Effect of Polyvinylpyrrolidone on Morphology and Performance of Hemodialysis Membranes Prepared from Polyether Sulfone

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ABSTRACT: Flat-sheet hemodialysis membranes were prepared by phase inversion technique using polyether sulfone (PES) dissolved in dimethylacetamide (DMAc) with and without the addition of polyvinylpyrrolidone (PVP). The effect of the composition of the casting solution on membrane morphology and performance were investigated. The performances of membranes were elucidated on the basis of removal of uremic toxins (urea, uric acid, and creatinine) from human blood serum. The membrane prepared from 12 wt % PES with 2.8 wt % PVP demonstrated better performance compared to the other compositions. The membrane performance is a consequence of membrane morphology. Membranes with channel-like or long finger-like structures provide superior removal efficiencies. If the morphology turns to a sponge structure, the effectiveness is diminished. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3804–3813, 2004

Key words: membranes; polyethers; morphology; polyvinylpyrrolidone; hemodialysis

INTRODUCTION

Polymeric membranes have been developed for a wide variety of applications in separation technology, such as condensation and purification of various liquids, desalination of sea water, biological processes, medical devices, and blood purification or hemodialysis.[1–6] In-depth understanding of polymer properties, membrane morphology, and formation process is necessary for the improvement of membrane performance.

Synthetic polymers such as polysulfone (PS), polyacrilonitrile (PAN), polymethyl methacrylate (PMMA), polyamide (PA), and polyvinylalcohol (PVA) in addition to cellulose-based materials such as cellulose acetate (CA) and regenerated cellulose (RC) are widely employed for the preparation of hemodialysis membranes.[7–13]

Recently polyether sulfone (PES) has been developed as a material for hemodialysis membranes due to its favorable mechanical strength, resistance to acids and alkalis, thermal and chemical resistance, and, most importantly, excellent biocompatibility.[14,15] As polyether sulfone is a hydrophobic material, several methods have been manipulated to modify the performance for aqueous applications such as hemodialysis. Sulfonation of PES or addition of a hydrophilic polymer or an inorganic salt in the polymer solution are some of the techniques used for enhancing the hydrophilicity of PES.[16,17]

Polyvinylpyrrolidone (PVP) is a common hydrophilic additive to enhance the hydrophilicity of PES membranes. This is a water-soluble polymer, which increases the membrane porosity. At the same time, a part of the remaining PVP magnifies the hydrophilicity of the membrane.[18,19]

Phase inversion is the usual procedure for fabrication of asymmetric polyether sulfone flat-sheet and hollow fiber membranes. For flat membranes, a thin layer of PES dissolved in an appropriate solvent is cast on a suitable support and is immersed into the nonsolvent coagulation bath.

In the present study, polyether sulfone (PES) was selected as the main polymer for hemodialysis flat membranes. Polymer solutions were prepared from PES with and without PVP in *N,N*-dimethylacetamide (DMAc) as solvent and pure water as nonsolvent.

Different recipes for fabrication of hemodialysis membranes using wet phase inversion have been manipulated. The morphology and performance of the membranes were investigated and specifically the effects of polyvinylpyrrolidone (PVP) were elucidated. The performance of membranes was estimated by measuring the removal of uremic toxins (urea, uric acid, and creatinine) from human blood serum. The relationships between membrane morphology and membrane performance were correlated.

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TABLE I
Composition of the Hemodialysis Membranes

Membrane type	Membrane solution compositions (wt %)		
	PES	PVP	DMAc
12 wt % PES	12	0	88
12 wt % PES, 2.8 wt % PVP	12	2.8	82.5
12 wt % PES, 5 wt % PVP	12	5	83
18 wt % PES	18	0	82
18 wt % PES, 2.8 wt % PVP	18	2.8	79.2
18 wt % PES, 5 wt % PVP	18	5	77
22 wt % PES	22	0	78
22 wt % PES, 2.8 wt % PVP	22	2.8	75.2
22 wt % PES, 5 wt % PVP	22	5	73

EXPERIMENTAL

Materials

The following materials were employed for preparation of membranes: Polyether sulfone Ultrason E6020P (M_w = 58,000 g/mol, porous flake) provided by BASF Co (Germany) as the membrane matrix, PVP (K = 90) supplied by Fluka Chemicals Co as additive, DMAc (purity 99%) supplied by Mark Co as solvent, and distilled water as nonsolvent.

Membrane preparation

Polyether sulfone was dried in a vacuum oven at 130°C for 4 h to remove absorbed water before use. Homogeneous membrane casting solutions were made from PES with and without PVP dissolved in DMAc solvent. The composition of casting solutions was adapted by changing the percentage of PES and PVP. Three concentrations for PES (12, 18, and 22 wt %) and three levels of PVP combinations (0, 2.8, and 5 wt %) were manipulated for preparation of hemodialysis membranes. The compositions of the membrane casting solutions are shown in Table I.

