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Preparation and Characterization of Composite Hollow Fiber Reverse Osmosis Membranes by Plasma Polymerization. 2. Reproducibility of the Plasma Polymerization Process and Durability of the Resulting Coated Membrane

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The reproducibility of the plasma polymerization process was examined in a semicontinuous coating of hollow fibers, 6 fibers in lengths of approximately 12–15 m, by evaluating the performance of reverse osmosis membranes. The uniformity of the coating along the length of hollow fibers, as well as the reproducibility of the process, was found to be satisfactory when electrodes were conditioned in the actual conditions of plasma polymerization to be employed and plasma polymerization conditions were carefully controlled. The durability of the coated hollow fibers was then investigated in the following test media: hot water, low pH, high pH, and 0.1% NaOCl solutions. A threshold value of glow discharge parameter W/FM was found to be crucial in the performance of the reverse osmosis membrane and durability of the coated hollow fibers. Plasma polymerized composite membranes showed remarkable durability.

Introduction

The semicontinuous plasma polymerization process has been discussed in part 1 of this series of papers (Heffernan et al., 1984). Control of the fundamental parameters for the coating operation was found to provide a satisfactory plasma polymer for composite reverse osmosis membranes. It has also been found that there is a critical coating thickness (~200 Å) which rejects salt most effectively. This thickness is dependent on the type of substrate and monomer used as well as glow discharge conditions. As observed in the previous paper, it is possible to continuously coat a long hollow fiber (~12 m long) with the semicontinuous system when the discharge parameters are well controlled, although the performance of the reverse osmosis membranes made with allylamine plasma polymer was not as good as it was hoped for (Hollahan and Wydeven, 1973; Bell et al., 1975; Peric et al., 1977). Preconditioning of the elctrodes also was found to be an important factor to achieve stable and continuous glow discharge in the plasma polymerization of allylamine. Since the repeatability of this process has not been thoroughly investigated until this time, it was considered essential to evaluate the factors which affect the process reproducibility, especially the electrical parameters for glow discharge which are known to fluctuate with time (Heffernan et al., 1984).

For further improvement of the reverse osmosis membrane, it is also important to test the durability of these membranes. For example, reverse osmosis membranes such as cellulose acetate and polyamide, etc., seem to have a weak chlorine resistance (0.5 ppm) (Channabasappa, 1977). This weak chlorine resistance is crucial in seawater application.

On the other hand, as seen in a previous paper (Bell et al., 1975), a plasma-polymerized allylamine deteriorated at elevated temperatures, although the reverse osmosis membrane performance was successful under normal conditions (water flux, 6–8 gfd and salt rejection, 99%). However, Yasuda et al. (1975a,b; 1976) reported that the chemical stability and temperature effect of reverse osmosis performance of a plasma polymerized membrane were excellent, and they also suggested that the nitrogen in the polymer could be a site of chlorine reaction resulting in a weak chlorine resistance.

In this study, we intended to investigate the reproducibility and the durability of composite membranes by studying the performance of membranes prepared with allylamine plasma polymer.

Experimental Section

Details of the plasma reactor and reverse osmosis equipment used were described in part 1 (Heffernan et al., 1984). The allylamine monomer used is a commercial product of the Aldrich Co. which is degassed by pumping prior to use. Polysulfone hollow fibers used as the substrate were the same as ones described in part 1.

In order to test the chemical and physical stability of the coated membrane, some test environments were prepared as follows: (a) free chlorine resistance, 0.1% NaOCl solution; (b) alkali resistance, NaOH solution of pH 11; (c) acid resistance, HCl solution of pH 2; (d) temperature resistance, distilled water at 95 °C; (e) combined temperature and chlorine resistance, hot water followed by 0.1% NaOCl solution.

Since the chlorine resistance is one of the important factors to develop reverse osmosis membranes in seawater application, a severe test condition, consecutive hot water and 0.1% NaOCl solution, was chosen to thoroughly test deterioration of plasma polymerized reverse osmosis membranes.

Before the reverse osmosis tests, the coated membrane was soaked in each of these media for 30 min and then rinsed with distilled water. These coated hollow fibers, as well as nontreated fibers, were loaded in the reverse osmosis test loops. A 2% salt solution at a pressure of 1300 psi was circulated through the loops.

