Effect of Hypochlorite Concentration on Properties of Posttreated Outer-Skin Ultrafiltration Membranes Spun from Cellulose Acetate/Poly(vinyl pyrrolidone) Blends

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ABSTRACT: An outer-skin hollow-fiber ultrafiltration (UF) membrane was spun from a new dope solution containing cellulose acetate (CA)/poly(vinyl pyrrolidone) (PVP 360K)/*N*-methyl-2-pyrrolidone (NMP)/water using a wet-spinning technique. The as-spun fibers were posttreated with a hypochlorite solution over a range of concentrations for a fixed period of 24 h. The experimental results showed that the pure water flux of the treated membrane increased with increasing hypochlorite concentration. The treated membrane experienced an increased fouling tendency with increasing hypochlorite concentration because the hydrophilicity of the treated membrane decreased as a result of the removal of PVP contents in the membrane matrix after hypochlorite treatment. SEM images revealed that the membrane had an outer dense skin, a porous inner surface, and a spongelike structure, which confirmed that addition of PVP favored the suppression of macrovoids in the membrane. The membrane pore size could be significantly increased when the hypochlorite concentration reached 200 mg/L. It was concluded that hypochlorite treatment provided an additional option to easily alter the pore size of UF membranes. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 227–231, 2005

Key words: ultrafiltration; membranes; blends; hypochlorite treatment; morphology

INTRODUCTION

Cellulose acetate (CA) membranes have been widely used for reverse osmosis, microfiltration (MF), and gas separation.[1–4] The major configurations of commercial CA membranes used are flat sheet or spiral-wound modules.[2,3] Nowadays the hollow-fiber configuration has become a favorite choice.[5–7] However, very few studies on CA hollow-fiber ultrafiltration (UF) membranes have been published. Hypochlorite treatment has been applied to increase the flux of MF/UF membranes made from blends of hydrophobic polymers and poly(vinyl pyrrolidone) (PVP).[8–12] Roesink[8] studied the effect of hypochlorite treatment on polyetherimide (PEI)/PVP (K90) hollow-fiber MF membranes with a sodium hypochlorite solution of 4000 mg/L and found that water flux of the treated membranes increased as a result of the partial removal of PVP content in the membrane matrix. Wienk et al.[9] treated a UF membrane spun from a blend of polyethersulfone (PES) and PVP (K90). They found that water flux increased linearly with increasing treatment time but bovine serum albumin (BSA) retention remained constant at around 90%. It was suggested then that hypochlorite treatment reduced the swelling of PVP in the pores of the membranes without substantially altering the pore structure. Xu et al.[10] investigated the effect of hypochlorite treatment on PEI/PVP hollow-fiber UF membranes for oil/water separation. They found that the membranes showed an obvious decreased solute retention or increased pores after the treatment. They also reported that a certain amount of PVP remained in the resulting membranes because the treated fibers were still wettable and all glass-transition (T_g) values of the treated fibers were less than the T_g of neat PEI. Recently, Qin et al.[11,12] prepared high-flux polysulfone (PSU)/PVP UF membranes by optimizing the hypochlorite concentration and posttreatment time.

To our best knowledge, a search of the open literature did not uncover any systematic investigations of how hypochlorite treatment influences hollow-fiber UF membranes fabricated from a blend of CA and PVP of high molecular mass, such as 360,000 Da. Very recently, the authors explored an optimum treatment time with hypochlorite to achieve a high-flux, inner-skin membrane made from a new dope containing

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TABLE I
Experimental Parameters Used in Spinning of Hollow-Fiber UF Membranes

Parameter	Range of variables
Dope solution composition, wt %	CA/NMP/PVP360K/Water (19 : 74.8 : 5 : 1.2)
Dope viscosity, cp	11,000
Dope flow rate, g/min	0.29
Bore fluid composition	85 wt % NMP in water
Bore fluid flow rate, cm^3/min	0.68
Air gap distance, mm	0
External coagulant	Water
Take-up speed, m/min	0.65
Coagulant temperature, °C	28
Dimensions of spinneret, mm	1.0/0.6 (OD/ID)
Spinneret temperature, °C	24

CA/PVP (360K)/*N*-methyl-2-pyrrolidone (NMP)/water.[13] The work described in this article continues the authors' earlier study and focuses on the effect of hypochlorite concentration on properties and morphology of an outer-skin CA hollow-fiber UF membrane treated for a fixed period of 24 h.

