

Preparation and Characterization of the Asymmetric Microporous Poly(vinylidene fluoride) (PVDF) Blend Membranes with Hydrophilic Surfaces

Jeong-Eun Hwang and Jonggeon Jegal[†]

Chemical Biotechnology Research Center, Korea Research Institute of Chemical Technology,
P. O. Box 100, Yusung, Daejeon 305-606, Korea
(Received October 8, 2007, Accepted November 14, 2007)

Abstract: To prepare chemically stable asymmetric microporous membranes with a hydrophilic surface, which would be expected to have better antifouling properties, poly(vinylidene fluoride) (PVDF) blend membranes were prepared by the phase inversion process. PVDF mixture solutions in N-methylpyrrolidone (NMP) blended with several polar potential ionic polymers such as polyacrylonitrile (PAN), poly(methylmethacrylate) (PMMA) and poly(N-isopropylacrylamide) (NIPAM) were used for the formation of the PVDF blend membranes. They were then characterized with several analytical methods such as FESEM, FTIR, contact angle measurement, pore size distribution and permeability measurement. Regardless of different polar polymers blended, they all showed a finger-like structure with more hydrophilic surface than the pristine PVDF membrane. For all the PVDF blend membrane, due to the polar potential ionic polymers used, the flux of those was improved. Especially the PVDF blend membrane with NIPAM showed the highest flux among the membranes prepared. Also antifouling property of the PVDF membrane was improved by the use of the polar polymers.

Keywords: hydrophilicity, membrane, contact angle, PVDF, polymer blend

1. Introduction

With increasing applications of membranes, chemically stable membranes are needed in many different fields. For a long period of time, engineering plastics with high mechanical strength and good chemical stability such as polysulfone and polyetherimide have been used for the preparation of microfiltration (MF) and ultrafiltration (UF) membranes. However, with the need for more chemically stable membranes for water treatment, recently, PVDF has started to be used as a membrane material, and some of the MF and UF membranes have been prepared, using PVDF. PVDF is a commercially available fluoropolymer with low surface energy and good physical, chemical and mechan-

ical properties. Because of its exceptional chemical stability and excellent resistance to aging, PVDF has been widely used in industry. However, as one knows, the PVDF is very hydrophobic material, and its strong hydrophobicity sometimes causes some problems such as membrane fouling by the organic component in the feed solutions. So, one of the best ways to avoid such negative property of the PVDF membrane is to make the surface of the membrane hydrophilic.

Generally speaking, the hydrophilic surface is much better than the hydrophobic surface especially for the antifouling property of the membrane. In other words, when the membrane surface is hydrophobic, hydrophobic-hydrophobic interaction between the membrane surface and the materials in the feed solution is high enough for the membrane fouling, but when the membrane surface is hydrophilic, such fouling problem can

[†] Author for all correspondences
(e-mail : jggegal@pado.kRICT.re.kr)

be reduced. One of the methods to make the surface of the PVDF membrane hydrophilic is to blend with hydrophilic polymers. Because it was reported that when a hydrophilic polymer is blend with a hydrophobic polymer, during the phase inversion process using water as a coagulant, the hydrophilic polymer tends to move to the outer-surface of the membrane, the blending with a hydrophilic polymer is a good way to make hydrophilic surface of the PVDF membrane. In recent years, the blend polymer membranes have been an attractive field and several blend membranes have been studied, manufactured and used [1].

Based on this, in this study, four polar potential hydrophilic polymers that can be converted into ionic polymers easily by the simple treatment with a basic solution were blended with PVDF to prepare PVDF asymmetric membranes by the phase inversion process. The prepared membranes were then treated with basic solution to make their surfaces hydrophilic, and then characterized with several analytical methods.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) bought from AKENA Co. and lithium chloride (LiCl) purchased from Junsei Chemical Co. were used as a membrane material and an additive, respectively. Polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and poly(N-isopropylacrylamide) (NIPAM) were purchased from Sigma-Aldrich Co. and used as potential ionic polymers for the modification of PVDF membrane surfaces. N-methyl-2-pyrrolidone (NMP) bought from Junsei Chemical Co. was used as a solvent. Polyethylene oxide (PEO) with a molecular weight of 100,000 g/mol and 300,000 g/mol and poly(ethylene glycol) (PEG) with a molecular weight of 35,000 g/mol obtained from Sigma-Aldrich Co. were used as solutes of feed solutions. Other chemicals were also used as purchased without further purification.

2.2. Preparation of PVDF Blend Membranes

PVDF blend asymmetric microporous membranes were prepared by the phase inversion process, using nonwoven polyester fabric as a support. First of all, a certain amount of PVDF was dissolved into NMP with small amount of LiCl to make a PVDF solution in NMP with composition of PVDF/LiCl/NMP of 13/7/80 (in wt%). Also 20 wt% solutions of potential ionic polymers were prepared by dissolving each of them into NMP. Then, a certain amount of each potential ionic polymer solution was blended with the PVDF solution to make PVDF/ionic polymer blend solutions with composition ratios of 90/10 and 80/20 in wt%. The prepared solutions were filtered and degassed before casting onto the nonwoven polyester fabric. After casting, it was immersed into the distilled water for the phase inversion, and then kept again in warm water for over 24 h to remove the solvent from the membranes completely. After the formation of the PVDF blend membranes, their surface was modified by reacting it with 0.01 M NaOH solution at 40°C for 1 h.