The technique employed for membrane performance measurements involved the accelerated degradation of membranes by exposure to extreme conditions for relatively short periods of time prior to insertion into the reverse osmosis test equipment. Although this static

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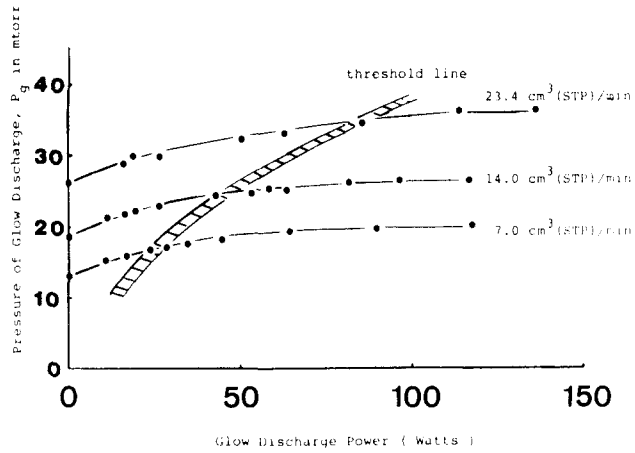

Figure 1. Relationship between pressure of glow discharge and discharge power.

Table I. Reproducibility of Fiber Membranes Prepared by Continuous Plasma Coating. Reaction Condition A[a]

coating time,[b] min	salt rejection, %	flux, gfd
10	85.4	5.57
25	85.5	4.26
50	87.7	3.61
85	81.9	5.60
100	87.4	4.77
115	88.3	3.58
135	83.6	6.20
155	89.0	3.68
	av 86.1 ± 2.30	av 4.66 ± 0.97

[a] Membrane preparation conditions: current, 105 mA; allylamine flow rate, 14.0 cm³(STP)/min; pressure, 18.0 m torr; fiber feed rate, 8.12 cm/min. Reverse osmosis test conditions: 2.0% NaCl; pressure, 1300 psig; time, 48 h. [b] The time elapsed from the start of the operation.

method is easy to apply, there are a number of differences between such experiments and long-term dynamic operation of membranes. The most important of these are that with static tests, no differential pressure exists across the hollow fiber, the test medium does not flow over the fiber surface, and no water flux occurs. However, in view of the fact that dynamic experiments take an excessive period of time to complete, the static approach has significant appeal where only first-order stability information is required. This is particularly true for composite membranes in which plasma polymer is only 200 Å thick.

The reproducibility of the polymerization process was tested by repeating the process under controlled discharge conditions. Since the process is simicontinuous, the uniformity of the coating was also examined over the entire length of the fibers at intervals along the 12-m fibers (the length of each test fiber was 80 cm). In the coating process, either wattage or current was closely controlled to obtain the uniform coating.

Results and Discussion

A. Threshold Value of Composite Glow Discharge Parameter, *W/FM*, and Reproducibility of the Plasma Polymerization Process. A rough estimate of the threshold value of *W/FM* (Yasuda and Hirotsu, 1978a) was made by measruing the system pressure during plasma polymerization (Yasuda and Hirotsu, 1978b). The system pressure at a given flux rate of monomer reaches its plateau as discharge power is increased (see Figure 1). Since no further pressure increase means no net increase in the total number of gaseous species in the reactor system, attaining this plateau means that more than sufficient discharge

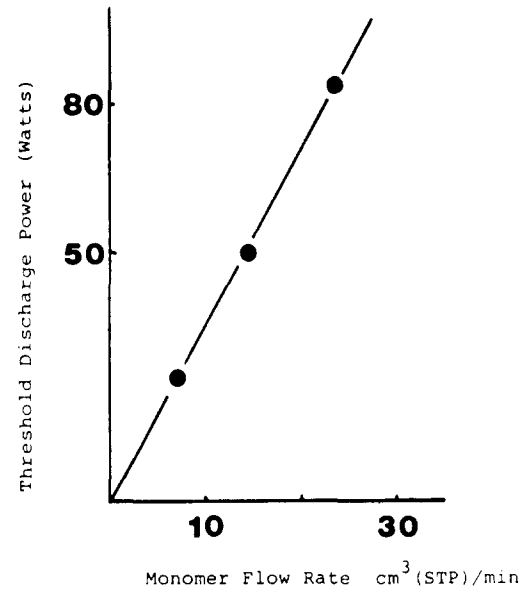

Figure 2. Relationship between threshold discharge power and monomer flow rate.

