Controlling the pore size of macroporous membranes by adding non-solvent

Se-Jong Shin, Se-Jun Im, Seung-Ryul Choi, Seung-Yun Lee, Byoung-Ryul Min†

Department of Chemical Engineering, Yonsei University, Shinchon-dong 134, Seodaemun-ku, Seoul 120-749, South Korea

Tel. +82-2-365-8570; Fax +82-2-365-8570; e-mail: minbr345@yonsei.ac.kr

Abstract

This study investigated the effect of 2-methoxy ethanol (2-Me) non-solvent as additive included in casting solution. Macroporous polymer membranes were prepared by using polyethersufone (PES)/N-methyl-2-pyrrolidone (NMP)/2-Me casting solution and water coagulant. The phase separation co-process of the vapor-induced phase separation (VIPS) and liquid-induced phase separation (LIPS) were used by means of membrane preparation method. The pore size and pore size distribution were controlled with additive (non-solvent), and measured with Automated Perm Porometer. By increasing additive (non-solvent) in the casting solution, the membranes produced changed from finger structure to sponge structure. That is due to the different diffusion rates. At slow diffusion process, sponge-like structure was formed and at fast diffusion process, finger-like structure was formed. Also relative humidity, evaporation time, temperature of casting solution and coagulation bath etc. had effects on the pore size distribution and the porosity of the membrane.

1. Introduction

There are several processes for the preparation of porous polymeric structures. Most common processes are based on phase separation of a polymer casting solution. In such processes, the composition or temperature of a casting solution is changed in such a way that it becomes thermodynamically unstable and separates into two phases. One of the two phases, containing most of the solvent components is then removed and the other phase, containing most of the polymer, becomes the porous structure. The types of phase separation processes are usually classified into four categories: 1) evaporation of the solvent and nonsolvent (dry process), 2) exposure to a nonsolvent vapor, such as water vapor, which absorbs on the exposed surface (VIPS), 3) quenching in a nonsolvent liquid, generally water (wet process or LIPS), and 4) thermally quenching a hot film so that the solubility of the polymer is suddenly greatly reduced (thermal process or thermally-induced phase separation; TIPS). By using the phase separation co-process of VIPS and LIPS, macroporous membranes were made at this study.

In this study, PES/NMP/2-Me casting solution and water coagulant system was investigated at

the viewpoint of membrane morphology and kinetics. It will be discussed how the membrane morphology can be changed with the ratio of 2-Me to NMP in the casting solution, evaporation, the temperature of coagulation bath, and the temperature of casting solution. This change of morphology will be observed through scanning microscopy (SEM) photographs, pure water flux (PWP) test, viscosity, porometer analysis, calculation of diffusion coefficient, and calculation of porosity.

2. Experimental

2.1. Materials

The membrane forming polymers, PES [Ultrason® E 6020P; weight-average molecular weight (Mw) = 58,000, density = 1.370g/cm^3] was produced by BASF (Ludwigshafen, Germany). This polymer flakes absorb moisture very rapidly. Therefore, the flakes were dried at least 4h at 130℃ to 150℃ prior to processing. The polyester non-woven fabrics were Sanko No. 10 from Japan. NMP and 2-Me was purchased from Aldrich (USA) and Fluka (Germany) respectively. The chemical structures of the materials were shown in Fig. 1.

2.2. Preparation of membrane

PES/NMP/2-Me casting solution consisted of PES 9~16 wt%, NMP 29~91 wt%, and 2-Me 0~61wt% mixture. The casting solution was poured on the non-woven fabric and cast with Sheen® four sided applicator. Precipitating this casting film into a membrane was normally carried out by exposure to a non-solvent vapor, such as water vapor, which was absorbed on the exposed surface, and then contacting the casting film with a non-solvent liquid (water) in a coagulation bath. The prepared membranes was washed with deionized water and dried in forced convection oven.

2.3. Determination of viscosity

Viscosity of the casting solution plays an important role in pore size control because it can affect remarkably the exchange rate of solvent and nonsolvent during phase separation. Therefore, it was used as an important parameter to influence the precipitation kinetics and the formation of resulting membrane morphology. It was measured by Brookfield LVDV-II+ viscometer (Brookfield, Middleboro, USA) at corresponding temperature.

2.4. Scanning electron microscopy photographs

Both the cross-sections and the surfaces of the prepared membranes were inspected with SEM using a JEOL-5410LV scanning electron microscope (JEOL, Tokyo, Japan). For this purpose, samples of the membranes were frozen in liquid nitrogen and fractured. If the membrane was not fractured in a dry state, the sample was soaked into a water bath for 1 sec before freeze-fracturing. After sputtering the parts with gold-palladium alloy, they were transferred into the microscope.