2.3. Characterization

The compatibility between PVDF and each ionic polymer was evaluated by the degree of polarization of the longitudinal Brillouin peaks, which can be measured by Fourier transform infrared (FTIR) spectroscopy (Bio-Rad, Digilab Division, FTS-80) [3]. The morphology and thickness of the membrane were observed with field emission scanning electron microscopy (FESEM) photographs (XL 30, Philips). The hydrophilicity of the membrane surface was evaluated based on the dynamic water contact angle (θ) measured using contact angle goniometer (SEO 300A) [4]. Calculation of average values was made with five measured values in different locations of the membrane surface. Each value was averaged from five measurements. The pore size and pore size distribution of the PVDF blend membranes were measured by a capillary flow porometry (CFP-1500-AEL, Porous Material Inc.).

2.4. Permeation Test

To test the performance of the membranes, an ultra-filtration test set-up was used. The used feed solutions were 1,000 ppm aqueous solutions of PEG 35,000, PEO 100,000 and PEO 300,000, and upstream pressure was controlled from 1 bar to 4 with back-pressure regulators. The flux was determined from the weight of permeates gathered for some time, and the rejection was calculated from the following equation:

$$\text{Rejection}(\%) = 100 \times \frac{C_f - C_p}{C_f}$$

Where C_f and C_p were the concentrations of the feed solution and permeate, respectively. The C_f and C_p were determined by the high-performance liquid chromatography (HPLC) equipment (Waters 501) with an R401 differential refractometer as a detector.

3. Results and Discussion

3.1. Membrane Preparation

Generally speaking, the membranes made from hydrophobic polymers such as PVDF show low water flux and are very easy to be contaminated by the organic materials in feed solutions as well. The low water flux is due to the resistance against water developed by the hydrophobic nature of the membrane surface, and the fouling is easy because of the hydrophobic-hydrophobic interaction between the membrane surface and the organic materials. To be used as a membrane for the water treatment, hydrophobic membranes such as PVDF membranes should be treated to have better hydrophilic surfaces. Even though the PVDF membrane has many good characteristics as a water treatment membrane such as good chemical stability, especially good ozone resistance, and good mechanical strength, its hydrophobic nature limits its application. To have better performance, the surface of the PVDF membrane has to be modified to have hydrophilic surface.

To figure out the effect of the ionic polymers on the performance of the PVDF membrane, PVDF blend microporous membranes were prepared by the conventional phase inversion process, using several potential ionic polymers such as PAN, PMMA, NIPAM and PDSA. To have homogeneous blend solutions, it is important to have right solvent that can dissolve both polymers together. In this case, it was NMP. In it, all the polymers used in this study were dissolved very well. As mentioned in the Experimental part, a certain amount of each 20 wt% of ionic polymer solution prepared was blended with PVDF solution at room temperature to have 90/10 and 80/20 ratios of PVDF/ionic polymer. Each blend solution was then cast with 150 μm thicknesses on the surface of the nonwoven polyester fabric. After which, they were solidified in the water via the phase inversion process to become microporous asymmetric PVDF blend membranes.

The speed of the phase inversion process of the PVDF membranes was much slower as compared with the case of polysulfone. Usually, the relatively hydrophilic polymers such as polysulfone and polyetherimide are fast for their phase inversion in water, but PVDF was very slow and took a relatively long time, because of its high hydrophobic nature. Also, the exchange between the solvent and nonsolvent in the phase inversion process is slow for the PVDF solution, thus the pore formation is not easy enough to form large number of small size pores. To overcome such difficulties, LiCl was used together with PVDF solution and its concentration was varied from 1.0 wt% to 10.0 wt%. As the concentration of LiCl was below 1.0 wt%, the phase inversion speed was too slow and as it was over 10 wt%, it was possible to cause recrystallization of LiCl in the PVDF solution, so that the concentration of the LiCl was fixed at 7.0 wt% for the formation of all the PVDF solutions. Therefore, the composition of the PVDF solution was fixed at 13/7/80 (wt%) of PVDF/LiCl/NMP.

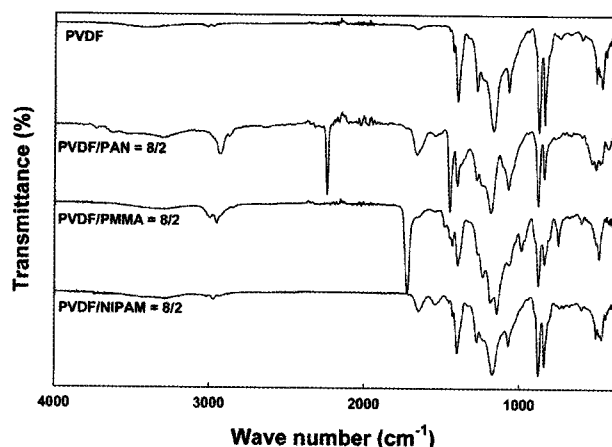


Fig. 1. FTIR spectra of the PVDF blend membranes: PVDF/potential ionic polymers = 8/2 (in wt%).