Table II. Reproducibility of Fiber Membranes Prepared by Continuous Plasma Coating. Reaction Condition B[a]

coating time,[b] min	salt rejection, %	flux, gfd
24	81.2	0.14
24	80.4	0.15
32	77.7	0.29
55	78.2	0.55
70	75.5	0.10
	av 78.6 ± 2.03	av 0.25 ± 0.16

[a] Membrane preparation conditions: current, 105 mA; allylamine flow rate, 7.0 cm³(STP)/min; pressure, 11.0 m torr; fiber feed rate, 10.9 cm/min. Reverse osmosis test conditions: 2.0% NaCl; pressure, 1300 psig; time, 48 h. [b] The time elspsed from the start of the operation.

Table III. Reproducibility of Fiber Membranes Prepared by Continuous Plasma Coating. Reaction Condition C[a]

coating time,[b] min	salt rejection, %	flux, gfd
7	79.8	2.53
7	81.1	2.38
7	79.0	2.49
32	82.6	1.10
58	84.9	2.00
	av 81.5 ± 2.10	av 2.10 ± 0.53

[a] Membrane preparation conditions: current, 105 mA; allylamine flow rate, 25.0 cm³(STP)/min; pressure, 23.0 m torr; fiber feed rate, 10.8 cm/min. Reverse osmosis test conditions: 2.0% NaCl; pressure, 1300 psig; time, 48 h. [b] The time elapsed from the start of the operation.

power (energy) is being supplied, and the mass flow rate becomes the rate-determining step of plasma polymerization. Plasma polymerization in this plateau region will be nearly independent of fluctuations in discharge power; i.e., plasma polymerization is independent of discharge power in this region. Because of this situation, minor changes in discharge conditions during the transient stage of plasma polymerization do no affect the rate of deposition. The pressure changes with discharge power are shown in Figure 1, and the empirical threshold discharge power (wattage) as a function of monomer flux rate is shown in Figure 2.

Table IV. Reproducibility of Fiber Membranes Prepared by Continuous Plasma Coating. Reaction Condition D[a]

coating time,[b] min	salt rejection, %	flux, gfd
64	73.0	13.2
118	71.0	11.5
	av 72.0 ± 1.0	av 12.4 ± 0.85

[a] Membrane preparation conditions: current 35 mA; allylamine flow rate, 14.0 cm³(STP)/min; pressure, 20.0 m torr; fiber feed rate, 4.24 cm/min. Reverse osmosis test conditions: 2.0% NaCl; pressure, 1300 psig; time, 48 h. [b] The time elapsed from the start of the operation.

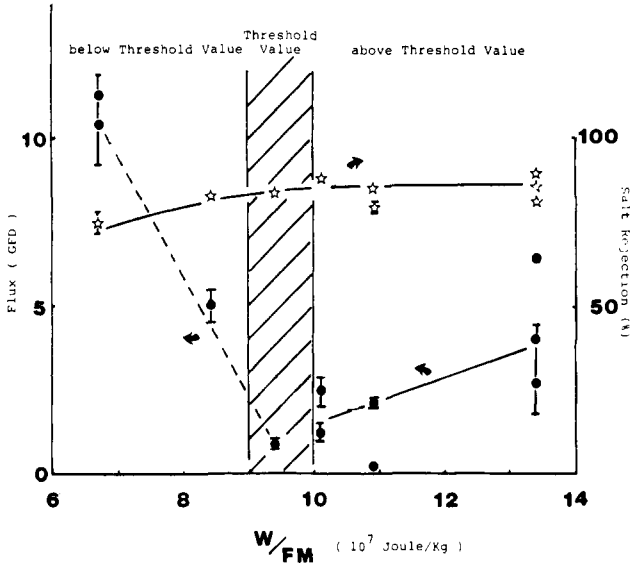

Figure 3. Relationship between flux and salt rejection vs. *W/FM*.