Asymmetric flat membranes were synthesized using phase inversion technique. Homogeneous solutions of membranes were cast on a smooth glass plate by a casting rod at room temperature with uniform speed. The wet thickness (gap between the glass plate and casting rod) was maintained at 120 μm for all membranes. The polymer solutions on glass plates were immediately immersed in the coagulation bath before any phase inversion in air. The coagulation bath consisted of distilled water at room temperature for all trials. After completion of coagulation, membranes were stored in distilled water for 48 h to allow

the water-soluble components in the membranes to be leached out. As a final stage, membranes were washed again with distilled water and were dried by placing them between two sheets of the filter paper for at least 48 h at room temperature.

Membrane performance

The capabilities of the prepared membranes were investigated on the basis of removal of uremic toxins with high potential toxicity (i.e., urea, uric acid, and creatinine) from human blood serum.

The experiments were carried out in a batch dialyzer (Fig. 1) consisting of two horizontal chambers with a volume of 100 ml for each chamber. Two identical stirrers were installed in the chambers. One of the chambers was filled with human blood serum. Distilled water was poured in the other chamber. The hemodialysis flat membrane was clamped between the two chambers.

The concentrations of urea, uric acid, and creatinine in human blood serum were measured before the trials. By starting the experiment, blood was in contact with membrane. The concentration gradients of uremic toxins in two sides of the hemodialysis membrane are the driving forces for the passage of urea, uric acid, and creatinine from the concentrated (i.e., blood serum) sector to the dilute (i.e., water) side. The concentrations of uremic toxin were measured after 1 and 5 h from the start of the experiments. The concentrations of uremic toxins were tested in a medical laboratory according to the standard methods.
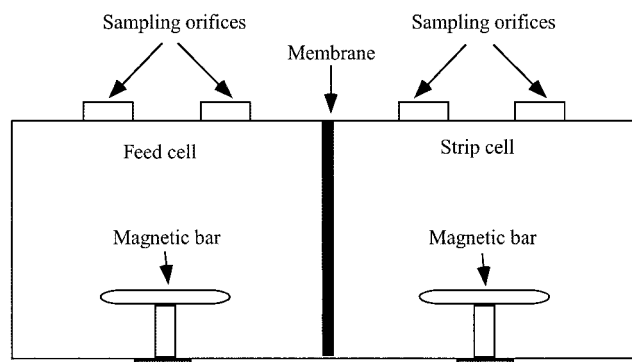
The membrane performance, i.e., concentration reduction (CR) of uremic toxins was calculated from eq. (1):

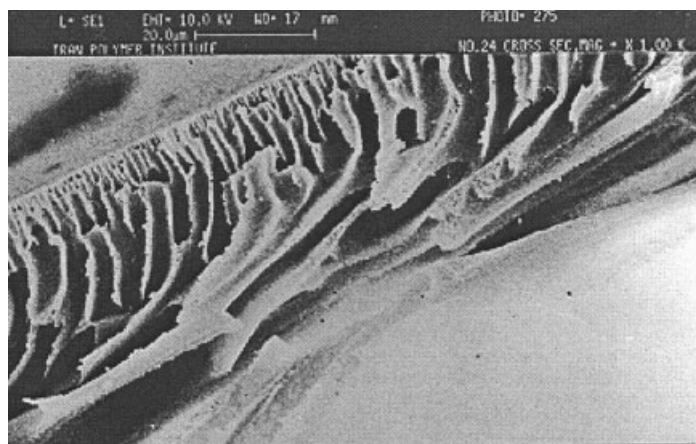$$CR = 100 \times (C_1 - C_2)/C_1 \qquad (1)$$

Where C_1 and C_2 are the uremic toxin concentrations in blood before and after the trial.
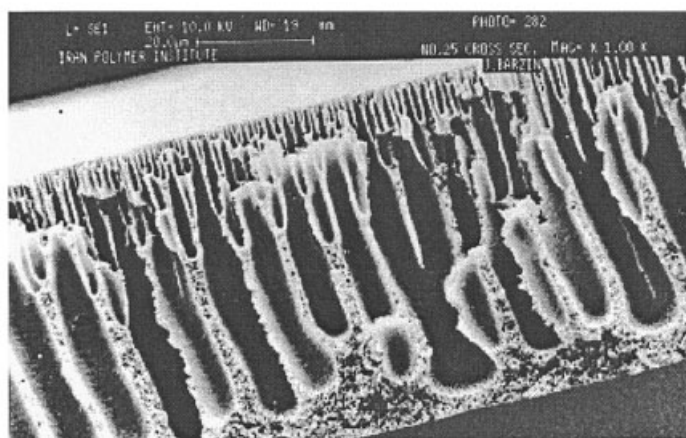
Scanning electron microscopy (SEM)

The cross-sections of the prepared membranes were observed with SEM using a Cambridge S360 scanning
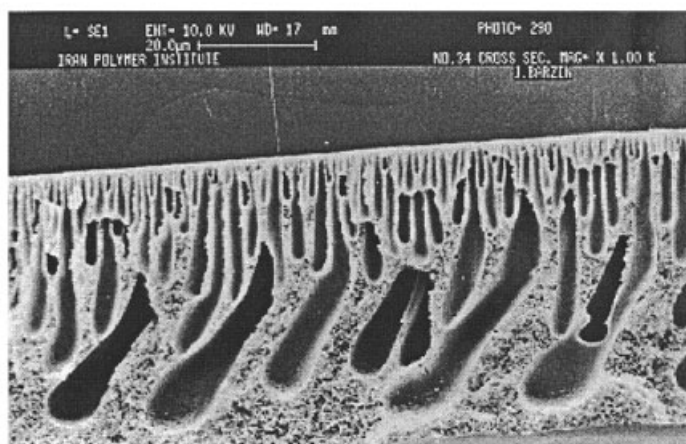

Figure 1 Experimental set-up.

