

Araştırma Makalesi / Research Article

Polisülfon Membranlarının Mikroyapı ve Performansı Üzerine Bir Gözenek Oluşturucu Olarak Polivinilpirolidonun Rolü

The Role of Polyvinylpyrrolidone as a Pore Former on Microstructure and Performance of Polysulfone Membranes

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Öz- Bu çalışmada, gözenek oluşturucu olarak polivinilpirrolidonun (PVP), polisülfon (PSF) membran performansı üzerindeki etkisi incelenmiştir. XRD spektrumları, artan PVP miktarı ile kristalin fazdan amorf faza geçişinin gerçekleştiğini ortaya koydu. SEM sonuçları, membranlardaki makro boşlukların şekli ve boyutunun, polimer çözeltisindeki artan PVP miktarı ile değiştiğini gösterdi. Saf PSF ve ağırlıkça % 5 PVP ilave edilmiş PSF membranı için Tg değerleri sırasıyla 189 °C ve 182 °C olarak ölçülmüştür. Membranların performansı, Saf Su Akışı (SSA) ölçümleri kullanılarak belirlendi. Membranların SSA'sı PSF polimer çözeltisinde PVP miktarının (ağırlıkça %0'dan %10'a) artmasıyla 36.76 L m⁻² s⁻¹'den 86.80 L m⁻² s⁻¹'e yükselmiştir. SSA ve PVP içeriği arasındaki ilişki artan termodinamik kararsızlık ve kinetik engel ile açıklanmıştır.

Anahtar Kelimeler: Membran, Gözenek Oluşturucu, Polisülfon, Polivinilpirolidon, SEM.

Abstract- In this study, the effect of polyvinylpyrrolidone (PVP) as a pore former on the performance of polysulfone (PSF) membrane was studied. XRD spectra revealed that a crystalline-to-amorphous phase transition occurred with the increasing PVP amount. SEM results indicated the shape and size of macrovoids in the membranes were altered with the increasing PVP amount in the polymer solution. The Tg values for the pure PSF and of 5 wt% PVP added PSF membrane were measured as 189 and 182 °C, respectively. The performances of the membranes were determined by using the pure water flux (PWF) measurements. The PWF of the membranes increased from 36.76 to 86.80 L m⁻² h⁻¹ with the increase of PVP amount (0 to 10 wt %) in PSF polymer solution. The relationship between PWF and PVP content was explained with the increased thermodynamic instability and kinetic hindrance.

Keywords: Membrane, Pore Former, Polysulfone, Polyvinylpyrrolidone, SEM.

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I. INTRODUCTION

Polysulfone (PSF) is a versatile membrane material in water treatment applications owing to its excellent mechanical, compaction-resistance, chemical and thermal properties [1]. The main problem in PSF membrane applications is the rapid decline of performance in water treatment applications due to its hydrophobic nature [2]. In literature, there are different methods to improve membrane performance such as surface coating, surface grafting, and blending with water-soluble polymers [3,4]. Among these methods, blending with water-soluble polymers is accepted simple and effective method to improve membrane permeability and antifouling property [4-8].

Polyvinylpyrrolidone (PVP) is used as water-soluble polymer in the preparation of filtration membranes using phase inversion method due to its good miscibility with polymers and high solubility in water [5-14]. PVP as a casting solution additive increases thermodynamic instability and kinetic hindrance of the casting solution during phase inversion process [5,6]. Due to these properties, PVP is an excellent pore former agent to increase the membrane performance [7-10]. Han and Nam [7] found that the pure water flux (PWF) enhanced about nine times in the presence of 5 wt % PVP comparing to that of 0 wt % PVP in the polymer solution. However, the lower PWF was obtained in the presence of PVP above 5 wt % in the polymer solution. Matsuyama et al [8] reported that the addition of PVP caused the low membrane formation rate. Also, they found that the membrane morphology changes macrovoid-to-sponge structure in the presence of high molecular weight PVP. Ding et al [9] found that the addition of PVP into polymer solution increased the porosity and hydrophilicity of the membrane. Also, the PWF increased initially with increasing PVP content, then it started to decrease when the PVP content reached to 4 %. The PWFs of PSF membranes including 5 and 10 wt % PVP were lower than that of pure PSF. The initial increase of PWF is due to the enhanced phase inversion induced by the thermodynamic instability of polymer solution. The low PWF in membranes having PVP amount above 4 % is attributed to the increased viscosity after introducing PVP. Lee et al. [10] investigated the effect of PVP addition on membrane performance. They reported a sharp increase in the PWF upto 7.5 wt % PVP due to its nonsolvent effect. However, the PWF decreased with the increasing PVP amount. Other researchers studied the performance of PSF/PVP membranes prepared at different experimental conditions [11-14].