2.5. Bubble Point Method with gas permeation

For the measurement of pore size and distribution, bubble point method using a CFP-1200AEL, Automated Perm Porometer (PMI, USA) was selected. Here at first the gas flow is measured through a dry membrane as a function of the pressure and generally a straight line obtained. Then the membrane is wetted with Porewick® (surface tension: 16 dynes/cm) and again the gas flow is determined as a function of the applied pressure. At the highest pressure the gas flow of the dry membrane must be equal to the wet membrane. This method is suitable for characterization of macropores and can be applied for microfiltration and ultrafiltration membranes with pore sizes up to 35nm [1, 2]. In this study, mean flow pore diameter (MFPD) (㎛) was acquired with Porometer.

2.6. Other membrane characterizations

A permeation test apparatus composed of a type 8050 Amicon stirred cell was used to measure the pure water flux and solute rejection of the PES membranes [3, 4]. PWP and solute rejection (R) were determined with de-ionized water and 500 ppm of aqueous polystyrene latex beads (PS) (0.2㎛) dispersion solutions at room temperature, respectively. The pure water flux is defined as,

PWP (l / m^2 hr, LMH) = $Q / (A \times T)$

Where Q is the volume of the permeate (l), A is the area of the membrane (m^2), and T is the permeation time (hr). The solute rejection (R) is defined as

R (%) = $(1 - C_p / C_f) \times 100$

Where C_p and C_f are the polystyrene concentration in the permeate and in the feed, respectively. PS concentration is measured with 2100P, Turbidimeter (HACH, USA).

After the area (A), the mass (W_m) and the thickness (D) of a PES membrane sample were measured, the overall porosity, or void volume can be estimated. The volume of the sample (V_m) equals $D \times A$ and the volume occupied by the polymer (V_p) can be expressed as W_m/ρ_p, where ρ_p is the density of the polymer and has a value of 1.370g/cm^3 for PES. Then, the porosity can be calculated [5]:

$$\text{Porosity} = \frac{V_m - V_p}{V_m} \times 100\% = \frac{D \times A - \frac{W_m}{\rho_p}}{D \times A} \times 100\%$$

3. Results and discussion

3.1. Effect of ambient humidity

During the initial exposure to the atmosphere, composition of a cast film is varied by water vapor sorption rather than by evaporation of the solvent, since NMP are a highly hygroscopic

and non-volatile (b.p. 202℃) solvents [6].

The skin region of the membranes consisted of nodule structures which are formed by aggregated polymer molecules. These structures were induced by the non-equilibrium phase separation due to the rapid composition change through the exchange between water and NMP in a coagulation bath. On the contrary, the membranes included cell-like structures on the whole cross-section as well as the skin region. These membranes represented the cast films immersed into a coagulation bath in a cloudy state.

3.2. Effect of concentration of additive (or non-solvent)

H. Strathmann et al added solvent to the coagulation bath [7]. As the concentration of solvent in the medium was increased, the rate of precipitation fell, resulting in a more sponge-like membrane structure [8]. At this study, some different method was used and was to add non-solvent to the casting solution. As to similar to, as the concentration of non-solvent in the casting solution was increased, the rate of precipitation decreased, resulting to change from finger-like structure to sponge-like structure [9]. For investigating these phenomena, Non-solvent was added in the casting solution to elevate the membrane porosity.

Additive (or non-solvent) should have only limited solubility in the coagulation liquid. This limited solubility is believed to be effective in increasing the asymmetry of the resulting membrane. The formation of membranes having larger pores (above about 0.05 microns) may be accomplished in various ways, but for convenience, the process by which these large pore membranes are produced is preferably facilitated by increasing the proportion of non-solvent in the casting solution. At constant homogeneity or colloidal dispersion stability, the amount of non-solvent that may be added to the system without causing prompt segregation of phases is higher at higher temperatures unless a non-solvent with reverse thermal gelation properties is employed. Such non-solvent with reverse thermal gelation properties includes 2-Me.

In Fig. 2, SEM photographs of a series of membranes cast from the different additive compositions of casting solution into pure water are shown. According to the additive amounts, the structure of membrane changed from a finger structure to a sponge [10]. Also, porosity and pore size were decreased by increasing viscosity of casting solution with same composition in Table 1.

3.3. Effect of temperature of coagulation bath

The temperature of the coagulation bath can affect the porosity of the membrane. In general, warmer coagulation baths result in more porous membranes. Generally, a wide temperature range can be utilized in the coagulation step, ranging from about 1℃ to about 60℃. The lower temperature limit is determined by the freezing point of the particular coagulation liquid. Preferably, the coagulation liquid is water and the temperature is between about 20℃ (or room temperature or slightly above room temperature) and about 40℃. The temperature of the

coagulation bath appears to cause marked changes in the pore diameters of the macroporous skin of the membrane and also in its asymmetry. Where higher coagulation temperatures are utilized, smaller pores form and asymmetry can be reduced.