Figure 2 SEM micrographs of cross-sections of hemodialysis membranes as a function of polyether sulfone percentage (0% PVP) (a) 12 wt %; (b) 18 wt %; (c) 22 wt %.

microscope. For this purpose, the membranes were frozen in liquid nitrogen and broken. They were transferred into the microscope with a sample holder after sputtering with gold as the conductive material. The SEM studies were carried out at room temperature and 10 kV with a magnification of 1,000.

RESULTS AND DISCUSSION

Membrane morphology

Morphology of the membranes prepared from ternary system (PES, DMAc, and water) is illustrated in Figure 2. The SEM micrographs indicate the typical asymmet-

(a)

(b)

(c)
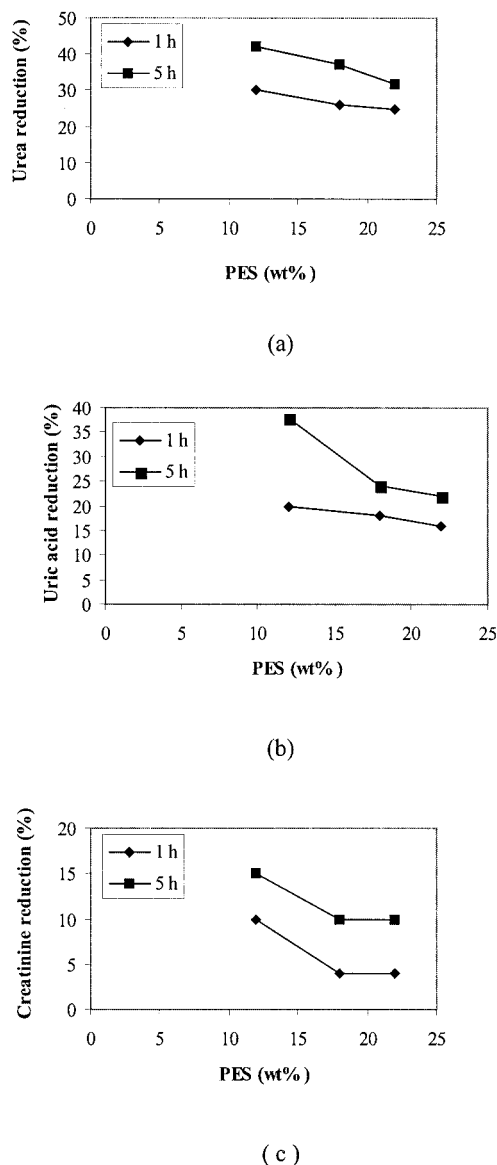
Figure 3 Reduction of uremic toxins as a function of polyether sulfone percentage using hemodialysis membrane after 1 and 5 h (0% PVP) (a) urea; (b) uric acid; (c) creatinine.

ric structure with a very thin and compact layer on the top (skin layer) and a porous and thicker layer as a support.

The membrane with 12 wt % PES [Fig 2(a)] demonstrates a structure, which looks like channels or large open pores from top to the bottom of the membrane. This morphology is named the channel-like structure.[20] The flat membranes obtained from 18 and 22 wt % PES [Figs. 2(b) and (c)], show the asymmetric structure with voids in the shape of a long tear or finger. This morphology is called the finger-like or macro voids structure.[20,21] These micrographs manifest that, when PES concentration increases in the polymer solution, the channel-like structure turns to a finger like configuration.

A comparison between the membranes with 18 wt % PES [Fig. 2(b)] and 22 wt % PES [Fig. 2(c)] indicates that the size and number of finger-like voids in the membrane decreases and turns to a more sponge-like structure when PES concentration increases in the preparation recipe. Similar observations have been reported by Stropnik et al.,[20] Barth et al.,[22] and Kaiser and Stropnik.[23] for polysulfone flat-sheet membranes.

Membrane performance

The membrane performances for different PES concentrations is depicted in Figure 3. A comparison between data for 1 and 5-h trials indicates that the removal of all uremic toxins (i.e., urea, uric acid, and creatinine) from blood serum increases for a longer term. Five hours corresponds to the hemodialysis process time currently used for patients with kidney failure.

Figure 3 shows that the removal of uremic toxins is lower for higher PES concentrations. This behavior indicates that the permeability of urea, uric acid, and creatinine through the membranes with a channel-like structure (PES 12 wt %) is higher than membranes with finger-like morphology (PES 18 and 22 wt %). The size and number of finger-like voids in membranes of 22 wt % PES decreases and turns to a more sponge-like structure [compare Fig. 2(b) and (c)]. This is responsible for the permeability decline of uremic toxin in the membrane with 22 wt % PES compared to the membrane with 18 wt % PES.

