Separation and Purification Technology 73 (2010) 188–193

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Effect of formamide additive on the structure and gas permeation performance of polyethermide membrane

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ARTICLE INFO

Article history:
Received 2 November 2009
Received in revised form 27 March 2010
Accepted 30 March 2010

Key words:
Gas separation membrane
PEI
FM
Viscosity
Solubility parameter difference

ABSTRACT

Asymmetric polyetherimide (PEI) membranes have been prepared by phase-inversion process from casting solution containing n-methyl-2-pyrrolidone as a solvent and formamide (FM) as an additive. The effects of FM concentration on the structure and gas separation performance of the PEI membranes have been investigated and analyzed in terms of the casting solution viscosity, phase diagram, and solubility parameter difference. With the increase of FM concentration, the casting solution becomes thermodynamically unstable and easier to cause casting solution demixing, but the precipitation rate decreases because of the increased casting solution viscosity. The experimental results reveal that the structure of the dense skin layer strongly depends on the content of FM in the casting solution, and the gas permeance of the PEI membrane is markedly improved by the addition of FM. After coated with silicone rubber, the membrane prepared from the casting solution with 28.0 wt.% of PEI and 3.0 wt.% of FM exhibits the H_2 permeance of 24.6 GPU (1 GPU = 10^{-6} cm^3/cm^2 s cmHg), combining with the O_2/N_2 and H_2/N_2 separation factors of 7.0 and 153.0, respectively.

1. Introduction

Membranes have been developed for a wide variety of applications in gas separation technology due to its efficient and economical feature [1–3]. Polymeric membrane material plays an important part in the performance of gas separation membranes. Among numerous polymer materials, polyetherimide (PEI) appears to be of particular interest in the fact that the aromatic imide units provide stiffness and heat resistance and the flexible ether linkages provide good process ability [4–6]. The studies on gas permeation in the PEI dense film reveal that PEI exhibits impressively high selectivity for all of the important gas pairs [7]. Therefore, many researches are devoted to the development of PEI membranes for gas separation [8–11].

PEI membranes are usually prepared by phase-inversion process, where a homogenous casting solution is cast as a thin film and then the film is immersed into a non-solvent coagulation bath. Due to the exchange of solvent and non-solvent between casting solution and coagulation bath, phase separation of casting solution is induced to form polymer-rich phase and polymer-lean phase, where the membrane is formed [12]. The final structure and the performance of the membrane largely depend on the properties of casting solution, including the type of polymer, solvent, additive, and their composition, as well as membrane formation conditions, such as solvent evaporation temperature, evaporation time, and coagulation media temperature [13]. Adding an additive into a casting solution is one of the important techniques in membrane preparation to regulate the morphology and develop the membrane performance [14]. Wang and co-workers have prepared PEI hollow fiber membranes with high gas selectivity by introducing methanol and acetone as additives into the casting solutions [8]. Kneifel and Peinemann have studied the effect of γ-butyrolactone in a PEI/NMP casting solution on the structure of gas separation membranes [9] and found that γ-butyrolactone suppressed the macrovoid formation. A well-interconnected porous network has been found to be formed after the additive of lithium nitrate leached out in the coagulation bath by Kurdi and Tremblay [10].

Low molecular weight component is frequently used as the additive in the membrane-forming system because it offers a convenient and effective way to obtain desired membrane structures [15]. As a low molecular component, formamide (FM) has good miscibility with solvent and high diffusivity in the coagulant. Therefore, it can easily diffuse into the coagulation bath during initial phase separation and modify the membrane structure. However, few studies have been reported on the influence of FM as additive on the properties of the membranes prepared by phase-inversion process. In this study, PEI asymmetric membranes with different FM contents have been prepared. We choose FM as additive and

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doi:10.1016/j.seppur.2010.03.024

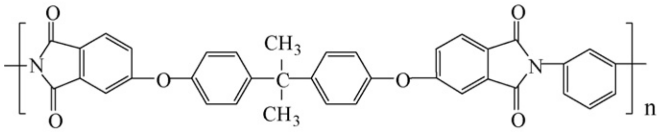

Fig. 1. Chemical structure of PEI.

n-methyl-2-pyrrolidone (NMP) as solvent to prepare the casting solution. The phase-inversion process takes place by using water as coagulant. The effects of FM concentration on the casting solution properties have been investigated in terms of cloud point curve, viscosity, and solubility parameter difference. Moreover, a dilute silicone solution is coated on the surface of the PEI substrates to eliminate defects in the skin layer. The gas separation performance of the PEI membrane has been examined and correlates with the membrane structure that is controlled by the phase-inversion thermodynamic and dynamics.

2. Experimental

2.1. Materials

Polyetherimide (PEI Ultem® 1000) in pellet form was purchased from General Electric Plastics (USA), and dried in a vacuum oven at 105 °C for 10 h prior to be used. The chemical structure of PEI is shown in Fig. 1. Polydimethylsiloxane (Sylgard-184), together with the proprietary crosslinker and catalyst system, were purchased from Dow Corning Corporation (USA). N-methyl-2-pyrrolidone (NMP, reagent grade) was purchased from Fuchen Chemical Co. (China), FM and pentane (reagent grade) were from Bodi Chemical Co. (China). All the solvents were dried using the activated molecular sieve (5A) purchased from Liaodong Chemical Reagent Company (China) before use. H_2, O_2, and N_2 with a purity of 99.99% were from Dalian Gas Co., Ltd. (China).