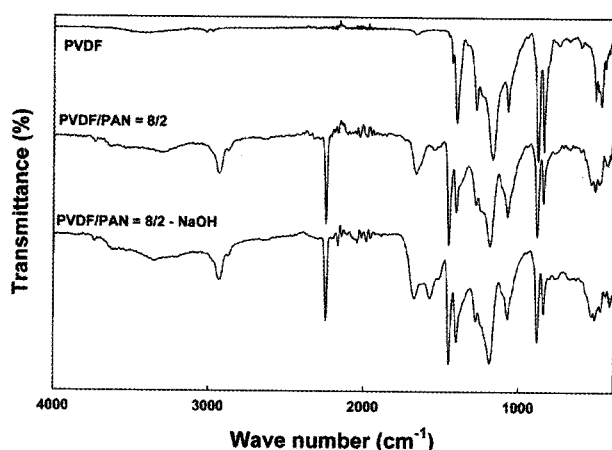


Fig. 2. FTIR spectra of the PVDF and PAN blend membranes with or without surface modification.

3.2. Characterization of the Membrane

3.2.1. FTIR Spectra

To observe the differences in the surface chemistry of the PVDF membranes caused by the blending with ionic polymers, FTIR spectra of PVDF membrane and PVDF-hydrophilic polymer blend membranes were taken and compared in Fig. 1. By the blending with hydrophilic polymers, the surface chemistry of the PVDF membranes changed. The absorption bands in the region of $840\sim 880\text{ cm}^{-1}$ and $1,070\sim 1,280\text{ cm}^{-1}$ of the FTIR spectrum of the PVDF membrane corresponded to $-\text{CF}_2$ and $-\text{CH}_2$ functional groups of the PVDF polymer chains, respectively [5-7]. The FTIR spectrum of PVDF-PAN blend membrane showed $-\text{CH}$ bond at

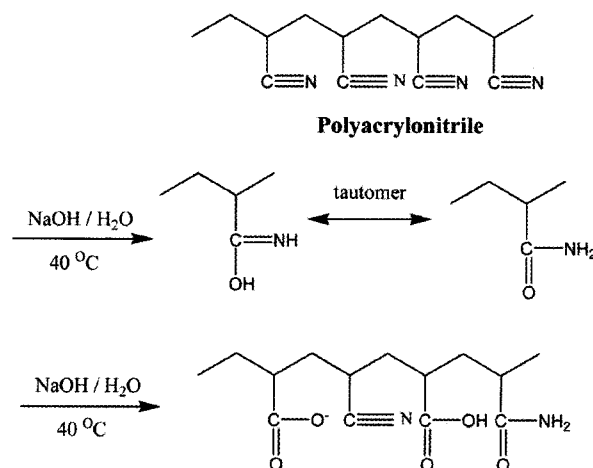


Fig. 3. A schematic reaction mechanism of PAN with NaOH at 40°C for 1 h.

$2,934\text{ cm}^{-1}$ and $-\text{C}\equiv\text{N}$ bond at $2,243\text{ cm}^{-1}$ derived from PAN polymer, indicating that the PAN appeared on the surface of the membrane. FTIR spectra of other PVDF-hydrophilic polymer blend membranes showed $-\text{CH}$ bond at $2,953\text{ cm}^{-1}$ and $-\text{C}=\text{O}$ bond at $1,724\text{ cm}^{-1}$ from PVDF-PMMA blend membrane and $-\text{C}=\text{O}$ bond at $1,650\text{ cm}^{-1}$ and $-\text{C}=\text{N}$ bond at $1,540\text{ cm}^{-1}$ from PVDF-NIPAM blend membrane [8].

After treatment of the blend membrane with 0.01 M NaOH aqueous solution at 40°C for 1 hr, the surface chemistry difference became even more distinctive and variations of the FTIR spectra after the surface modification were as shown in Fig. 2. When the PAN blend membrane was treated with NaOH solution, the spectrum showed the broad adsorption band at $3,350\text{ cm}^{-1}$ corresponded to the stretching vibration of the $-\text{NH}_2$ group [9]. The bands of $-\text{C}=\text{O}$ at $1,673\text{ cm}^{-1}$ and $-\text{NH}$ band at $1,574\text{ cm}^{-1}$ indicated the introduction of the $-\text{COO}^-$ and $-\text{CONH}_2$ groups represented the intermediate between $-\text{CN}$ and $-\text{COOH}$ groups after the surfacial modification of the blend membrane. The reaction between the $-\text{CN}$ groups of PAN with NaOH was shown in Fig. 3 [10]. It is in fact known reaction mechanism that by the reaction of $-\text{CN}$ with NaOH to produce $-\text{CONH}_2$ and $-\text{COO}^-$ groups.