PSF membranes used in this study were prepared by the means of phase inversion method from the solution consist of PSF, N-Methyl-2-pyrrolidone (NMP), and PVP. The effect of PVP was studied on PSF membrane performance by changing the amount of PVP from 0 to 10 wt % in the solution. The obtained PSF membranes were characterized by using SEM, DSC, and PWF techniques.

II. EXPERIMENTAL

Polysulfone (PSF), N-Methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP) (MW 360.000) were used to the preparation of membranes. The phase inversion method was used to prepare the PSF membranes. The polymer solution was prepared with 17 wt % PSF, 0 – 10 wt % PVP, and 86-80 wt% of NMP (m/m) and stirred with heating at 60 °C for 10 h. The polymer solution was degassed in an ultrasonic water bath for 2 h. The solution was then cast on glass plate using a doctor blade for a fixed thickness of 200 µm, and the plate immediately immersed into a coagulation bath at ambient temperature. Then, the membrane was washed using water and dried at room temperature to remove residual NMP. Finally, the membrane was dried at ambient temperature before testing. The membrane sample designations and compositions are given in Table 1.

Table 1. Preparation conditions for PSF membranes.

Membrane	Casting Solution (wt.%)		
	PSf	NMP	PVP
PSF	17	83.00	0.0
PSF-0.5	17	82.50	0.5
PSF-1	17	82.00	1.0
PSF-2	17	81.00	2.0
PSF-5	17	78.00	5.0
PSF-10	17	73.00	10.0

Morphologies of the membranes were determined by SEM (Carl Zeiss Sigma VP). All images were taken at an accelerating voltage of 15 kV and magnification of 5.0 kx. The thermal behaviors of membranes were investigated by DSC (Shimadzu DSC-60). The XRD measurements were done with PAN Analytical X-ray systems

(XRD Rigaku Miniflex) (Cu K α radiation, $\lambda = 1.54 \text{ \AA}$). The crystalline size is calculated using the Debye–Scherer equation [15]:

$$L = \frac{K\lambda}{\beta(2\theta)\cos(\theta)} \quad (1)$$

where $\lambda = 1.5418 \text{ \AA}$ (Cu K α), β is full width at half maximum, $K = 0.89$, and θ is the Bragg diffraction angle. All the PWF experiments were carried out in a cross-flow ultrafiltration cell with a membrane diameter of 47 mm. The PWF, porosity, compaction properties of membrane were determined as previously described [16].

III. RESULTS AND DISCUSSION

The glass transition temperature (T_g) values from the DSC curves for the control and PVP added PSF membranes have been given in Table 2. According to Table 2, the T_g value for pure PSF decreased from 187 °C to 182 °C when the addition of 10 wt % PVP into casting solution. The decreasing glass transition temperature means the loosened packing density in solid polymer structures since PVP molecules intercalate between PSF chains reducing the intermolecular forces, which results in an increase of mobility [17-19].

Table 2. DSC and XRD characteristics of PSF membranes.

Sample	T_g (°C)	Intensity	Crystalline
PSF	187	1.699	4.54
PSF-0.5	188	1.732	4.54
PSF-1	189	1.749	4.63
PSF-2	187	1.464	2.75
PSF-5	187	1.881	5.65
PSF-10	182	1.63	4.07

^a Obtained from DSC. ^{b,c} the main X-ray diffraction peak at $2\theta = 16.55^\circ$.

The XRD analysis was studied to obtain further information about the effect of pore former on the physicochemical properties of studied membranes (Fig. 1). PSF control membrane showed a broad band at $2\theta = 16.55^\circ$ and a shoulder at $2\theta = 24^\circ$ indicating the amorphous nature of the polymer. After the addition of PVP into the PSF polymer solution, the shift in the main XRD peak from $2\theta = 16.55^\circ$ to $2\theta = 17.85^\circ$ indicated a distorted crystal structure. In addition, the observed decrease in the intensity of main diffraction peak suggest the increased amorphous phase in the PVP added PSF membrane samples. As given in Table 2, the intensity of the broad peak fluctuates with the variation of the PVP amount.