Tables I through IV compare desalination data over a period of plasma coating time under four sets of glow discharge conditions. Here, discharge current was carefully controlled but discharge power was permitted to fluctuate. The fiber speed was adjusted (the substrate moves through the glow zone at a fixed velocity in this system) so that the same amount of film was deposited for each set of conditions. The standard deviation in salt rejection by these samples is 2.7, 2.6, 2.6, and 1.4%, respectively. The scatter in the water flux level is greater.

However, when one of the other glow discharge parameters (discharge power) is well controlled during the coating process, the scatter in the reverse osmosis membrane performances is much reduced as shown in Table V. Control of the discharge power is thus shown to be more effective in maintaining uniformity of the coating than control of discharge current.

Tables I through V also establish the effect of reaction conditions on the reverse osmosis membrane performances. The reaction conditions corresponding to series 108-2 in Table V represent the optimum combination of salt rejection (88.0 ± 0.7%) and water flux (1.29 ± 0.26 gfd). This optimum reaction condition can be obtained in the zone above the threshold value in Figure 3, representing a relationship between water flux and salt rejection versus W/FM values. The trends we can observe in Figure 3 are (1) salt rejection increases with increasing *W/FM* but tends to level off above the threshold value indicated by the hatched zone, and (2) water flux declines sharply with increasing *W/FM* and reaches the minimum value at around the threshold value and increases slightly with further increases in *W/FM*. Therefore, it is seen that a

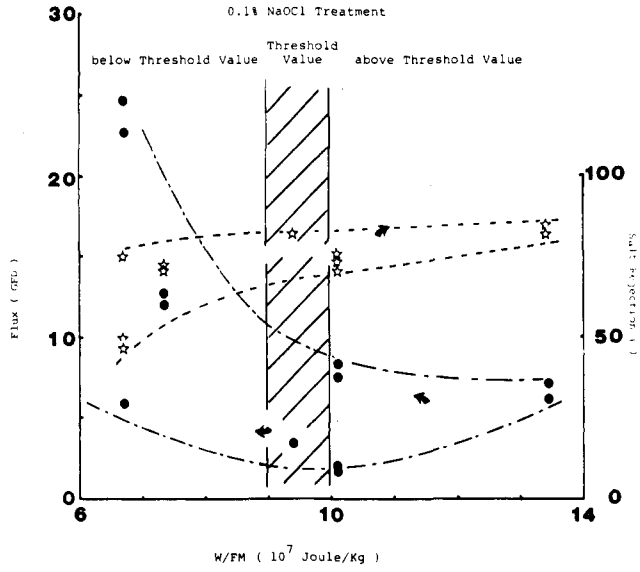

Figure 4. Relationship between flux and salt rejection vs. *W/FM* after 0.1% NaOCl treatment.

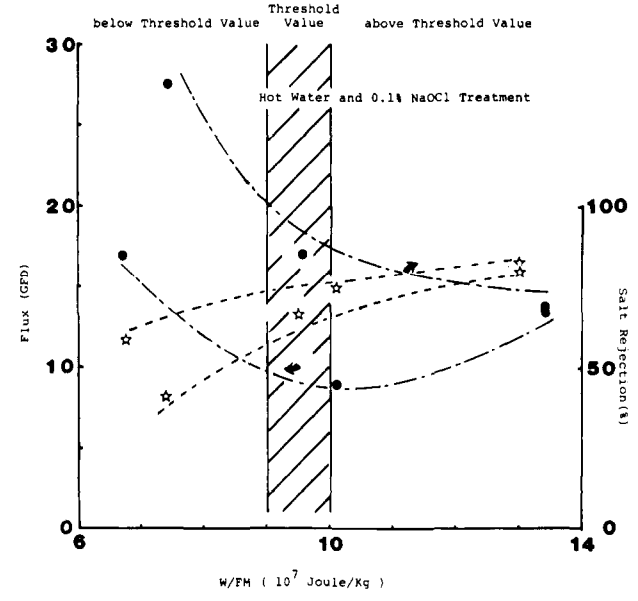

Figure 5. Relationship between flux and salt rejection vs. *W/FM* after a treatment with hot water and 0.1% NaOCl.

critical discharge condition exists to obtain an optimum combination of water flux and salt rejection in the reverse osmosis membrane performances.