Table 1. Variations of the Water Contact Angles on the Surface of the Blend Membranes

Membrane	Without surface modification	Surface modification with NaOH
PVDF	81.6	-
PVDF/PAN = 9/1	71.4	70.8
PVDF/PAN = 8/2	65.0	63.6
PVDF/PMMA = 9/1	64.8	65.2
PVDF/PMMA = 8/2	64.4	65.8
PVDF/NIPAM = 9/1	66.4	68.4
PVDF/NIPAM = 8/2	64.2	66.0

Contact angle (θ) : °

3.2.2. Contact Angles

Hydrophilicity is one of the most important parameters of the characteristics of the membrane surface, and the water contact angle (θ) is a regular measurement of surface hydrophilicity. To see the effect of the blending with potential ionic polymers on the hydrophilicity of the PVDF membrane, water contact angles of the blend membranes were measured and compared with that of the PVDF membrane (Table 1). In general, high contact angle with a water droplet means that the surface is hydrophobic. As one can see from the Table 1, the contact angle of the PVDF membrane without any potential ionic polymers blended was the highest, and the reason for its high hydrophobicity is mainly due to the fluorine atom of the $-\text{CF}_2$ groups with high electronegativity (4.0), small atomic size (0.135 nm) and high bond energy [11]. However, as the amount of the potential ionic polymers increased, the contact angle decreased, indicating that the surface of the blended membranes became more hydrophilic with the content of the potential ionic polymers used [12,13]. However, when the blend membranes were treated further with basic- or acidic-solutions, the contact angles of those membranes did not change much. From this result, it can be suggested that the hydrophilicity of the PVDF membrane can be substantially improved by the introduction of the ionic polymers into the membranes, depending on the amount of ionic polymers used.

3.3. Morphologies of the Membrane

3.3.1. SEM Photographs of the Membrane

Fig. 4 shows the FESEM photographs of the surfaces and cross-sections of the PVDF blend membranes. All of the blend membranes show a finger structure, but their surface morphologies appeared to be dependent strongly on the compositions of the PVDF/polar potential ionic polymers. However, there was no structural trend according to the different kinds of potential ionic polymers used.

3.3.2. Pore Size Distributions of the Membrane

The FESEM photographs showed the actual morphology and structure of the membranes. However, it is not possible to know the complicated shape and structure of the pores by using FESEM alone. Therefore, to figure out the exact pore sizes and porosities of the membranes, special method is needed to be used.

In fact, there have been two different methods that can be used for the determination of the pore size distribution. One is mercury intrusion method and the other is a liquid displacement method. In a liquid displacement method, the flow rates are measured with liquid at the same pressures as the pressures applied to penetrate the dry pores. Generally speaking, the liquid displacement method is only applicable to the pores which connect both ends of the membrane. Such pores are defined as active pores. In the case of mercury intrusion method, there may exist the pores one end of which is blocked so that the liquid cannot pass through it. They are called as inactive pores and cannot contribute to the pore size distribution measured by any liquid displacement method [14].

So, in this study, a capillary flow porometry, a convenient method to characterize membrane pore size, pore size distribution and structure variability, was used [15]. The membrane sample was first thoroughly wetted with 'Galwick', a liquid of a low surface tension ($\sigma = 15.9 \times 10^{-3}$ N/m) and a vapor pressure. The gas pressure was applied to one side of the wetted sample. As the gas pressure increases, it will reach a

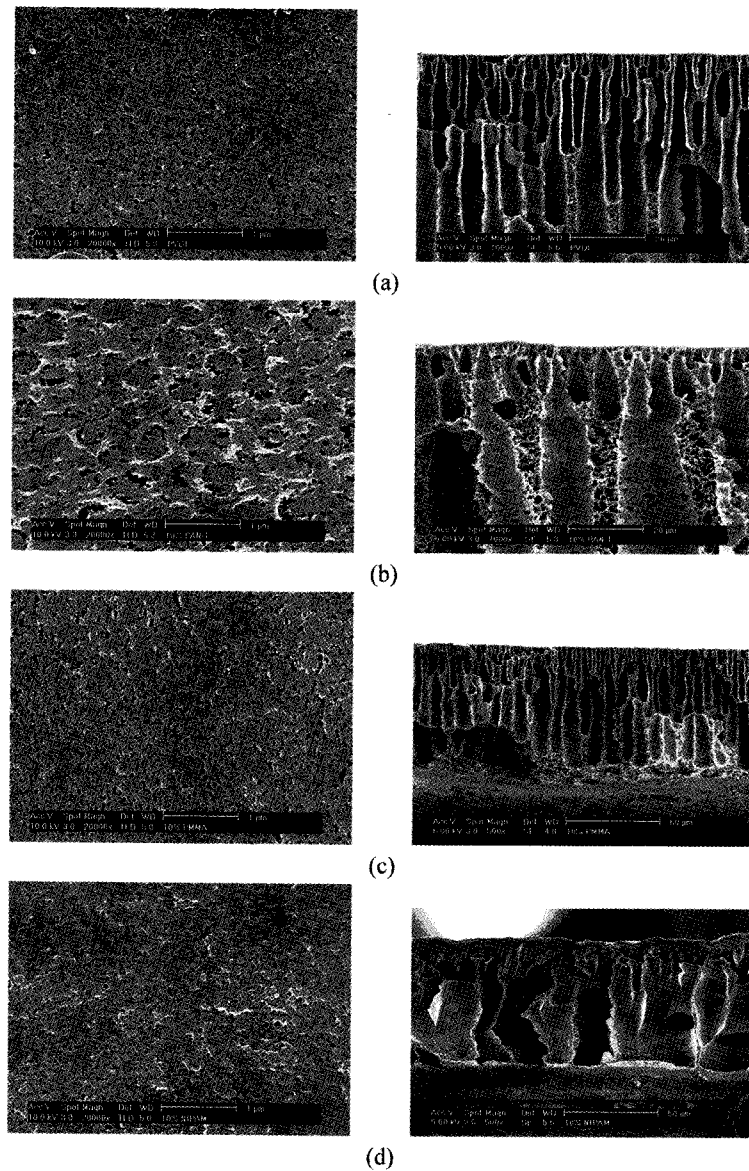


Fig. 4. FESEM photographs of the surface and cross-section of the blend membranes with different compositions: (a) PVDF membrane, (b) PVDF/PAN = 9/1 (in wt%), (c) PVDF/PMMA = 9/1 (in wt%), (d) PVDF/NIPAM = 9/1 (in wt%).