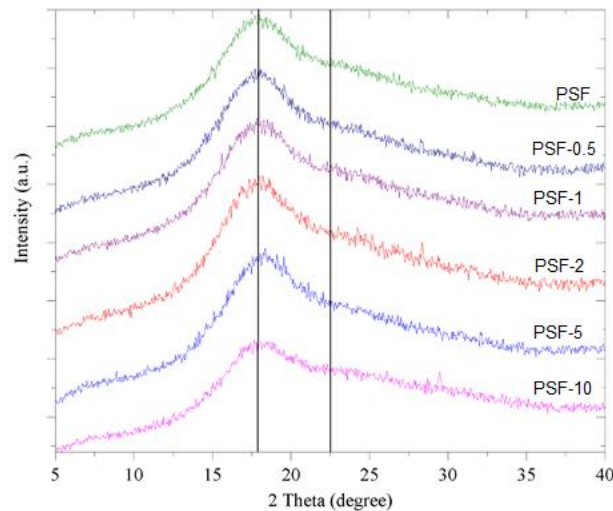


Fig. 1. XRD patterns of PSF membranes

Fig. 2 shows SEM micrographs of the cross-section of control PSF membrane and PVP added PSF membranes. As shown in Fig. 2, the size, number, and shape of macrovoids changed after the addition of PVP into the polymer solution. It is known that PVP is compatible with PSF and increases the polymer solution viscosity. Therefore, the addition of PVP leads to decrease in the thermodynamic stability of the casting solution and thus the kinetics of the phase separation increases and resulting in big cavities and macropores. Also, the hydrophilicity of PVP in the membrane solution reduce the exchange rate of NMP and water and affects the precipitation kinetics and membrane morphology [20-23]. In the pure PSF membrane sample, the finger-like voids in the asymmetric membrane structure point out the formation of a skin layer at an early stage of the phase inversion process due to a slow exchange rate between NMP and water. With a further increase of PVP concentration, the increased viscosity can delay the diffusion and the enhancement of phase separation. Therefore, the change on membrane morphology with increasing PVP concentration can be explained by the relationship between the thermodynamic instability and kinetic hindrance.