The results of this reproducibility study also show that it is possible to prepare composite membranes in a reproducible manner by the continuous coating process described here.

B. Durability Tests on Composite Reverse Osmosis Membrane. In order to see the effect of a variety of test environments on the performance of reverse osmosis of the coated fibers after they have been exposed to accelerate test media, these prestressed fibers were compared with unstressed coated fibers. When the coated membranes are exposed to severe accelerated test conditions, (1) a noticeable increase in water flux but (2) relatively small decline in salt rejection was generally observed. The dependence of reverse osmosis characteristics on *W/FM* found for control samples was still found in the prestressed samples, but the deviation (scattering of data) became more pronounced as shown in Figure 4 for NaOCl-treated membrane. The deviation becomes narrower as the value of *W/FM* increases. The dependence of salt rejection on

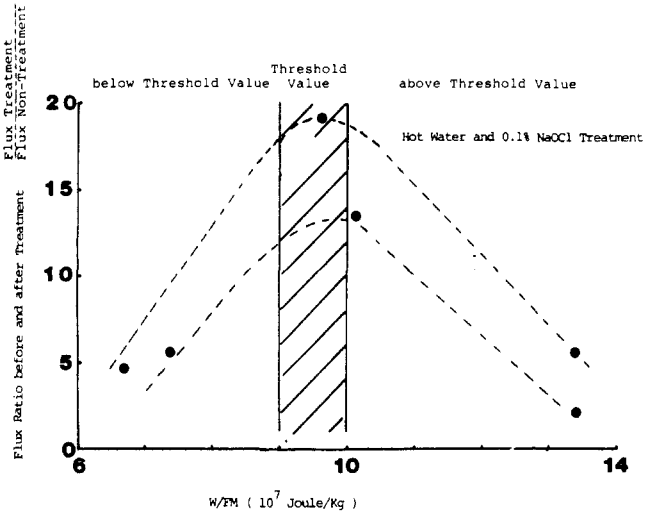

Figure 6. Changes of flux ratio before and after a treatment with hot water and NaOCl (0.1%).

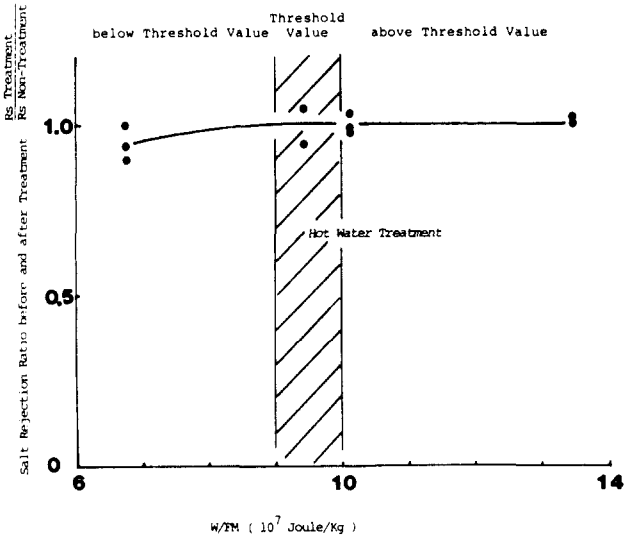

Figure 7. Changes of salt rejection ratio before and after hot water treatment.