EXPERIMENTAL

Materials

Cellulose acetate (CA) was purchased from Eastman Chemical (Kingsport, TN). Poly(vinyl pyrrolidone) (PVP360K, average MW 360,000) was supplied by Sigma-Aldrich (St. Louis, MO). *N*-Methyl-2-pyrrolidone (NMP, >99%) was supplied by Merck (Darmstadt, Germany). Bovine serum albumin (BSA, MW 66,000; Calbiochem, La Jolla, CA) was used to characterize the separation performance of the hollow-fiber UF membranes. Sodium hypochlorite solution (10–12%) from Sino Chemical Co. (Taipei, Taiwan) was used for the posttreatment of the UF hollow-fiber membranes.

Fabrication and posttreatment of hollow-fiber UF membranes

Hollow-fiber UF membranes were spun from a spinning dope of CA/PVP (360K)/NMP/water with a mass ratio of 19.0 : 5.0 : 74.8 : 1.2 using a wet-spinning process, as described elsewhere.[14,15] The experimental parameters used in spinning of UF hollow-fiber membranes are summarized in Table I.

The as-spun fibers were rinsed in flowing town water at room temperature for 16 h. After rinsing, the fibers were immersed in a 50% aqueous glycerol solution for 48 h and then dried in air at room temperature for making test modules. To investigate the effect of hypochlorite treatment on membrane properties, the rinsed fibers were immersed in a hypochlorite solution over a range of concentrations for a fixed period of 24 h. Before the treatment, the pH of the hypochlorite solution had to be adjusted from 11.4 to 7.0 by using H_2SO_4 because CA membranes could not tolerate high pH. The treated fibers were then rinsed again in flowing town water. After that, the same procedure as described above was followed.

Characterization of prepared hollow-fiber UF membranes

Flux and retention measurements of the UF membranes were carried out in a cross-flow filtration setup at room temperature of 25 ± 1°C, as shown in Figure 1.[14] Because the hollow fibers have an outer dense skin, the feed was pumped into the shell side of the module and the permeate was collected at the lumen side of fibers. Five 20-cm-long fibers were assembled into a test module. Three modules were freshly prepared and tested for each membrane sample and the average of their performance was reported. Ultrapure water was used to characterize the pure water flux and also used to prepare the feed solutions containing 100 mg/L of the different solutes used. The average transmembrane pressure was 100 kPa and the feed velocity was 0.6 m/s. The solute concentration in the feed or in the solution of permeate was determined using a TOC-V Analyser (Shimadzu, Kyoto, Japan). The permeate flux and percentage retention of the hollow-fiber UF membranes were calculated by using eqs. (1) and (2), respectively, as follows:

$$\text{Permeate flux} = Q/(A \times \Delta P) = Q/(N\ \pi d_o l \times \Delta P) \quad (1)$$

where Q is the volume flow rate of permeate (L/h), A is the effective membrane area (m^2), ΔP is transmembrane pressure (Pa), N is the number of fibers, d_o is the

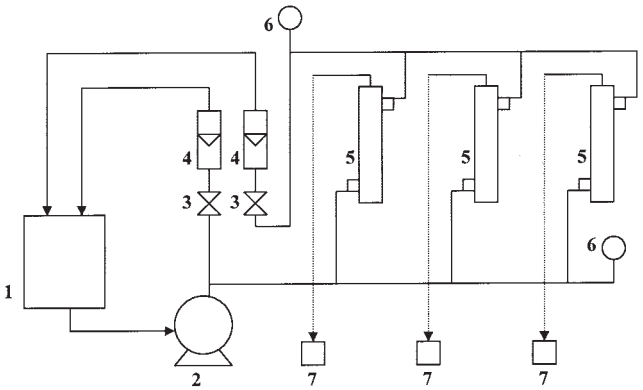

Figure 1 Experimental setup in testing of hollow-fiber UF membranes with an outer skin. 1: Feed tank; 2: pump; 3: valve; 4: flow meter; 5: hollow-fiber membrane module; 6: pressure gauge; 7: beaker for collecting permeate.