There is a limitation for the preparation of membranes with low polymer concentration (less than 12 wt % PES) by phase inversion due to the difficulty of casting solutions and membrane handling, as they are easily broken.

## Effect of PVP on membrane morphology

The morphology of membranes prepared from quaternary systems (PES/PVP/DMAc/water) is presented in Figure 4. The micrographs indicate that, when PVP is added to the casting solution, the size and number of channel and finger-like voids are changed.

For membranes prepared from 12 wt % of PES with addition of PVP [Fig. 4(a)], the size and number of channel-like voids increased compare to the membrane without PVP [Fig. 2(a)]. Similarly for higher (18 and 22 wt %) PES concentrations [Figs 4(b) and (c)], the size and number of finger-like voids increased compared to the same PES concentration without PVP [Fig 2(b) and (c)].
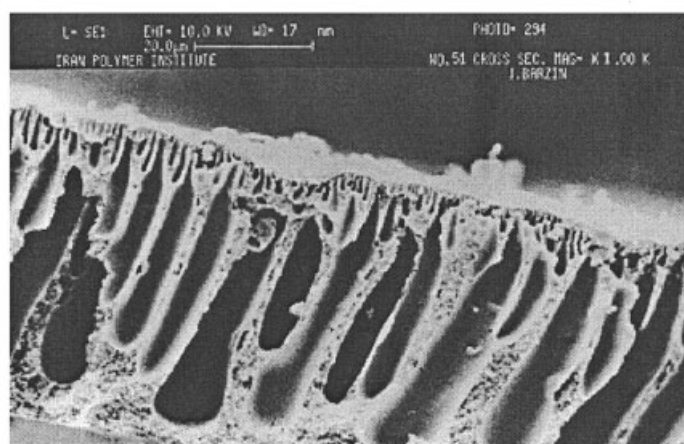
An important conclusion from Figure 4 is that, as the PES concentration in polymer solution increases, channel-like structures turn to finger-like configurations. The same trend was observed in membranes
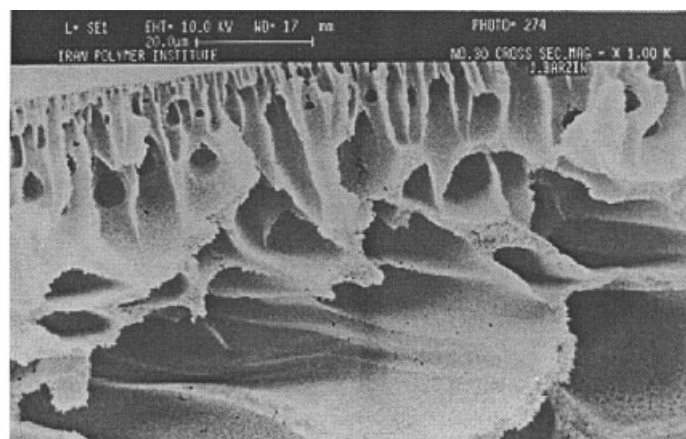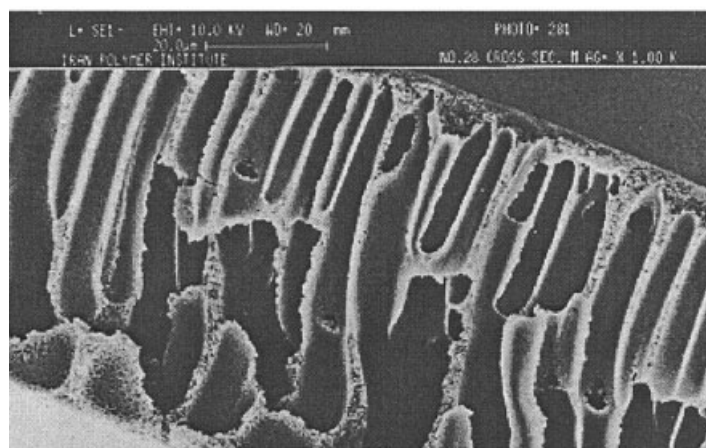
Figure 4 SEM micrographs of cross-sections of hemodialysis membranes as a function of polyether sulfone percentage (2.8% PVP) (a) 12 wt % (b) 18 wt % (c) 22 wt %.

without PVP (Fig. 2). Tam et al.[24] observed similar phenomena for polyether sulfone membranes containing PVP.

When a hydrophilic additive is added to the polymer solution, the solvent–water exchange rate in a water coagulation bath increases at the phase inversion stage.[25] As the PVP is a hydrophilic polymer, the water–DMAc exchange rate in the coagulation bath increases. On the other hand, PVP is also a water-soluble pore-forming polymer. Thus, the membrane structure exhibits more and larger channel- and finger-like voids.

