

Porometry Studies of the Polysulfone Membranes on Addition of Poly(ethylene Glycol) in Gelation Bath During Preparation

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Abstract. Polysulfone membranes are prepared through phase separation technique, introduced by Loeb-Sourirajan. The viscous polymer solution (in dimethyl formamide) is first spread into the thin film, and then immersed in gelation medium (water). The influence of polymeric additive, poly(ethylene glycol) (PEG) in the formation of the pores during phase separation in gelation bath (i.e. from the polymer poor phase, which appears at the phase separation) is explored. The effects of different molecular weight (Mw) of PEG in the gelation bath regarding the differential filter flows of nitrogen as well as their concentration are reflected from the porometry studies. The pore distribution is shifted as the molecular weight of PEG used in the gelation bath. The bubble point and mean flow pore diameters vary with the concentration as well as their molecular weight of PEG.

Key words: Membrane, poly(ethylene glycol), wet phase inversion, gelation bath, pore diameter

Resumen. Se prepararon membranas de polisulfona mediante la técnica de separación de fase, introducida por Loeb-Sourirajan. La solución del polímero viscoso (en dimetilformamida) se esparce dentro de la película delgada, y se sigue por una inmersión en el medio de gelación (agua). Se explora la influencia del aditivo polimérico (poli(etilenglicol) (PEG)) en la formación de los poros durante la fase de separación en el baño de gelación (desde la fase escasa en polímero, la cual aparece en la separación de fases). De los estudios de porometría, se observan los efectos en las diferencias en peso molecular del PEG en el baño de gelación sobre los flujos diferenciales de nitrógeno así como de la concentración. La distribución de poros se desplaza de acuerdo con el peso molecular del PEG empleado en el baño de gelación. El punto de burbujeo y la media en los diámetros de los poros de flujo varían en función de la concentración y del peso molecular del PEG.

Palabras clave: Membrana, poli(etilenglicol), inversión de la fase húmeda, baño de gelación, diámetro de poro.

Introduction

The recent era of separation science and technology is mostly based on membranes, as they are of economic and require low energy. As a result, there are various attempts to develop the membranes. The invention of "asymmetric polymer membrane" by Loeb and Sourirajan is treated one of the best findings in field of membrane science. The asymmetric membranes are of two or more structural planes of non-identical morphologies of polymers. They are achieved through four principal methods: immersion-precipitation (wet phase inversion), vapor-induced phase separation, thermally induced phase separation and dry casting [1]. The structures of these type of membranes are greatly influenced by the changes in membrane preparation conditions whatever slight may be. In the present investigation, wet-phase inversion technique is followed to prepare the asymmetric membranes (Figure 1). In this technique, an initially homogeneous polymer solution becomes thermodynamically unstable and phase separates into "polymer-poor" and "polymer-rich" phases [2-6]. The polymer poor phase forms the membrane pores and polymer rich solid phase forms the membrane homogeneous structure. The diffusion exchange of solvent and non-solvent in the polymeric substrate is the basic mechanism of formation of the membrane. The polymer rich phase (top layer) is first formed at the polymer-nonsolvent interface, and then polymer poor phase (sub layer). Thus, in the present study, it is focused on phase separation pores, i.e. the characteristics of the polymer poor phase.

The preparation of asymmetric membranes by phase inversion is advantageous to generate pore structures of the

membranes. It is done by using additives (organic or inorganic) as well [7-11]. Additives are also helpful in inhibition of macrovoids, to improve the pore connectivity and to increase hydrophilicity [8]. The conventional approach is adding the additives as the third component to the casting solution. But, here, in this study poly(ethylene glycol) is added in water-gelation bath as additive. The polymeric additives of different molecular weight are also varied to investigate whether it can change the pore characteristic or not.