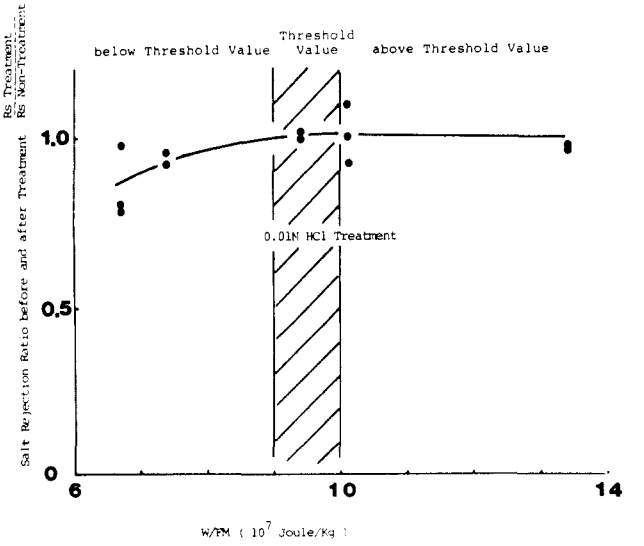

Figure 8. Changes of salt rejection ratio before and after 0.01 N HCl treatment.

W/FM is most evident for the most severe case of consecutive hot water and NaOCl treatments (see Figure 5). The most pronounced increase in water flux after prestressing (compared to corresponding unstressed samples)

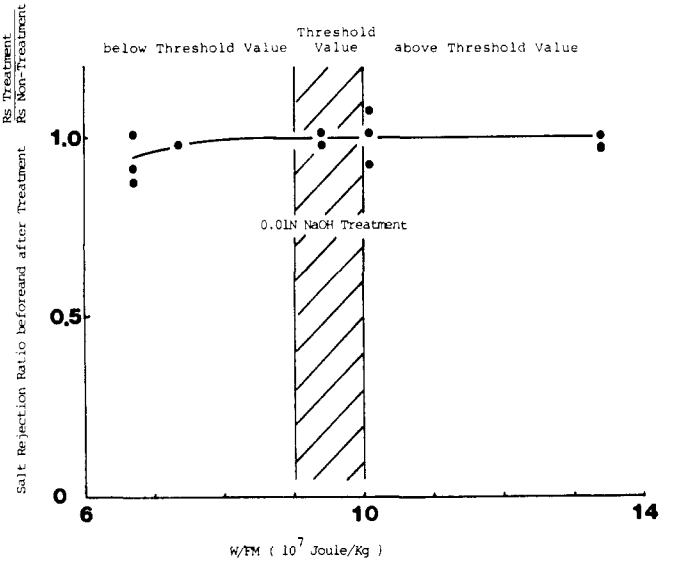

Figure 9. Changes of salt rejection ratio before and after 0.01 N NaOH treatment.

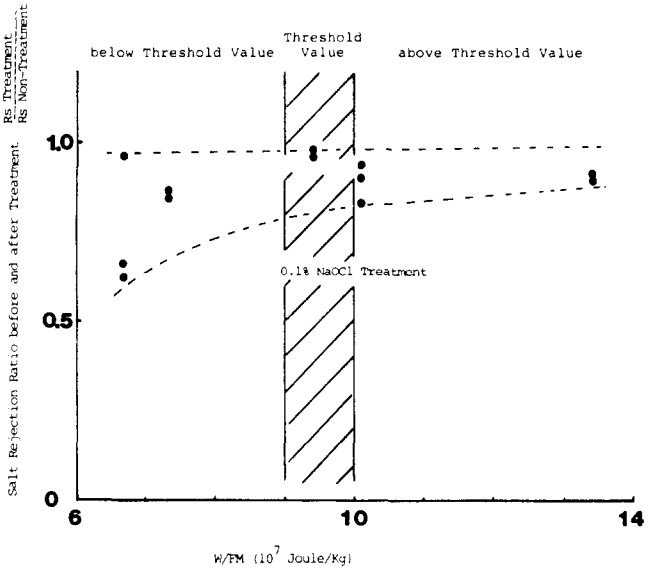

Figure 10. Changes of salt rejection ratio before and after 0.1% NaOCl treatment.