(a)

(b)

(c)
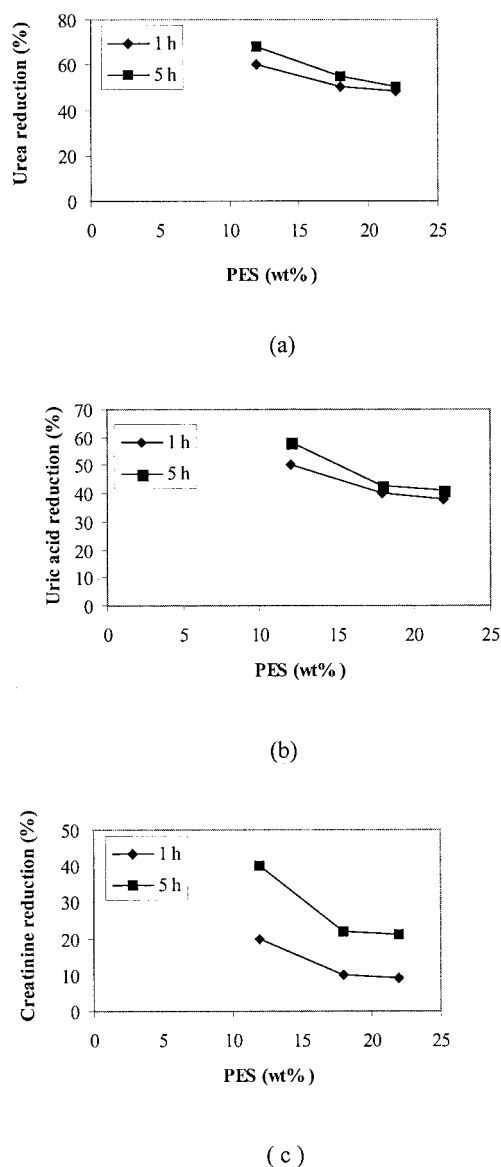
Figure 5 Reduction of uremic toxins as a function of polyether sulfone percentage using hemodialysis membrane after 1 and 5 h (2.8% PVP) (a) urea; (b) uric acid; (c) creatinine.

Effect of PVP on membrane performance

The performance of membranes containing 2.8 wt % PVP is designated in Figure 5. For membranes with 12 wt % PES, the removal of urea was 60% after 1 h and around 70% after 5 h. Uric acid declined 50% after 1 h and 60% after 5 h. Creatinine decreased around 20% after 1 h and more than 40% after 5 h. These results show that the manufactured membranes are capable for the removal of uremic toxins to the desired level.

The removal efficiencies for all uremic toxins, i.e., urea, uric acid, and creatinine, were increased for a longer time (compare data for 1 and 5 h in Fig. 5) or with the addition of PVP (compare Fig. 3 and 5). However, similar to membranes prepared without PVP, the removal of uremic toxins decreased as the PES concentration increased.

The important point is that the removal of urea, uric acid, and creatinine increased tremendously for the membranes with 2.8 wt % PVP compared to the membranes without PVP.

Addition of PVP to the membranes results in an increase in size and number of channel-and finger-like voids. On the other hand, a part of PVP remains in the membrane matrix after membrane washing in the final preparation stage. PVP is a hydrophilic polymer and the remaining amount increases the hydrophilicity of membrane. This leads to a higher passage of water through the membrane. The uremic toxins, which are dissolved in water, are carried with water and pass through the membrane more easily. In other words, in addition to the concentration gradient, which is the major driving force for removal of uremic toxins, convection of water plays a role.

Effect of PVP concentration

To elucidate the effect of higher concentration, the PVP was increased to 5 wt % in the polymer solution. The membrane morphology was changed (Fig. 6). For membranes with 12 wt % PES and 5 wt % PVP, a finger-like structures [Fig 6(a)] appeared instead of the channel-like configuration that was observed in 12 wt % PES without PVP [Fig 2(a)] and with 2.8 wt % PVP [Fig 4(a)]. When the concentration of PVP increased to 5 wt %, finger-like voids decreased in size and number [Figs. 6(b) and (c)] compared to the same PES concentration without PVP [(Figs. 2(b) and (c)] and with 2.8 wt % PVP [Figs. 4(b) and (c)].

It is well known that a slow exchange rate between solvent and nonsolvents in a coagulation bath, results in more sponge-like structures in membrane morphology.[26,27] In our experiments with higher PVP concentrations, the viscosity of the polymer solution was increased, leading to a slow water–DMAc exchange rate in the coagulation bath and resulting in more sponge-like and fewer finger-like voids in the membrane structure. Similarly Dal-Cin et al.[25] observed more sponge-like areas for polyethersulfone and polyvinylpyrrolidone membranes in high PES and PVP concentrations.