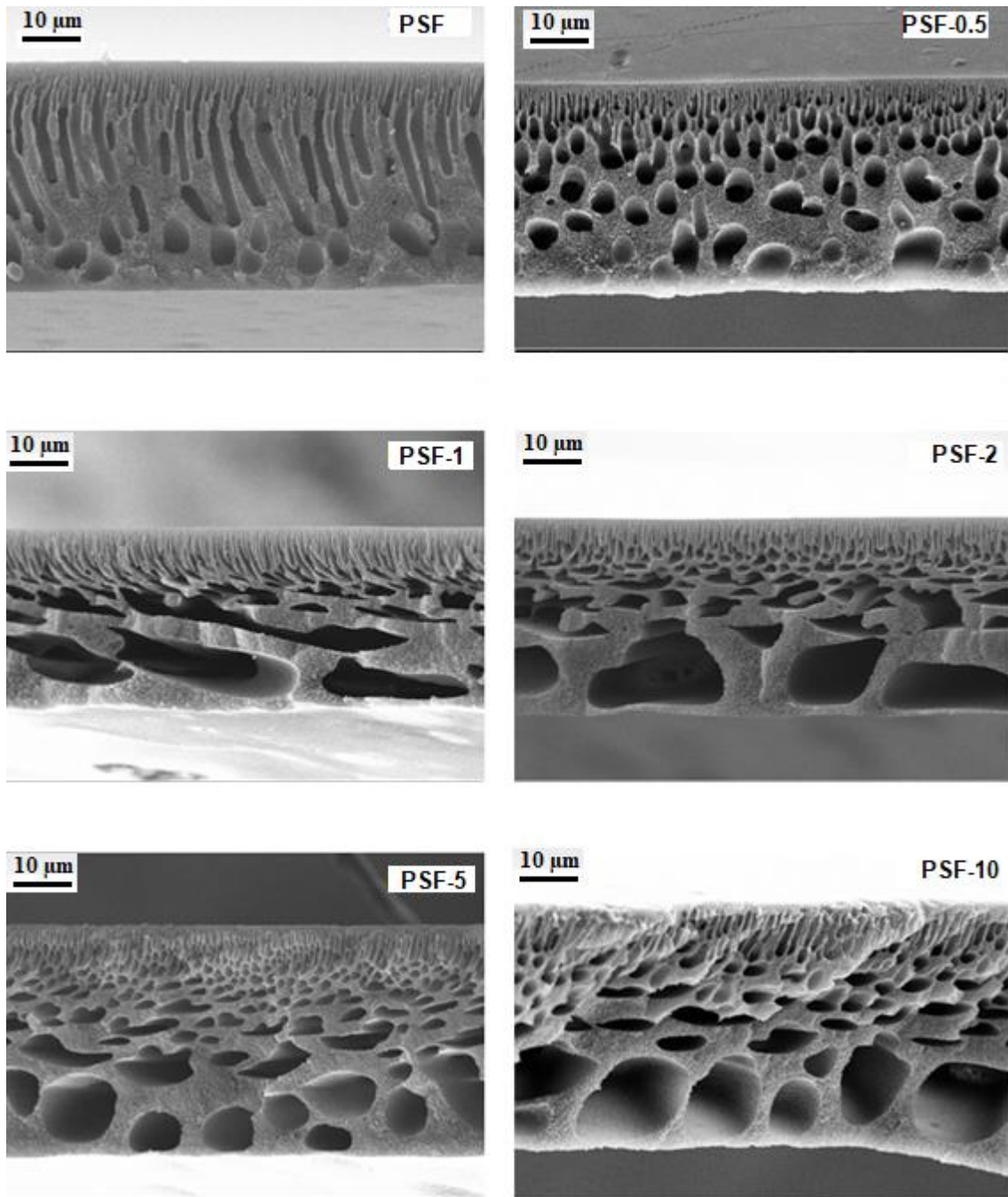


Fig. 2. Cross-sectional SEM images of the PSF membranes

The measurement results of porosity and PWF of PSF membranes were given in Table 3. This result confirmed the increase in porosity and macrovoid size after the addition of PVP into the polymer solution. The PWF decreased initially with up to the PVP amount of 5% and then started to increase. It was found that the PWF values of PSF membranes including 5, 7 and 10 % of PVP were high than that of the PSF control membrane. It was concluded that the initial increase of PWF was attributed to the increased phase separation induced by the thermodynamic instability of the polymer solution as mentioned above. At constant operating pressure (1 bar), the compaction properties of studied PSF membranes upon compaction were given in Fig. 3.

Table 3. Some characterization parameter values of PSF and PSF/PVP membranes.

Membrane	% Water content	% Porosity	PWF at 1 bar (L/m ² h)	Hydraulic resistance (R _m) (m ² hkPa/L)
PSF	77.48±1.22	91.96±5.17	36.76	5.44
PSF-0.5	76.73±1.27	86.00±2.59	24.14	8.29
PSF-1	77.71±0.89	89.12±5.32	24.69	8.10
PSF-2	80.26±0.79	98.67±3.58	28.12	7.11
PSF-5	79.93±0.73	89.25±3.72	46.61	4.29
PSF-10	81.83±0.98	89.09±3.44	86.80	2.30

According to Fig. 3, the PWF was high initially and then reduced gradually and reached stability after 4 h of compaction. This initial decrease in PWF points out the compacted membrane macropores.

PWF of PSF control membrane at 1 bar is 36.76 Lm⁻²h⁻¹. After the addition of 5 wt% PVP into PSF casting solution, the PWF increased from 36.76 to 46.6 l Lm⁻²h⁻¹. The increase in PWF is not only due to the hydrophilicity of PVP but is also due to the change in the structure of membrane crystalline-to-amorphous resulting to the formation of pores. As given in Table 3, the highest water content determined was 81.83% and the minimum of 77.48%. This result showed that the increase of PVP content in the membrane increased the hydrophilic character of the membrane. The thermodynamic instability controls the enhanced phase inversion in the presence of PVP below 5 wt.%. However, at higher PVP amounts, the solution demixing delays and the increased viscosity suppress the thermodynamic instability.