Results and Discussion

In the "phase inversion" step polysulfone turns into solid state from the solution state in proper solvents (viz. DMF). As soon as the polymer in casting form contacts to the non-solvent (water), it forms skin layer. Phase inversion as well as skin layer formation depends upon the surface tension gradients [12]. In other words, surface tension gradients are the driving forces accounting for the pore structure as well as the formation of asymmetric layer in which side. As in this case $\gamma_P < \gamma_S$ (P : Polymer and S : solvent), it tends to form on the gelation bath side [13]. Thus, the presence of water (non-solvent to the polysulfone) in gelation bath results the dense skin on the topmost layer. Dimethyl formamide in the casting solution desolvates rapidly into the water gelation bath as there is strong interaction of dimethyl formamide (solvent) and water (non-solvent). When the casting solution and water come into contact, little water (non-solvent) diffuses into the casting solution since it is a non-solvent for Polysulfone. On the other

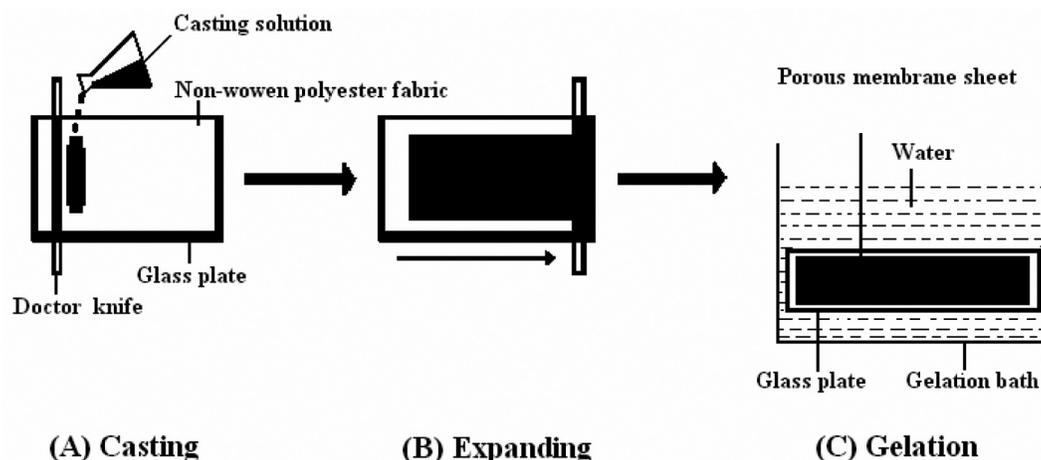


Fig. 1. Schematic diagram of preparation of porous asymmetric membrane.

hand, polysulfone molecules at the interface aggregate rapidly to form a dense skin without pores. Thus, the casting solution enters the solidification region directly. As DMF molecules must diffuse through the dense skin layer, the diffusion of DMF into the water gelation bath from the sub-layer solution is much slower than from the top layer

The poly(ethylene glycol) (additive) in the gelation bath decreases the activities of demixing of both the solvent in the casting solution and the water in the gelation bath, enhancing the conditions for delayed de-mixing, which slows down the gelation process. Thus, there are the possibilities of achieving different pore distribution by adding poly(ethylene glycol) having different molecular weight.

The pore, whose constricted size is the maximum, requires minimum pressure to be emptied and is emptied first. This minimum pressure is known as the bubble point pressure. The related pore diameter is called bubble point pore diameter. Figure 2 shows the trend of bubble point diameters with the concentrations of poly(ethylene glycol) used in the gelation bath. Almost similar trend is observed for all the molecular weights of poly(ethylene glycol) used in the gelation bath. The bubble point pore diameters for all the molecular weights of poly(ethylene glycol) are showing its maximum for 1%. Probably, comparatively higher concentration (2%) poly(ethylene glycol) hinders the solvent and non-solvent exchange process and lower bubble point pore diameter is reflected (compared to 1% poly(ethylene glycol)) except the membranes prepared in gelation bath comprised of molecular weight 6000. The bubble point pressure data are in ensemble (Table 1). The corresponding bubble pressures trend is reverse of bubble point pore diameters, as expected.

Figure 3 shows the variation of mean flow pore diameters with the molecular weight of poly(ethylene glycol) used in gelation bath. The mean flow pore diameters trend is more or less similar for all the concentrations of poly(ethylene glycol) studied. The mean flow pore diameter increases as the concentrations for the membranes prepared in PEG 3000. The membranes prepared in gelation bath containing PEG

3000 shows maximum mean flow pore diameter. The figure shows there is a decreasing trend of pore diameter for the membranes prepared in PEG 6000. This is possibly due to relatively higher molecular weight factor, which slows down the diffusional solvent-non-solvent exchange during membrane formation.