TABLE II
Dimension of Hollow-Fiber UF Membrane

Outer diameter (μm)	Inner diameter (μm)	Wall thickness (μm)
1140	730	205

outer diameter of fiber (m), and l is the effective fiber length (m).

$$\text{Retention} = (1 - C_p/C_f) \times 100\% \quad (2)$$

in which C_f (mg/L) and C_p (mg/L) represent the solute concentrations in the feed and permeate, respectively.

The structure and morphology of the fibers were studied using a JSM 5310 LV model SEM apparatus (JEOL, Tokyo, Japan), as described in previous work.[12]

Study of fouling tendency of hollow-fiber membranes

The pure water flux through a fresh membrane, the solution flux, and pure water flux through a fouled membrane were measured as J_{vw}, J_v, and J_{va}, respectively. The membrane fouling tendency was analyzed using the osmotic-pressure–adsorption model[16] in which it was assumed that the decline in flux would result from two main mechanisms: (1) reduction in hydrodynamic driving force by osmotic pressure ($\sigma\Delta\Pi$) and (2) increase in fouling resistance (R_a) from surface adsorption and pore plugging. The detailed description on study of fouling tendency of hollow-fiber membranes was introduced elsewhere.[13]

RESULTS AND DISCUSSION

Effect of hypochlorite concentration on flux and retention

The dimension of the hollow-fiber UF membrane was measured as shown in Table II. Measurements of pure water fluxes and BSA retentions of the membranes treated with a hypochlorite solution over different concentrations are summarized in Table III. It can be seen that the pure water flux of the final membrane increased with increasing hypochlorite concentration. This could be explained by the fact that the removal of PVP from the membrane increased with increasing hypochlorite concentration, attributed to the reaction between hypochlorite and PVP that caused chain scission of PVP molecules and eventually the leaching of PVP from the membrane, resulting in reduction of the swelling of PVP in the pores of the membrane. The result was also in agreement with previous work.[12] The retention of BSA slightly decreased from 98 to 96.2% when the hypochlorite concentration increased from 0 to 100 mg/L, although it dropped sharply to 85.8% when the hypochlorite concentration reached 200 mg/L. The latter may imply that the membrane pore size could be significantly increased, which was subsequently supported by SEM images.

Fouling tendencies of hollow-fiber membranes

Table IV shows experimental measurements of J_{vw}, J_v, and J_{va} and the calculated values of R_m (the hydraulic resistance of the membrane), R_a, $\sigma\Delta\Pi$, and J_{rt} (the total relative flux reduction) of the membranes treated with different hypochlorite concentrations. It can be seen that R_m decreased with increasing hypochlorite concentration, which was consistent with the results of pure water flux in Table III. It also shows that R_a significantly increased compared to R_m, whereas osmotic pressure $\sigma\Delta\Pi$ slightly decreased, in comparison to operating pressure (100 kPa), with increasing hypochlorite concentration. In other words, the contribution of R_a to J_{rt} was predominant compared with the contribution of $\sigma\Delta\Pi$ to J_{rt}. As a result, the total relative flux reduction J_{rt} increased with increasing hypochlorite concentration. These results indicate that the treated membrane experienced an increased fouling tendency with increasing hypochlorite concentration. The increased fouling tendency could be attributed to the reduced hydrophilicity of the treated membrane as a result of the removal of PVP contents in the membrane matrix after hypochlorite treatment, which was also supported by SEM images of the membranes. It should be pointed out that for the CA/PVP membranes, J_{rt} values of untreated H01 and treated H04 were only 0.029 and 0.102 (max), respectively, which were much lower than values for untreated (0.107) and treated (0.780) PSU/PVP membranes.[12] The results indicated that hydrophilic CA membranes had a much lower fouling tendency than that of hydrophobic PSU membranes.