point where it can overcome the surface tension of the liquid in the largest pores and will push the liquid out. The pressure is termed the minimum bubble point and corresponds to the measurement of maximum effective pore size. The most widely used non-destructive integrity test for membranes is bubble point analysis, which is based on the retention of liquids in pores by surface tension and capillary forces. By measuring the bubble point, the average pore diameter of the membrane can be quantitatively determined [16].

Table 2 shows the characteristics of effective pore such as minimum and mean bubble points, and maximum and mean pore sizes of the blend membranes. The mean pore size of the pristine PVDF membrane was about $0.56 \mu\text{m}$, and it decreased by the blending with the polar polymers and it became about $0.02 \mu\text{m}$ for the PVDF/PAN blend membrane. Fig. 5 shows the pore size distribution of the blend membranes. From this data, it was found that the pore size of the PVDF membrane was decreased by the blending with polar

Table 2. Characteristics of Effective Pore Size of the Blend Membranes

Membrane	Minimum bubble point (psi)	Maximum pore size (μm)	Mean bubble point (psi)	Mean pore size (μm)
PVDF	148.8	0.0443	357.7	0.0184
PVDF/PAN = 8/2	4.218	1.5642	11.70	0.5639
PVDF/PMMA = 8/2	12.78	0.5164	226.2	0.0292
PVDF/NIPAM = 8/2	13.54	0.4875	69.98	0.0943

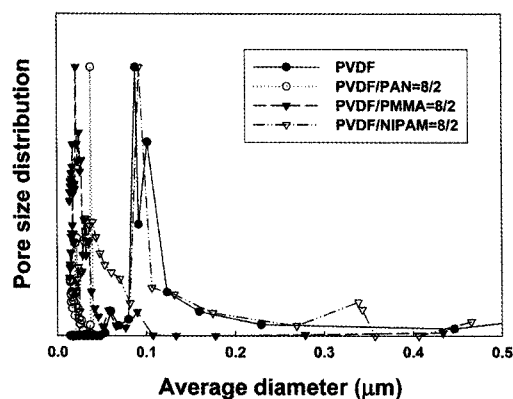


Fig. 5. The average pore diameter and the size distribution of pores on the surface of the PVDF blend membranes: PVDF/potential ionic polymers = 8/2 (in wt%).

polymers and pore size distribution also became narrower by the polar polymers.

3.4. Permeation Properties

3.4.1. Pure Water Flux

In order to see how the blending with polar polymers affect on the formation of pores and consequently on the water flux of the PVDF microporous mem-

branes, pure water flux through the membranes was measured. Fig. 6 shows the pure water flux of the PVDF blend membranes prepared from different conditions.

Except for the PVDF/NIPAM blend membrane, all of the blend membranes showed lower pure water flux than the pure PVDF membrane, due to their smaller pore sizes as found from Fig. 5. For the case of the PVDF/NIPAM blend membrane, as the composition of PVDF/NIPAM was 8/2, the flux was about $40 \text{ m}^3/\text{m}^2 \text{ day}$, which was more than 50% increase of that of pure PVDF membrane. From this data, it was found that the pure water flux data reflect the pore sizes of the membrane well.

However, when the blend membranes were chemically treated with NaOH solution, it became different. Most of the blend membranes showed flux increase, and some of them showed very high flux increase. For PVDF/PAN blend membranes, when they were treated with NaOH solution, the flux improved substantially and became much higher than the pure PVDF membrane. This kind of phenomenon was also found from

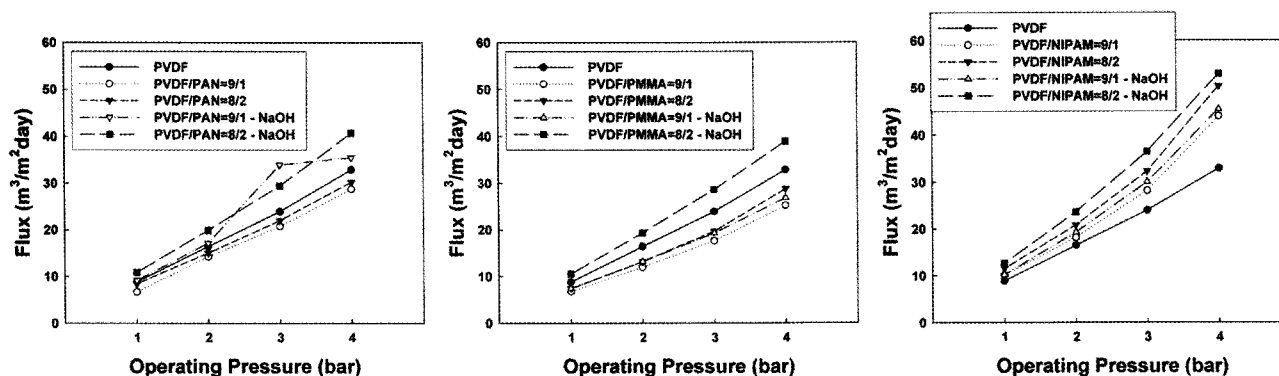


Fig. 6. Pure water flux of the blend membranes prepared different compositions, where -NaOH and -HCl mean that the each blend membrane was treated with NaOH or HCl, respectively.