In figure 4, the histograms of the differential flow parameter (%) for the membranes prepared in PEG (1%) of different molecular weight 400 to 6000 are displayed. It shows that, the porosities or pore diameters are shifted to higher side with the increase of molecular weight of PEG additives. The differential filter flow of nitrogen for the Polysulfone membranes prepared in absence of PEG is only in water is ~55% at 0.4 μm pore diameter. The differential filter flow is ~32.5% at 0.4 μm and >0.1 μm it is 34% for the membranes prepared in PEG 400. The differential filter flow for PEG 1500 is shifted more (to 55% at 0.5 μm). For PEG 3000, the maximum differential

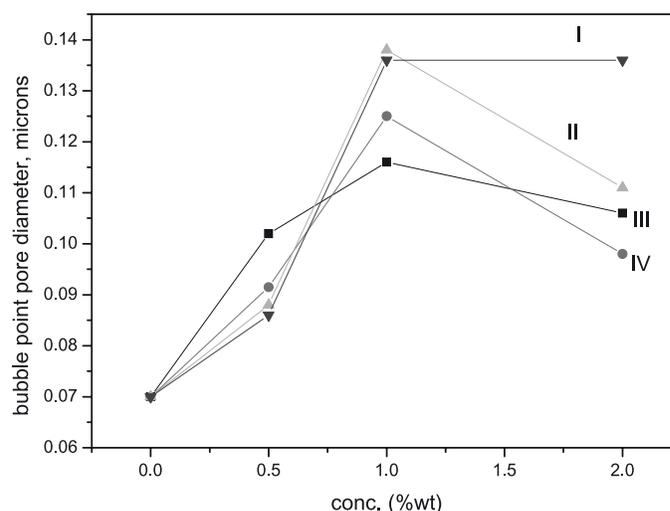


Fig. 2. Variation of Bubble point pore diameter with the concentration of PEG in gelation bath (I. PEG 6000, II PEG 3000, III PEG 400 and IV PEG 1500).

Table 1. Bubble point and mean flow pore pressure for the corresponding molecular weight of PEG in gelation bath.

Molecular weight and concentration of PEG in gelation bath	Bubble point pore pressure (MPa)	Mean flow pore pressure (MPa)
Polysulfone (without additive in gelation bath)	0.652	1.28
PEG (400)		
0.5 %	0.447	0.91
1 %	0.394	0.904
2 %	0.432	1.068
PEG (1500)		
0.5 %	0.5	1.195
1 %	0.367	0.919
2 %	0.450	1.005
PEG (3000)		
0.5 %	0.524	0.917
1 %	0.467	0.877
2 %	0.413	0.422
PEG (6000)		
0.5 %	0.534	1.267
1 %	0.337	0.743
2 %	0.337	0.766

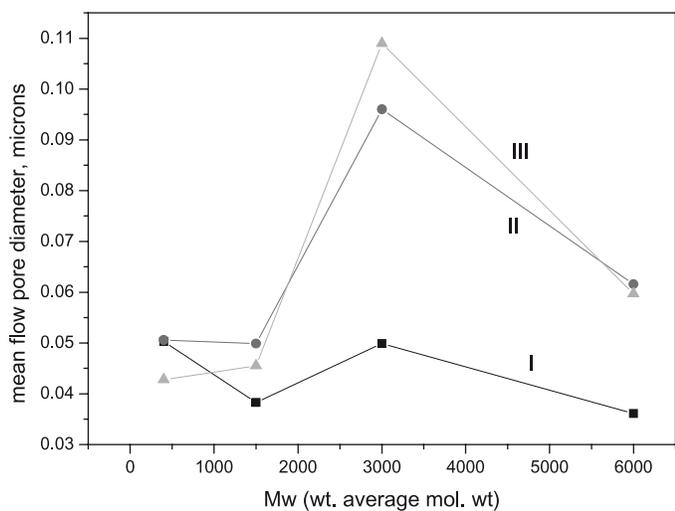


Fig. 3. Variation of mean flow pore diameter with the molecular weight of PEG in gelation bath (I. 0.5%, II. 1% and III. 2%).