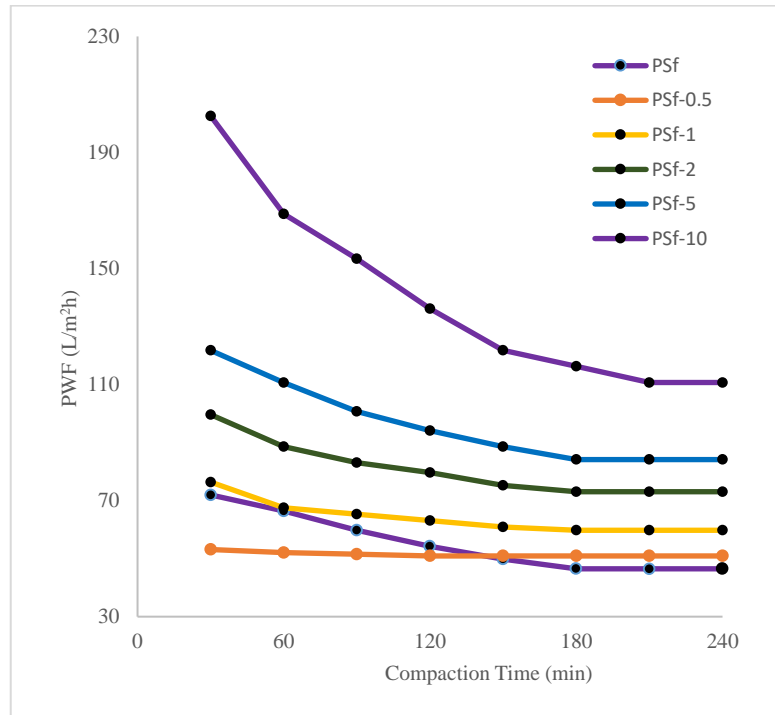


Fig. 3. The effect of compaction time on PWF values for PSF and PSF/PVP blend membranes

It is known that PWF is mainly influenced by the morphology of the membrane [24-27]. At a high pore former amount, the rate of phase separation is reduced by the increased viscosity, thus a dense and thick top layer with low porosity is occurred [25]. This kind of membrane structure restricts water diffusion into the membrane structure [26]. Also, the presence of large macrovoids in the membrane causes in substantial compaction and high flux resistance [27].

As shown in Fig. 2, SEM results revealed that the size of macrovoids in the membranes increased with the addition of PVP to PSF solution. The values of PWF for all the PVP added PSF membranes are higher than that of PSF membrane and fluctuate in linearity (Table 3). For the membranes with PVP content below 5 wt%, the increased PWF may arise from the enhanced phase inversion induced by the thermodynamic instability of the polymer solution. However, the PWF decreased from 36.76 to 28.12 $\text{Lm}^{-2}\text{h}^{-1}$ with the increasing amount of PVP from 0.5 to 2 wt% in the polymer solution rather than improved. The observed low PWF for PSF membranes including below 2.5 wt % PVP showed the reduced the pore size due to closer segmental arrangements of the PSF and PVP polymer. This is also supported by SEMs of prepared membranes (Fig. 2).

The PWF of PSF membranes was compared with the reported in literature (Table 4). On comparison, we find that the PWF of the PSF membranes is comparable with the reported values.

Table 4. Comparison of PSF membranes with literature.

PSf Membrane	PWF ($\text{L}/\text{m}^2\text{hbar}$)	Ref.
PSf/PEG	72.22-114.97	[28]
PSf	0.25	[29]
PSf/PVP	33.6	[29]
PSf/PEG	2.80	[29]
PSf/NMP/PVP (24-360K)	355.4-118.5	[30]
PSf/DMAC/PVP (24-360K)	149-68.8	[30]
PSf/PEG	4	[31]
PSf	63.7	[32]
PSf/PEG	34.6-45.7	[32]
PSf/PVP	29.1-4.1	[32]
PSf/DMAC/PVP	6.56	[33]
PSf/DMAC/PVP/Ascorbic acid	12.72-13.12	[33]
PSf/DMAC/PVP/Citric acid	11.24-12.03	[33]
PSf/DMAC/PVP/Malic acid	12.31-15.83	[33]
PSf	38.5	[34]
PSf (15 wt%)/Tetronic-1107 (4 wt%)	65.7	[34]
PSf/TiO ₂ (2 wt%)	488	[35]
PSf/DMAC/PVP	27.5 (1 bar)	[36]
PSf/PVP	36.76-86.80	In this study

IV. CONCLUSION

The XRD patterns indicated that PVP influenced the recrystallization kinetics of PSF chain. SEM images showed that the addition of PVP into PSF solution increased the number and size of macrovoids in the membrane. The increase in PWF is not only due to the hydrophilicity of PVP but is also due to the change in the crystalline structure of PSF. The convex relationship between T_g , XRD intensity and PWF with the variation of PVP amount are explained with the increased thermodynamic instability and kinetic hindrance.

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