSf/PI. Liang et al. [18] reported the miscibility properties of PES/PI blend by studying thermal and rheological properties. The hollow fibers of PES/PI blends with different compositions were studied by several groups [19–21]. However, the flat sheet dense membrane of the same blends has very few reports. Ekiner [22] reported blends of PES with aromatic polyimides, polyamides and polyamide-imide. In this patent they reported PES/PI blend composition for O_2/N_2 separation.

In this paper we studied the preparation of flat sheet blend membranes consisting of PES and MI by spin casting and then the

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Abbreviations: $\alpha_{A/B}$, the ideal separation factor A over B; P/L, the permeance (GPU); PI, polyimide; PES, polyethersulfone; MI, Matrimid® 5218; EM, polyethersulfone/Matrimid® 5218 blend polymer; NMP, N-methyl-2-pyrrolidinone; DMF, dimethylformamide; SEM, scanning electron microscope; TGA, thermal gravimetrical analyzer; GPU, gas permeation unit; STP, standard temperature and pressure.

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dry/wet induced phase inversion process. The effect of polymer concentration, composition and solvent in the dope solution on the membrane morphology was studied by SEM. Gas permeance and selectivity, miscibility and thermal stability were studied by gas permeation analyzer, FTIR and TGA respectively.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Ultrason E 6020P) was procured from BASF (Mn = 58,000 g/mol, 1.37 specific gravity) and Matrimid® 5218 (MI, 5(6)-amino-1-(4′-aminophenyl)-1,3-trimethylindane (BTDA-DAPI)) from Ciba-Geigy Co. (Mn = 46,000 g/mol) is prepared from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and diaminophenylindane. The polymer structures are shown in Fig. 1. N-methyl-2-pyrrolidinone (NMP and purity 99%) and dimethylformamide (DMF) were purchased from Lancaster Co. and Aldrich Co. and used without purification. Ultra purified water was prepared by Millipore filtration systems (ELGA STAT and UHQ).

2.2. Preparation of PES/MI blend membrane and characterization

2.2.1. Characterization

Fourier transform infrared (FTIR) spectra of the samples were collected by an Excalibur series FTIR instrument (ATI Mattson, Genesis Series) in the frequency ranges of 4000–400 cm^{-1} with an attenuated total reflection facility. TGA (Shimadzu, TGA-50, Japan) was performed under nitrogen environment at a rate of 10 °C/min in the temperature ranges of 35–1000 °C. The surface and cross-section (fractured in liquid nitrogen) morphology of the blend membranes were examined by scanning electron microscopy (SEM, JEOL, JSM-5010LV). The membranes were platinum-coated prior to SEM measurements.

2.2.2. Phase diagrams

Cloud point lines were determined by visual observation of the turbidity change of polymer solution. Nonsolvent was slowly added in drops to the mechanically stirred polymer solution until the solution became turbid. The cloud point was assigned when the turbidity of the solution persisted for at least 5 min. Then the solution was diluted with solvent and the experiment was repeated. Cloud point curve was illustrated by titration method [23,24]. Polymer solutions were prepared with 1, 2, 5, 8, 10, 15, 20, 25, and 30 wt.% and titrated by using water as nonsolvent at 24 °C. Ternary phase diagram was illustrated by calculating each fraction of components which was represented from titration.

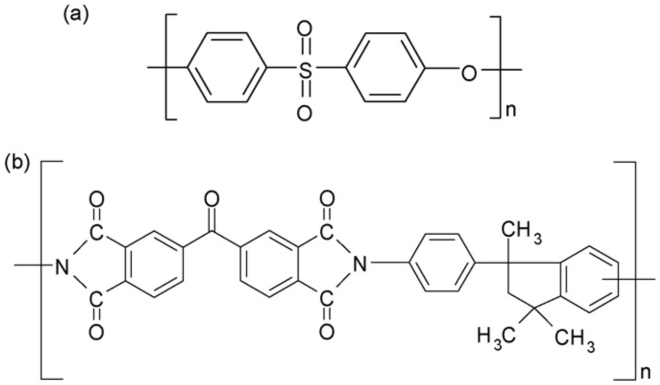

Fig. 1. Structure of polymers: (a) polyethersulfone (PES) and (b) Matrimid® 5218 (MI).

2.2.3. Precipitation kinetics and anticipation of morphology: apparent diffusion coefficient of nonsolvent

The forming behavior was investigated by an optical microscope with PES, MI and PES/MI blend (5:5). Many kinetic parameters of a membrane formation can be observed, but during the immersion step in the phase inversion process, precipitation kinetic provides very important information on the membrane formation process. In order to obtain the apparent diffusion coefficient of a nonsolvent, the optical microscopy measurement techniques described by Chun et al. [24] and Strathmann et al. [25] were used and are detailed as follows: a drop of polymer solution was placed between two optical glass slides, and then a drop of the nonsolvent was placed near the edge of polymer solution with a micropipette. As the nonsolvent makes contact, it immediately diffusion into the polymer solution and the precipitation started with its front moved inward. The moving distance, d, of the precipitation front was measured by optical photographs at different times. The apparent diffusion coefficient, D_e, of a nonsolvent can be calculated as formulated by Strathmann et al. [25] in the following manner:

$$d = 2(D_e t)^{1/2}$$

where D_e is the apparent diffusion coefficient of a nonsolvent.

2.2.4. Membrane preparation by dry/wet induced phase inversion process

Polymer blend membranes were fabricated by the dry/wet phase inversion process. Polymers were pretreated in a vacuum oven at 100 °C for 12 h prior to the polymer solution preparation. The polymer blend compositions of PES/MI were varied from 90/10 to 10/90 in NMP as solvent. These solutions are named as EM9010, EM8020, EM7030, EM6040, EM5050 and EM1090 respectively. Three different concentrations of 15, 20, 25 wt.% of dope solution were chosen for the preparation of membrane. Spin casting was done on a glass plate at 850 rpm. Casted films were evaporated for 30 s under the relative humidity 55 ± 5% and at a temperature of 24 °C. Then they were immersed into the water coagulation bath at 15 ± 1 °C. The casted membranes were kept in a vacuum oven at 80 °C for 1 day to remove the residual solvent present. In this study, the effect of solvent on cross-section morphology was fabricated in NMP and DMF.

2.2.5. Characterization of gas permeance

Gas permeance was measured by apparatus consisting of a bubble flow meter, and pressure gauge at the bottom of the cell. Operating pressure was controlled between 20 and 50 psig and temperature at 24 °C. A permeation cell made up of stainless steel consists of double O-ring to prevent gas leakage at high pressure. Effective cell area was 12.57 cm^2. Gas permeance was measured five times. As a result, the pressure-normalized fluxes $(P/L)_i$, can be calculated as follows:

$$\left(\frac{P}{L}\right)_i = \frac{Q_i}{\Delta p_i A}$$

where Q_i is the volumetric flow rate of gas i at STP, Δp is the trans-membrane pressure drop, and A is the membrane surface area. Pressure-normalized fluxes are often reported in permeation units, GPU, as given blow:

$$\text{GPU} = 1 \times 10^{-6}\,\frac{\text{cm}^3\,(\text{STP})}{\text{cm}^2\,\text{s}\,\text{cmHg}}$$

The ideal separation factor of a gas separation membrane can be determined from:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/L)_A}{(P/L)_B}$$