filter flow is 65% at 0.1 μm where as the maximum differential filter flow is 90% at 0.13 μm pore diameter for membranes prepared in PEG 6000. This signifies that with the increase of molecular size of poly(ethylene glycol) additives (as the molecular weight), the pore diameters increase. The pure water fluxes of the membranes are also supports the observation. The pure water flux of polysulfone membranes increases with

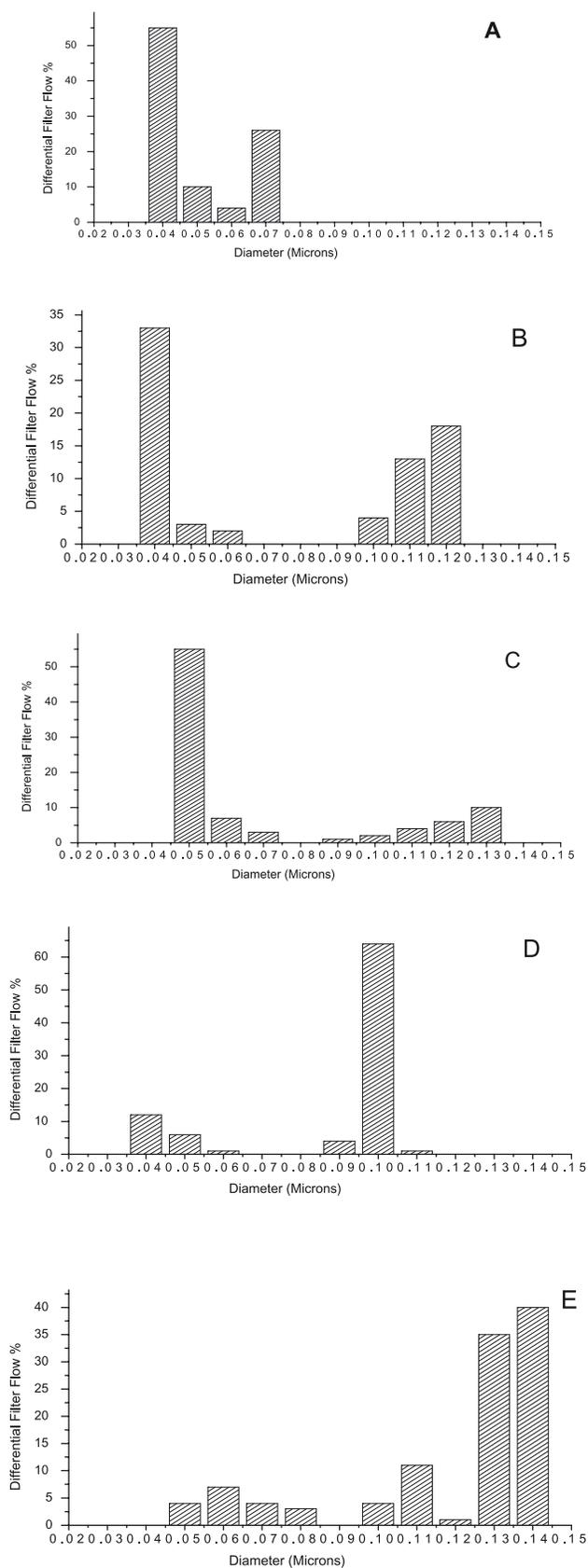


Fig. 4. Histogram of differential filter flow (%) with the pore diameter of the membranes (A: in water, B: in PEG 400, C: in PEG1500, D: in PEG 3000, E: in PEG 6000).

the molecular weight of PEG used as well as their concentrations (Table 2).

Experimental

Materials

Polysulfone (Udel, P-3500; Solvay Advanced Polymers, USA), Dimethylformamide (Qualigen, India), were used to prepare the asymmetric membranes. Polyethylene glycol (Loba, India) of different molecular weight 400, 1500, 3000, 6000 were used as additives in the gelation bath. In all the experiments reverse osmosis treated water was used.