Morphology of hollow-fiber membranes

Figure 2 shows SEM images of the as-spun hollow-fiber membrane without hypochlorite treatment. Figure 2(a) and (b) indicate that the cross section of the

TABLE III
Effect of Hypochlorite Concentration on Membrane Flux and Retention

Fiber ID	Hypochlorite concentration (mg/L)	Pure water flux ($\times 10^{-5}$ L m^{-2} h^{-1} Pa^{-1})	Retention (%)
H01	0	22.7	98.0
H02	50	29.3	97.6
H03	100	44.2	96.2
H04	200	77.5	85.8

TABLE IV
Experimental Measurements of J_{vw}, J_v, and J_{va} and the Calculated Values of R_m, R_a, $\sigma\Delta\Pi$, and J_{rt}

Hypochlorite concentration (mg/L)	Flux ($\times 10^{-6}$ ms^{-1})			Resistance ($\times 10^{11}$ m^{-1})		$\sigma\Delta\Pi$ (Pa)	J_{rt}
	J_{vw}	J_v	J_{va}	R_m	R_a		
0	6.31	6.13	6.25	178	1.71	1920	0.029
50	8.14	7.85	8.00	138	2.41	1870	0.036
100	12.3	11.6	11.8	91.3	3.87	1690	0.057
200	21.5	19.3	19.6	52.2	5.06	1530	0.102

as-spun fiber had a spongelike structure, which confirmed that addition of PVP favored the suppression of macrovoids in the membrane.[8,10–13] Figure 2(c) shows that the inner edge of the fiber was porous, whereas Figure 2(d) shows that the outer edge was very dense, with a thickness of about 3 μm. Figure 2(e) and (f) also reveal that the inner surface of the fiber was porous and the outer surface was very dense, even at a high magnification of $\times$10,000, in agreement with the structures of Figure 2(c) and (d), respectively. These images indicate that the fiber had an outer dense skin responsible for the retention, which confirmed our design objective that water as a strong coagulant started to precipitate the nascent fiber from the outside and the precipitation moved to the inside until the whole fiber matrix was incorporated, whereas a bore fluid with high solvent concentration (85% NMP in water) was used to delay the liquid–liquid phase inversion at the inner surface of the nascent fiber.

As a typical example, Figure 3 shows SEM images of the hollow-fiber membrane treated with a hypochlorite solution of 200 mg/L. It is evident that, after the hypochlorite treatment, the thickness of the dense region near the outer edge of the fiber decreased [comparing Fig. 3(d) to Fig. 2(d)], the network pore size on the inner surface increased [comparing Fig. 3(e) to Fig. 2(e)], and especially the outer dense surface became microporous [comparing Fig. 3(f) to Fig. 2(f)], which supported the results of flux and retention measured above. These changes in the membrane surface morphology could be attributed to the removal of PVP contents in the membrane. It might be concluded that hypochlorite treatment could increase the membrane