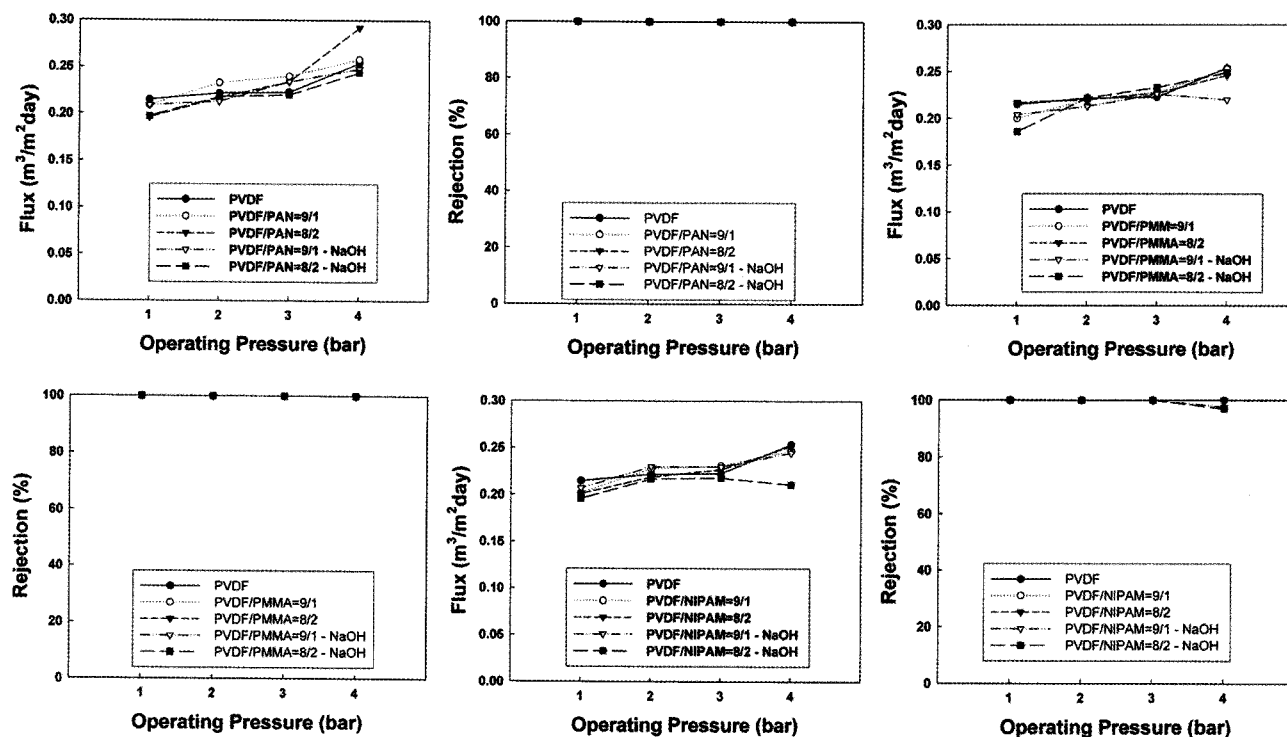


Fig. 7. Performance of the blend membranes prepared under different conditions, as a 1,000 ppm PEO 300,000 aqueous solution was used as a feed, where -NaOH means that the each blend membrane was treated with NaOH.

the other blend membranes, and can be explained by the improved surface hydrophilicity of the membranes. The improved surface hydrophilicity decreased the resistance against water at the membrane surface, and it became easy for water to wet the membrane surface, eventually increasing the water flux through the membranes.

3.4.2. Permselective Properties

Figs. 7, 8, and 9 show the permselective properties of the PVDF blend membranes as a function of operating pressure, using three different feed solutions such as 1,000 ppm aqueous solutions of PEO 300,000, PEO 100,000 and PEG 35,000.

Fig. 7 shows the performance of the membranes with a 1,000 ppm aqueous solution of PEO 300,000. For all of the membranes, the rejection was almost over 95%. However, the flux became very low, especially as compared with pure water flux. It was almost less than 2% of that, strongly suggesting that serious fouling of the membrane by the PEO 300,000 blocking

almost all the pores was involved. Despite the different kinds of membranes used, all of the flux was in the range from 0.2~0.3 $\text{m}^3/\text{m}^2\text{day}$ slightly increasing with operating pressure.

Fig. 8 shows the results from the test with 1,000 ppm aqueous solution of PEO 100,000 as a feed. As compared with the data shown in Fig. 7, flux increased a little, but the rejection decreased due to the smaller molecular weight of the PEO 100,000 than that of the PEO 300,000. Overall behavior of the membranes, effect of the polar polymer on the flux and rejection of the blend membrane, was more or less same as the solution of PEO 300,000 was used as a feed, flux not depending on the composition of the blend membranes and rejection being decreased slightly by the polar polymers.