The membrane morphology is reflected in membrane performance. For 5 wt % PVP, the membrane performance, i.e., removal of uremic toxins, is represented in Figure 7. As expected, the removal percentage decreases with increasing PES concentration.
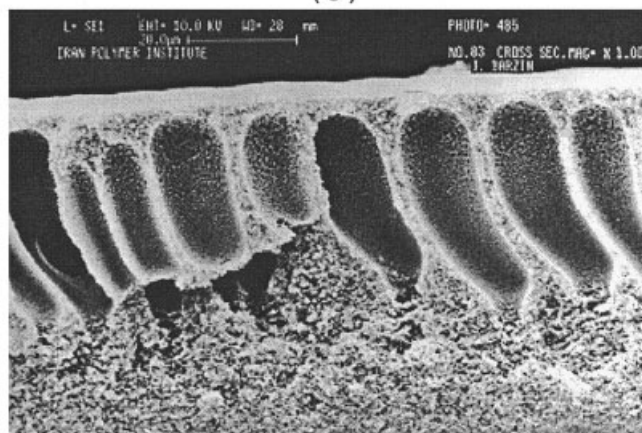
The removal of urea, uric acid, and creatinine was decreased compared to 2.8 wt % PVP in the same PES concentration. For 12 wt % PES (Fig. 8) after 1 h, removal of urea was around 45%, whereas, for 2.8 wt % PVP, removal of urea was 60%. For 5-h experiments, the removal of urea was around 50% for 5 wt % PVP
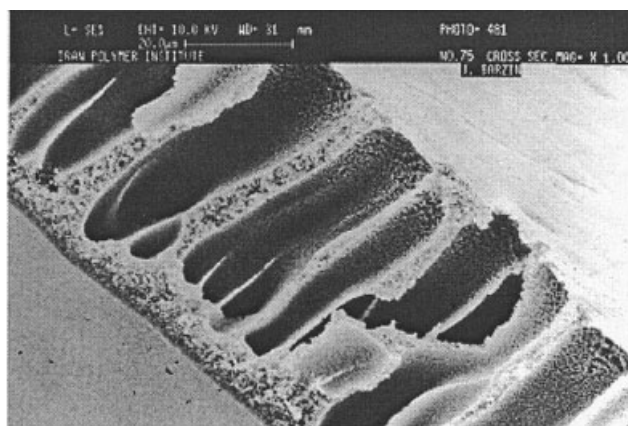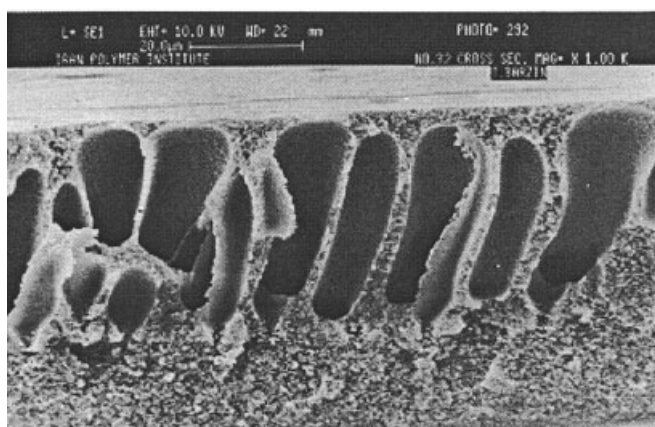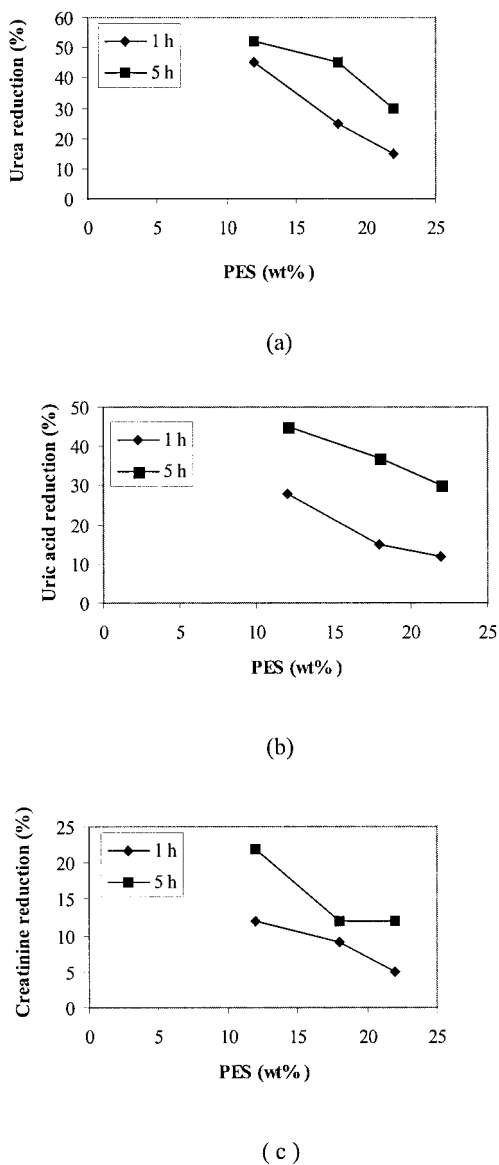
Figure 6 SEM micrographs of cross-sections of hemodialysis membranes as a function of polyether sulfone percentage (5% PVP) (a) 12 wt %; (b) 18 wt %; (c) 22 wt %.

membrane, which is lower than 70% (for 2.8 wt % PVP) but higher than 42% (for the membrane without PVP). The same trend was observed for the removal of other uremic toxins or for the membranes prepared with 18 wt % (Fig. 9) and 22 wt % (Fig. 10) PES.