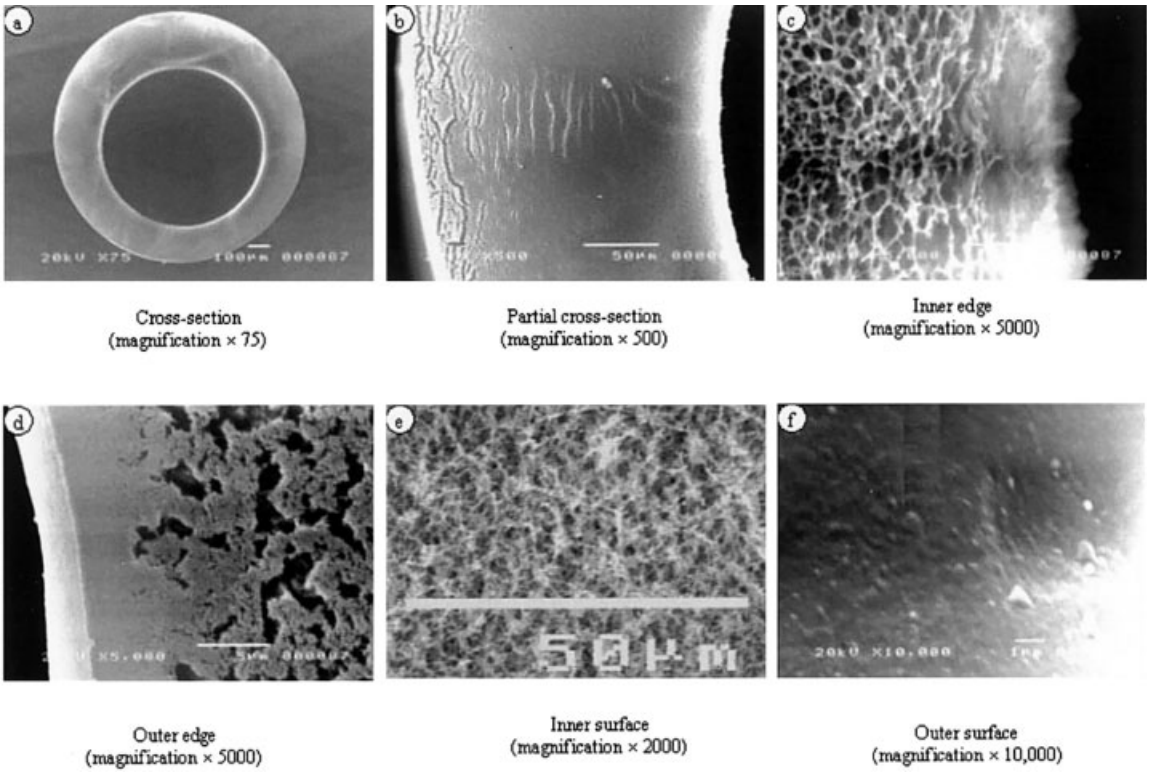

Figure 2 SEM images of hollow-fiber membrane without hypochlorite treatment.