4. Conclusions

The addition of non-solvent in casting solution was proved to be an efficient method to elevate the porosity of PES membranes. According to the increase of non-solvent amount in casting solution, the morphology of membrane changed from finger form to sponge.

The effect of the exposure of casting solution could have drastic influence on the membrane surface morphology. The duration of the liquid-liquid phase separation during exposure was proportional to the pore size of the top surface of the membrane. The lower temperature of coagulation bath was, the more uniform pore size was.

Acknowledgement

This work was supported by BK21. The authors appreciate the materials and technical supports of BK21.

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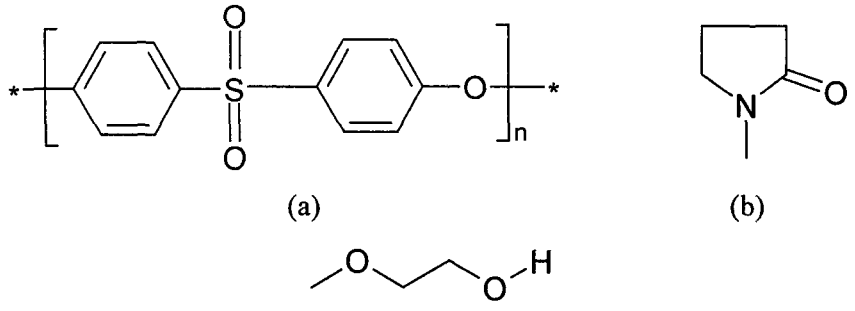

(a) (b)

(c)

Fig. 1. Molecular structures of the chemicals; (a) PES, (b) NMP, (c) 2-Me

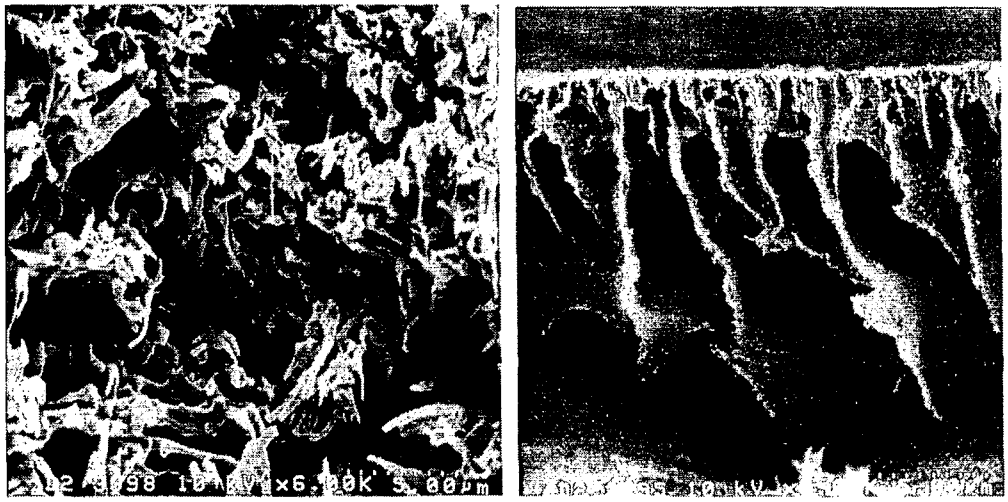

Fig. 2. SEM showing membranes with the transition from sponge to finger structure: prepared from 10wt% PES in casting solution including NMP and 2-Me mixtures of B: PES/NMP/2-Me (10/60/30 wt%), F: PES/NMP/2-Me (10/30/60 wt%).

Table 1. Characterization of PES macroporous membranes

Example #	Viscosity (cp)	R (%) PS (0.2㎛)	PWP (LMH)	MFPD (㎛)	Porosity (%)
A: PES/NMP/2-Me (10/60/30 wt%)	80.08	71.5	310.2	0.875	86.9
B: PES/NMP/2-Me (10/60/30 wt%)	148.77	98.9	718.3	0.348	84.7
C: PES/NMP/2-Me (11/60/29 wt%)	223.95	98.2	1236.0	1.316	84.3
D: PES/NMP/2-Me (9/60/31 wt%)	95.08	99.79	216.4	0.110	86.9

E: PES/NMP/2-Me (10/50/40 wt%)	141.85	99.21	23.1	0.112	85.7
F: PES/NMP/2-Me (10/30/60 wt%)	152.96	100	8.1	0.096	86.7
G: PES/NMP/2-Me (10/5/85 wt%)	167.84	100	4.0	0.123	92.13