Fig. 9 shows the results obtained as a 1,000 ppm aqueous solution of PEG 35,000 was used as a feed. Being different from the two cases explained above, as the PEG 35,000 was used, membrane fouling was not that serious. The slope of the line of flux as a function

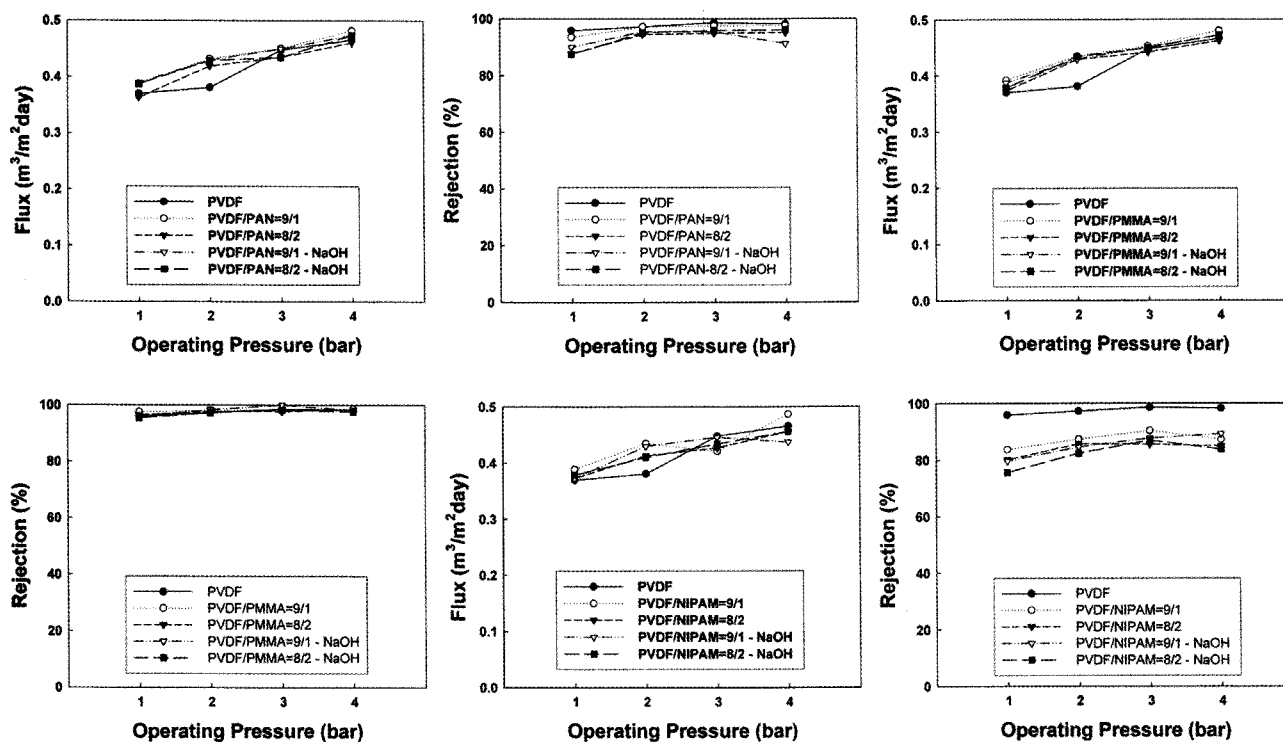


Fig. 8. Performance of the blend membranes prepared under different conditions, as a 1,000 ppm PEO 100,000 aqueous solution was used as a feed, where -NaOH means that the each blend membrane was treated with NaOH.