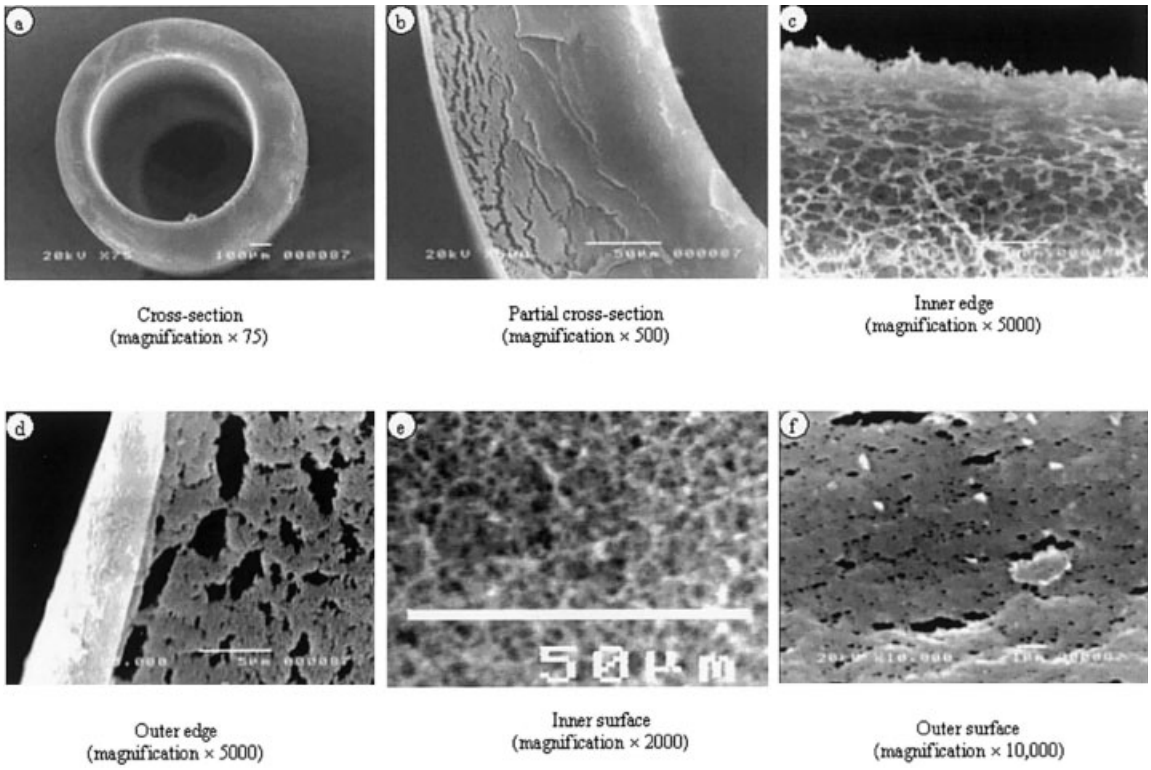

Figure 3 SEM images of hollow-fiber membrane treated with hypochlorite (200 mg/L).

pore size, which provided an additional option of altering the pore size of UF membranes more easily than other methods such as controlling the spinning conditions, dope composition, and additives, for example. It should be pointed out that the increase in pore size, from Figure 2(f) to Figure 3(f), seems greater compared to the enhancement in flux from H01 to H04, the cause for which needs further investigation.

CONCLUSIONS

A cellulose acetate hollow-fiber ultrafiltration membrane was developed from a dope solution containing CA/PVP360K/NMP/water using a wet-spinning process. The experimental results showed that the pure water flux of the treated membrane increased with increasing hypochlorite concentration. The treated membrane experienced an increased fouling tendency with increasing hypochlorite concentration because the hydrophilicity of the treated membrane decreased as a result of the removal of PVP contents in the membrane matrix after hypochlorite treatment. SEM images revealed that the membrane had an outer dense skin and a porous inner surface and had a spongelike structure, which confirmed that addition of PVP favored the suppression of macrovoids in the membrane. The membrane pore size was significantly increased when the hypochlorite concentration reached 200 mg/L.

References

1. Sourirajan, S.; Matsuura, T. Reverse Osmosis/Ultrafiltration Process Principles; NRCC Publications: Ottawa, Canada, 1985.
2. Osmonics, 2″, 4″, and 8″ RO Cellulose Acetate, Catalogue of Products; Osmonics, Inc.: Minnetonka, MN, 2001.
3. Millipore Corp. MF-Millipore™ Membrane Filters, Catalogue of Products; Millipore Corp.: Bedford, MA, 2001.
4. Schell, W. J. ACS Div Fuel Chem Prepr 1975, 20, 253.
5. Zhu, G. H.; Chung, T. S.; Loh, K. C. J Appl Polym Sci 2000, 76, 695.
6. Jie, X. M.; Cao, Y. M.; Lin, B.; Yuan, Q. J Appl Polym Sci 2004, 91, 1873.
7. Qin, J.-J.; Cao, Y. M.; Li, Y. Q.; Li, Y.; Oo, M. H.; Lee, H. Sep Purif Technol 2004, 36, 149.
8. Roesink, H. D. K. PhD Thesis, University of Twente, The Netherlands, 1989.
9. Wienk, I. M.; Meuleman, E. E. B.; Borneman, Z.; vanden Boomgaard, A.; Smolders, C. A. J Polym Sci Part A: Polym Chem 1995, 33, 49.
10. Xu, Z. L.; Chung, T. S.; Huang, Y. J Appl Polym Sci 1999, 74, 2220.
11. Qin, J.-J.; Wong, F. S. Desalination 2002, 146, 307.
12. Qin, J.-J.; Wong, F. S.; Li, Y.; Liu, Y. T. J Membr Sci 2003, 211, 139.
13. Qin, J.-J.; Li, Y.; Lee, L. S.; Lee, H. J Membr Sci 2003, 218, 173.
14. Qin, J.-J.; Chung, T. S. J Membr Sci 1999, 157, 35.
15. Qin, J.-J.; Wang, R.; Chung, T. S. J Membr Sci 2000, 175, 197.
16. Ko, M. K.; Pellegrino, J. J. J Membr Sci 1992, 74, 141.