A conclusion from the above results (Figs. 8–10) is that the membrane performance for 5 wt % PVP is in between membranes prepared with 2.8 wt % PVP and without the addition of PVP. The benefits of using PVP, i.e., increasing the size and number of channel- and finger-like voids and enhancing the hydrophilicity of membrane, were explained in the previous section. The higher removal efficiency for membranes prepared with 5 wt % PVP compared to membranes without the addition of PVP is due to the higher hydrophilicity of the membrane.

tween the hydrophilicities of the membranes to influence the convection of the species through the membranes.

CONCLUSIONS

When PES concentration increases in the ternary system (PES, DMAc, and water), the channel-like structure turns to a finger-like configuration. By adding more PES, the size and number of finger-like voids in the membrane decrease and turn to a more sponge-like structure. The removal of uremic toxins is lower for higher PES concentrations due to the higher permeability of urea, uric acid, and creatinine through the

(a)

(b)

(c)

Figure 7 Reduction of uremic toxins as a function of polyether sulfone percentage using hemodialysis membrane after 1 and 5 h (5% PVP) (a) urea; (b) uric acid; (c) creatinine.

The superior performance of membranes produced from 2.8 wt % PVP compared to the membranes with 5 wt % PVP may be explained in terms of morphology of the membrane. The membrane with lower PVP (2.8 wt %) acquired a greater solvent and nonsolvent exchange rate providing favorable channel- and finger-like structure. Higher PVP (5 wt %) results in a lower solvent and nonsolvent exchange rate, accommodating the hindering sponge-like structure.

The additional PVP, which acts as a hydrophilic agent, is expected to produce more hydrophilicity leading to greater removal efficiency. However, for both membranes (2.8 and 5 wt % PVP), the same portion of PVP remains in the membrane matrix, consequently, there is not a prodigious difference be-
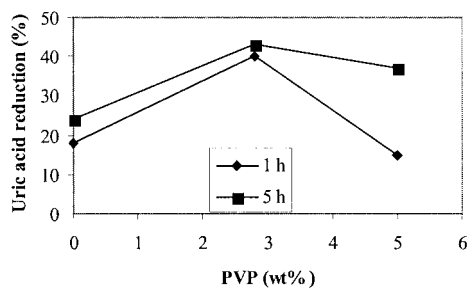
(a)

(b)

(c)

Figure 8 Reduction of uremic toxins as a function of polyvinylpyrrolidone percentage using hemodialysis membrane after 1 and 5 h (12 wt % PES) (a) urea; (b) uric acid; (c) creatinine.
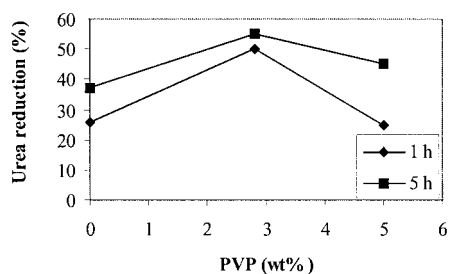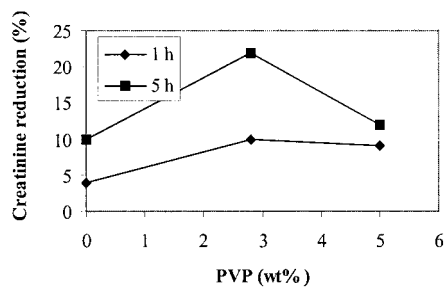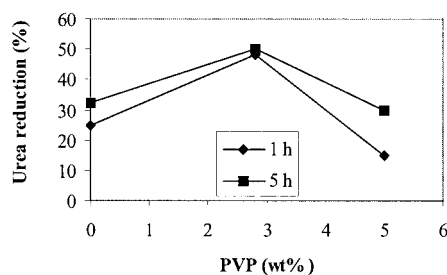
(a)

(b)

(c)

Figure 9 Reduction of uremic toxins as a function of poly-vinylpyrrolidone percentage using hemodialysis membrane after 1 and 5 h (18 wt % PES) (a) urea; (b) uric acid; (c) creatinine.

configurations and/or finger-like voids decreased in size and number. This is due to a slow exchange rate between the solvent and nonsolvent, resulting from an increase in the viscosity of the polymer solution. The membrane performance for 5 wt % PVP was in between membranes prepared with 2.8 wt % PVP and without the addition of PVP. The membrane with lower PVP (2.8 wt %) acquired greater solvent and nonsolvent exchange rates providing favorable channel- and finger-like structures. Higher PVP (5 wt %) results in a lower solvent and nonsolvent exchange rate, which accommodates the hindering sponge-like structure.