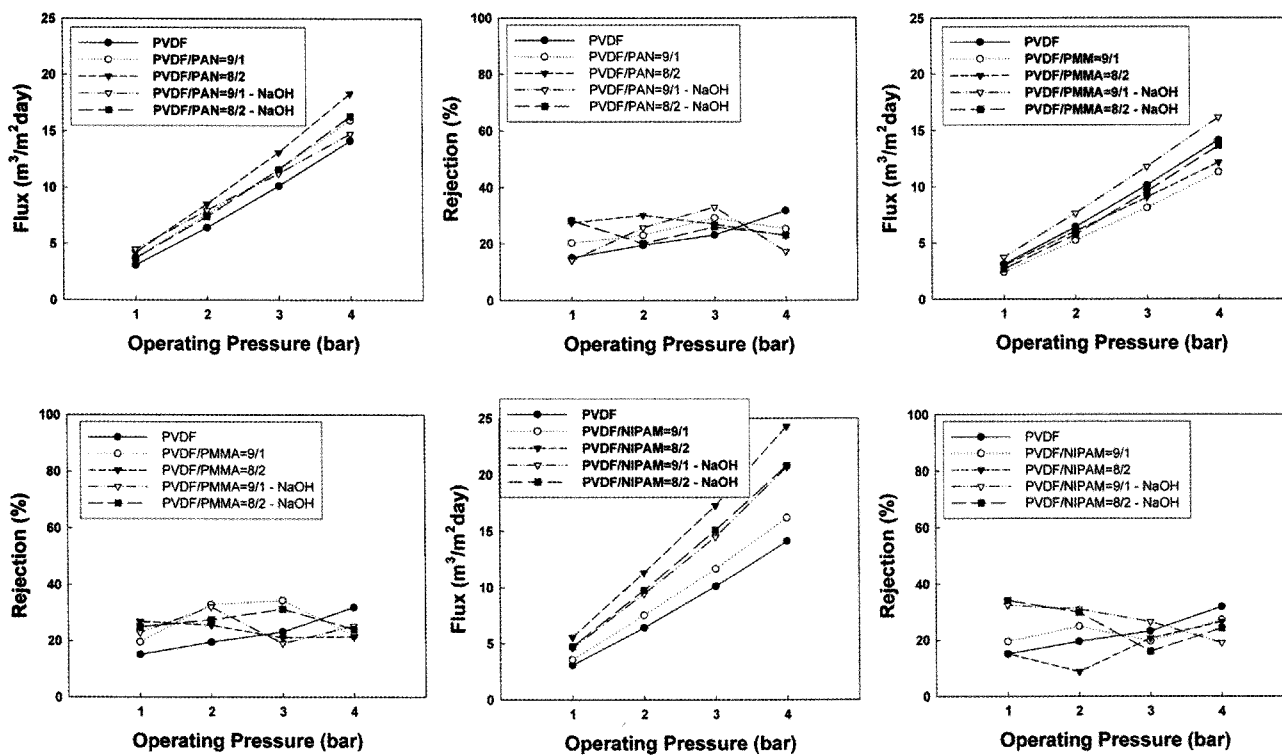


Fig. 9. Performance of the blend membranes prepared under different conditions, as a 1,000 ppm PEG 35,000 aqueous solution was used as a feed, where -NaOH means that the each blend membrane was treated with NaOH.

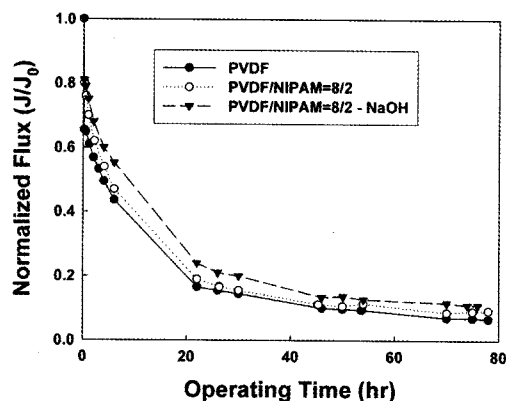


Fig. 10. Flux decline of the PVDF/NIPAM blend membranes along the operating time as a 1,000 ppm PEG 35,000 aqueous solution was used as a feed.

of operating pressure became high and normal, the flux being increased linearly with the operating pressure. This phenomenon is due to the smaller size of the PEG 35,000 so that the rejection was fairly low, almost less than 40%, but the flux was fairly high and increased by the potential ionic polymers blended. The extent of the increase in the flux was the highest when NIPAM was blended. From these results, it was found that NIPAM is the best to increase the flux of the membrane.

Considering the data from Figs. 7, 8, and 9, it can be suggested that even though polar potential ionic polymer be blended with PVDF, membrane fouling by the solutes in the feed solutions was still so serious, especially when the solute was large enough to show relatively high rejection, say 80%, that the flux of the PVDF membrane is not improved. However, when the solute of the feed solution was small, the improvement of the flux by the use of polar polymers was substantial.

3.4.3. Long Time Tests

Effect of the blending with polar polymers on the fouling of the PVDF membrane was studied using a 1,000 ppm aqueous solution of PEG 35,000 as shown in Fig. 10. Fig. 10 shows the result obtained when PVDF-NIPAM blend membrane was used. As one can see, there is positive effect of the blending with

NIPAM on the antifouling effect of the PVDF membrane. Though the degree of flux decline was not improved very much, the flux decline of the PVDF/NIPAM blend membrane was less than that of the PVDF membrane. The effect was even better when the PVDF-NIPAM blend membrane was treated with 0.01 M NaOH solution. From this result, it can be suggested that blending with ionic polymers such as NIPAM is favorable to improve antifouling property of the PVDF membrane, but it is not good enough to solve major membrane fouling problems of the PVDF membrane.

4. Conclusions

PVDF asymmetric microporous membranes with a polar surface can be prepared by the conventional phase inversion process, using PVDF/polar potential ionic polymer blend solutions as dope solutions. The permselective properties of the PVDF blend membrane such as flux and solute rejection depended on the polar polymers blended with PVDF. Among the polar polymers used such as PAN, PMMA and NIPAM, NIPAM showed the best performance in the improvement of the membrane flux. Most of all the potential ionic polymers turned out to be favorable for the formation of a PVDF membrane with a better flux. However, antifouling property of the PVDF membrane was not highly improved by the use of those potential ionic polymers. It seemed that there is limitation to improve antifouling property of the PVDF membrane by blending polar polymers to increase hydrophilicity of the membrane. The membrane fouling was proved to be very dependent on the solutes used: larger solute causing more fouling by the more selective permeation of water, resulting in higher rejection ratios.

Acknowledgement

This research was supported by a grant (code #: 05K1501-01210) from 'Center for Nanostructured Ma-

terials Technology' under '21st Century Frontier R&D Programs' of the Ministry of Science and Technology, Korea.

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