Methods

Polysulfone solutions in dimethyl formamide (15% w/w) were prepared through slow dissolution in heating condition over a long time. The solutions were cast on non-woven polyester fabric fitted on glass plate and then immediately immersed in a gelation bath comprised of water (non-solvent)/mixed with poly(ethylene glycol) bath at laboratory temperature (30 °C). All the membranes are kept in gelation bath for 1 h. The solidified membranes were rinsed with reverse osmosis treated water for 18 h to remove solvents and then dried for 48 h at the room temperature before their characterization and performance study.

Techniques used

Capillary flow porometer (Porous Materials Inc, USA, Model 1500 AEX) was used to determine the distribution of pores. The nitrogen gas permeation was measured up to 1.29 MPa. The water flux experiments were performed in a dead end filtration unit. The surface tension of the gelation bath was measured by Tensiometer (DCAT 21 from Dataphysics, Germany).

Theory

The porometric data was measured by Capillary Flow Porometer, considering the pores as capillaries. In this tech-

Table 2. Pure water flux of the membranes (at 0.069MPa) prepared using PEG, having different molecular weight in different concentrations used in gelation bath.

Membrane Conc. of PEG	(l/m ² /h)	0.5% (l/m ² /h)	1% (l/m ² /h)	2% (l/m ² /h)
PS	32.6			
PS-400		38	48.9	54.3
PS-1500		50.2	74.7	80.1
PS-3000		66.5	95	115.4
PS-6000		95	111.3	135.7

nique, the membrane samples are soaked overnight in a liquid, Porewick having $\gamma \Rightarrow 16$ dynes/cm² and contact angle is zero i.e. it wets the membrane samples fully and spontaneously fills all the pores in the sample. Such a liquid is known as the wetting liquid. Pressure of the gas on one side of the wet sample is then gradually increased. When the pressure is sufficient to empty the largest pore in the sample, the gas begins to flow through the membrane. With increasing pressure, the gas removes liquid from smaller pores and the gas flow rate increases. The pressure required emptying the pores [14-16] was as follows

$$P = \gamma_{lg} \cos\theta (dS_{sg} / dV) \tag{1}$$

Where dV is increase in volume of gas in pore and ds_{sg} is increase in solid/gas surface area, γ_{lg} is the surface tension of the liquid, θ is the contact angle

The measurement of the porosity and pore properties of the membrane on the capillary flow porometer was based on the physical phenomenon of surface tension of the liquids.

For a pore of circular cross-section of diameter D

$$(dS/dV) = (4/D)$$

Hence, with decrease in pore size (dS/dV) increase and the pressure required displacing the liquid inside the pore also increased.

The minimum force required to empty the fluid from the pore of the membrane was calculated using the fundamental equation of porometry.

$$D = \frac{4 \gamma \cos \theta}{p} \tag{2}$$

D is the diameter of a pore of circular cross-section having the same value of (dS/dV) as that of the pore at its most constricted part

When $\theta = 0^\circ$, the equation becomes

$$D = 4\gamma/p \tag{3}$$

Here θ is the contact angle, γ surface tension, p is the differential pressure.

Conclusions

The study regarding the influence of PEG additive in gelation bath leads to the following conclusions:

1. The influence of PEG in the gelation of the Polysulfone membrane shows different porosities, as the differential filter flow of nitrogen suggests. The differential flow through the membranes shows that there is a maximum (at M_w 3000) in the pore diameter (i.e. mean flow) with

the increase in molecular weight.

2. The bubble point diameters are maximizing in 1% for all the molecular weight of PEG studied. Beyond 1%, the higher viscosity of the gelation bath hinders the solvent- non-solvent exchange. The mean flow pore diameter shows its maximum for PEG, M_w 3000.
3. The increase in molecular weight (apparently molecular size) of poly(ethylene glycol), added to gelation bath results the pore distribution to the higher side.
4. The water flux of the membranes also increases with the molecular weight as well as their concentration of poly(ethylene glycol), used in gelation bath.

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