2.2. Membrane preparation

28 wt.% PEI casting solution was prepared by dissolving PEI in a binary mixture solvent of NMP and FM by magnetically stirring at 90 °C for 8 h. Air bubbles in the homogeneous solution were removed with a vacuum pump. The casting solution was kept at room temperature for 24 h and then was cast onto a non-woven fabric to form a thin film with a knife gap of 380 μm thickness at 25 °C. After exposed to the atmosphere of 60% average relative humidity for 5 s, the film coupled with the non-woven fabric was immersed in a coagulation bath, where polymer precipitation occurred and a membrane formed. The membrane was kept in an aqueous bath for at least one day to remove solvents.

The as-prepared membrane was coated with a 3.0 wt.% of silicone rubber solution in pentane to plug the pinhole defects on the membrane surface. During the coating process, a vacuum was applied to facilitate the filling of the silicone-coating material into the pores on the PEI substrate. After about 5 min, the residual solution was poured out and the membrane was set aside to let pentane evaporate gradually. Then, the silicone layer was further cross-linked by keeping the membrane in an oven at 50 °C for 12 h.

2.3. Measurement of cloud point and casting solution viscosity

The cloud point curves were measured by titration method at 25 °C. A binary polymer solution (PEI/NMP) was added to a thermostatic flask with a rubber septum stopper. The addition of FM was dropwise added into the solution by a syringe through a septum, while thorough mixing was applied using a magnetic stirrer. The addition of FM was continued until the clear polymer solution visually turned to a cloudy solution from visual observations. After the first sign of turbidity was observed, the addition of FM was stopped. The cloudy solution was stirred for an additional 30 min while examined whether the turbid solution changed to be clear. If the cloudy solution turned clear, more FM was added, otherwise the titration process was terminated.

The viscosity of the casting solution was measured using a Brookfield LVT DV-III viscometer (USA) at 25 °C.

2.4. Solubility parameter difference calculation

Solubility parameter difference provides an easy numerical method of rapidly prediction the extent of interaction between solvents and polymers [16]. The higher is the solubility parameter difference between solvent and polymer, the more intense the interaction of solvent and polymer, and the solubility of solvent to polymer will decrease. The solubility parameter difference between the binary mixture solvent of FM/NMP and PEI, $\Delta\delta_{s-p}$ can be calculated by the following equation [17]

$$\Delta\delta_{s-p} = \left[\sum_i (\delta_{i,s} - \delta_{i,p})^2\right]^{0.5} \qquad (i = d, p, h)$$

where $\delta_{i,p}$ and $\delta_{i,s}$ represent the solubility parameter of PEI and the binary mixture solvent, $\mathrm{MPa}^{1/2}$. The subscript i stands for the dispersion interaction ($i = d$), the polar bonding ($i = p$), and the hydrogen bonding ($i = h$).

The solubility parameter of binary mixture solvent of NMP and FM can be calculated by the volume average of the solubility parameters of pure components, which is calculated by the following equation [18]:

$$\delta_{i,s} = \phi_1 \delta_{i,\mathrm{NMP}} + \phi_2 \delta_{i,\mathrm{FM}} \quad (i = d, p, h)$$

where ϕ_1 and ϕ_2 are the volume fraction of NMP and FM in the casting solvent, respectively.

In the calculation, $\delta_{i,\mathrm{NMP}}$ and $\delta_{i,\mathrm{FM}}$ are determined from the literatures [19]. The solubility parameters of PEI are calculated using the group contribution method for polymers [20,21].

2.5. Characterization of membrane morphology

The morphology of the substrate membrane was viewed by a KYKY-2000B scanning electron microscopy (SEM) at an accelerating voltage of 30 kV under magnifications ranging from 500 to 10,000. The samples were freeze-fractured in liquid nitrogen to guarantee a sharp brittle fracture, and were successively sputter coated with a thin gold film prior to SEM observation.

2.6. Gas permeation measurements

Gas permeation measurements were performed with a permeation cell by a single gas feed at 20 °C. Circular membrane discs with an effective area of 9.61 cm^2 were used. The feed pressure was controlled at 0.5 MPa while the permeate side pressure was atmosphere. The gas permeance was measured with a soap bubble flow meter. The permeance of gas i, J_i, in GPU ($1\ \mathrm{GPU} = 10^{-6}\ \mathrm{cm}^3/\mathrm{cm}^2\,\mathrm{s\,cmHg}$) is determined by the following equation:

$$J_i = \frac{Q_i}{\Delta p_i A}$$

where Q_i is the gas permeate volumetric flow rate (cm^3/s), ΔP_i is pressure difference across the membrane (cmHg), A is membrane effective surface area (cm^2). $\alpha_{i/j}$ as the separation factor of gas pair