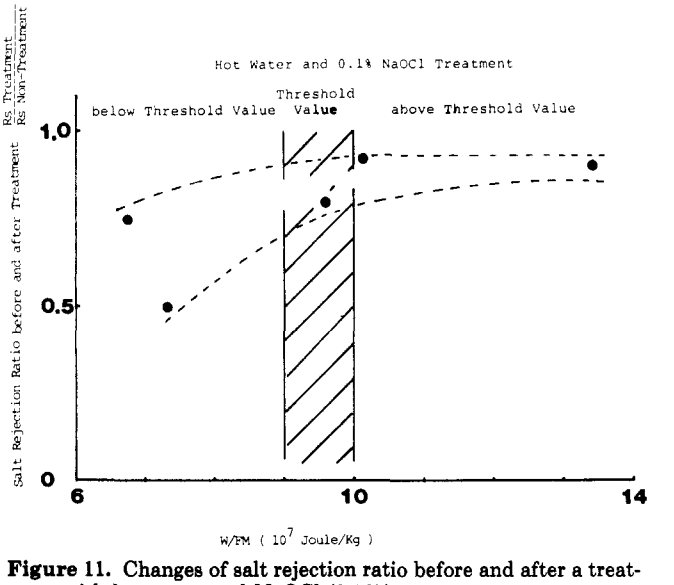

Figure 11. Changes of salt rejection ratio before and after a treatment with hot water and NaOCl (0.1%).

Table V. Effect of Coating Location on Reverse Osmosis Tests[a]

fiber no.	fiber feed, cm/min	total length, cm	reverse osmosis tests: flux	av and std dev	R_s	av and std dev
106-1-E[b]	7	1200	5.33		82.8	
G			5.56		83.9	
I			4.92		84.0	
K			4.94	5.00 ± 0.45	82.8	83.0 ± 1.1
O			4.39		83.3	
Q			4.37		83.5	
R		4.92	4.92		84.0	
S			5.48		80.6	
108-2-C	7	1200	1.50		87.3	
G			0.93		87.0	
K			1.07		88.7	
M			1.11	1.29 ± 0.26	88.7	88.0 ± 0.7
Q			1.26		88.9	
S			1.73		87.6	
U			1.44		87.7	

[a] 106 series: discharge power, 20 W; monomer flow rate, 7 cm³(STP)/min; 108 series: discharge power, 60 W; monomer flow rate, 14 cm³(STP)/min; R.O. test conditions, feed soln, 2% NaCl soln; applied press., 1300 psi. [b] Coating position of fiber.

is observed with samples prepared with the threshold W/FM value. This trend is shown in Figure 6 for membrane treated by the consecutive hot water and NaOCl solution.

The durability of membranes may be visualized by the ratio of salt rejection before and after the various prestresses. This ratio as a function of glow discharge parameter (W/FM) is shown in Figures 7 through 11. From these figures, particularly for Figures 10 and 11, it is obvious that W/FM is a very important parameter which determines the durability of reverse osmosis membranes.

Although the maximum value of salt rejection obtained by this particular combination of allylamine and polysulfone porous hollow fibers is not high enough for seawater application, these data seem to demonstrate that remarkably good durability can be obtained by plasma polymerization. Incidentally, in addition to the chemical stability of allylamine plasma polymerized membrane, it was found that they can be stored without any special care.

Conclusions

1. Hollow fiber reverse osmosis membranes prepared by plasma polymerization have been shown to exhibit good salt rejection with high water flux. Although further improvement should be possible in the maximum salt rejection (90%), the water flux obtained is very good for hollow fiber membranes.

2. Allylamine plasma polymers have been shown to possess a high degree of chemical stability under extreme conditions of pH and in free chslorine oxidizing environments. If most commercially available reverse osmosis membranes were exposed to these test media, severe deterioration of their performance would result almost immediately.

3. Plasma polymerization parameter given by W/FM plays an important role in obtaining excellent durability of membrane. A critical value of W/FM exists above which good durability can be obtained.

4. Plasma polymerization can be utilized in a continuous operation and its reproducibility is very good, particularly when a steady-state operation is maintained.

5. Overall performance of plasma polymerized composite hollow fiber membranes depends on the matching of substrate hollow fibers and plasma polymers. Therefore, further improvement may be possible by improving the hollow fibers suitable for the process. Excellent durability of plasma polymer layers found in this study seems to support this point; i.e., not high enough salt rejection is not due to the inferior semipermeable layer but perhaps it is due to incomplete coverage of excessively large pores, which exist on the surface of substrate fibers.

Registry No. Poly(allylamine) (homopolymer), 30551-89-4.

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