(a)

(b)

(c)

Figure 10 Reduction of uremic toxins as a function of polyvinylpyrrolidone percentage using hemodialysis membrane after 1 and 5 h (22 wt % PES) (a) urea; (b) uric acid; (c) creatinine.

membranes with the channel-like structure compared to the membranes with a finger-like morphology.
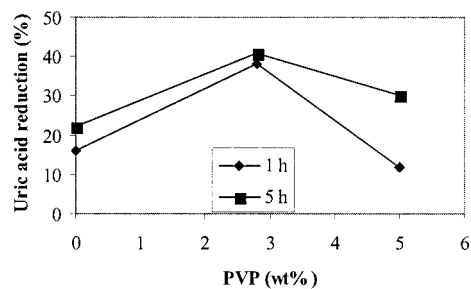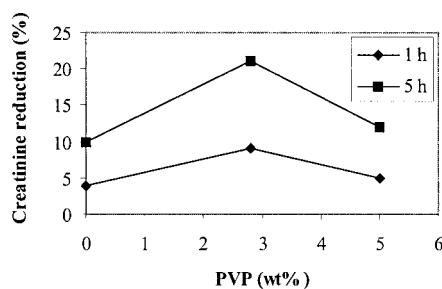
The membranes prepared from quaternary systems (PES/PVP/DMAc/water) showed higher performance. The benefits of using PVP are increasing the size and number of channel- and finger-like voids and enhancing the hydrophilicity of membrane. This can be explained by an increment in solvent–water exchange due to the presence of PVP. In addition, PVP is a water-soluble pore-forming polymer leading to the membranes with more and larger channel- and finger-like openings.

By increasing the concentration of PVP to 5 wt %, finger-like structure appeared instead of channel-like

References

1. Daufin, G.; Escudier, J. P.; Carrere, H.; Berot, S.; Fillaudeau L.; Decloux, M. Food Bioprod Proc 2001, 79, 88.
2. Girard B.; Fukumoto, L. R. Food Sci Technol 1999, 32, 290.
3. Matsuura, T. Synthetic Membranes and Membrane Separation Processes; CRC Press: Boca Raton, FL, 1994.
4. Sourirajan, S.; Matsuura, T. Reverse Osmosis and Ultrafiltration Process Principles; National Research Council of Canada: Ottawa, Canada, 1989.
5. Mulder, M. Basic Principles of Membrane Technology; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.
6. Wenthold, R. M.; Hall, R. T.; Andrus, R. G.; Brinda, P. D.; Cosentino, L. C.; Reggin R. F.; Pigott, D. T. U.S. Patent 1998, 5, 762–798.
7. Bonomini V.; Berland, Y. Dialysis Membranes Structure and Predictions: Karger: Basel, Switzerland, 1995.
8. Sakai, K.; J Membr Sci 1994, 96, 91.
9. Etheve, J.; Dejardin P.; Boissiere, M. Desalination 2002, 146, 111.
10. Kataoka, H.; Kunitomo, T.; Kobayashi, T.; U.S. Patent 4,834,882 (1989).
11. Mochizuki, A.; Seita, Y.; Nakashima, T. Endo, F. Yamashita, S. J Appl Polym Sci 1998, 67, 1253.
12. Yamamoto, K.; Kawai, S.; Ohmori, A. U.S. Patent 4,071,454 (1978).
13. Abe, Y.; Mochizuki, A. J Appl Polym Sci 2003, 89, 333.
14. Sluma, H. D.; Passlack, J.; Buttner, B.; Scherf, M.; U.S. Patent 5,246,582 (1993).
15. Bell, C. M.; Pirner, M.; Buck, R.; Gohl, H. J. U.S. Patent 5,543,465 (1996).
16. Lee, S. H.; Kim, J. J.; Kim, S. S.; Kim, U. Y. J Appl Polym Sci 1993, 49, 539.
17. Shimagaki, M.; Fukui, F.; Sonoda, T.; Sugita, K. U.S. Patent 5 938 929, 1999.
18. Kawata, I.; Okamoto, T.; Akasu, H.; Komatsu, K. U.S. Patent 5,340,480 (1994).
19. Kobayashi, T.; Tanaka, K. U.S. Patent 5,436,068 (1995).
20. Stropnik, C.; Germic, L.; Zerjal, B. J Appl Polym Sci 1996, 61, 1821.
21. Barton, B. F.; Reeve, J. L.; and Mahugh, A. J. J Polym Sci: Polym Phys Ed 1997, 35, 562.
22. Barth, C.; Goncalves, M. C.; Pires, A. T. N.; Roeder, J.; Wolf, B. A. J Membr Sci, 2000, 196, 287.
23. Kaiser, V.; Stropnik, C. Acta Chim Slov 2000, 47, 205.
24. Tam, C. M.; Dal-Cin, M. M.; Guiver, M. D.; J Membr Sci 1993, 78, 123.
25. Dal-Cin, M. M.; Tam, C. M.; Guiver, M. D.; Tweddle, T. A. J Appl Polym Sci 1994, 54, 783.
26. Strathmann, H. In Synthetic Membranes: Science, Engineering and Applications; Bungay, P. M.; Lonsdale, H. K.; de Pinho, M. N. Eds.; NATO ASI Series 181: Dordrecht, The Netherlands, 1986.
27. Munari, S.; Buttino, A.; Capannelli, G.; Moretti, P.; Bon, P. P.; Desalination 1988, 70, 265.