

Truly Chlorine-Resistant Polyamide Reverse Osmosis Composite Membrane

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SYNOPSIS

Truly chlorine-resistant polyamide reverse osmosis composite membranes were prepared by cross-linking the interface of the composite membrane. Such membranes possessed chlorine resistance one order of magnitude more than those of the commercially used polyamide composite membranes. The effect of the degree of cross-linking on chlorine resistance was also described. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Because of their superior performance in separation, polyamide reverse osmosis composite membranes have developed rapidly.¹ However, due to the limitation of the chemical structure of polyamide ultra-thin layers, their resistance to active chlorine is low. Scientists have invented various methods to improve them, but, because of overemphasis on the thin film itself, they did not obtain satisfactory results.²⁻⁴ To our knowledge, the effect of the interface of the composite membrane on chlorine resistance has been neglected. Through introducing reactive groups into the interface and cross-linking the interface, we have obtained membranes that possess chlorine resistance one order of magnitude more than those of the commercially used composite membranes and that are truly chlorine-resistant polyamide composite membranes.

EXPERIMENTAL

A polysulfone substrate membrane was prepared by the phase inversion process.² Its pore diameter is about 20 nm. Reactive groups were introduced to its surface by a chemical method.

A poly(phenylene-trimesoylamide) thin film composite membrane was deposited onto the polysulfone surface by interfacial polycondensation.² A

heat treatment was required to cross-link the molecules of the interface.

Chlorine resistance of the composite membrane was tested in 50 ppm NaClO (aq) for a certain time, then its rejection and water flux was tested under conditions of 5000 ppm NaCl (aq) at 1.5 MPa pressure.

Characterization of the degree of cross-linking at the interface was as follows: the O/C was measured by XPS with a VG ESCA-LAB MK-II using a pass energy of 10kV-20mA with a MgK α X-ray source.

RESULTS AND DISCUSSION

Figure 1 shows the effect of chlorine treatment of the composite membrane without cross-linking at the interface on salt rejection of the composite membrane. We found that the rejection decreased rapidly. Its chlorine resistance was about 500 ppm · h, which means that, even for short time use in seawater, its performance will be deteriorated. Even when the structure of the polyamide was cross-linked by trimesoyl chloride, its resistance to chlorine did not improve well; perhaps the cross-linking is not extensive because of its low reactivity. Figure 2 shows the effect of free chlorine on the salt rejection of the composite membrane with cross-linking of the interface. This membrane possesses very high resistance to free chlorine up to the level of a true chlorine resistance membrane, which must possess more than 20,000 ppm · h according to the present standard.² By suitable control of the interface, we

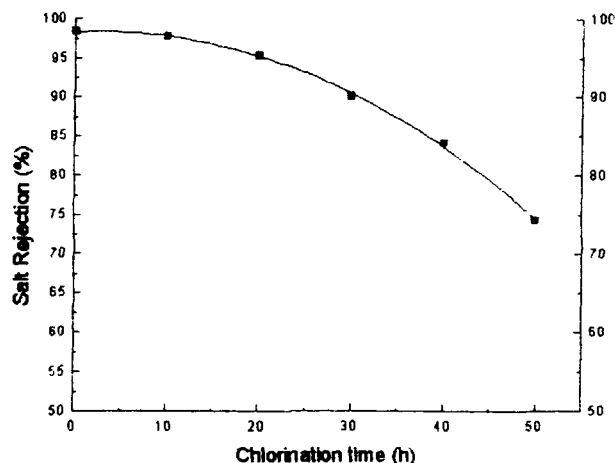


Figure 1 Effect of free chlorine on salt rejection of polyamide composite membrane without cross-linked interface. Test conditions: 5000 ppm NaCl; 50 ppm NaClO (aq); 1.5 MPa; 20°C.

could obtain such a membrane possessing chlorine resistance of 35,000 ppm·h; that is more than one order of magnitude of that of an ordinary polyamide membrane. The effect of Fe^{3+} ion on chlorine resistance is also shown in Figure 2. It is found that it still exhibits chlorine resistance of 25,000 ppm·h. But the performance of ordinary polyamide composite membranes rapidly decreased after chlorination treatment in Fe^{3+} conditions because of its catalysis. This means that cross-linking the molecules between polyamide and polysulfone in the in-

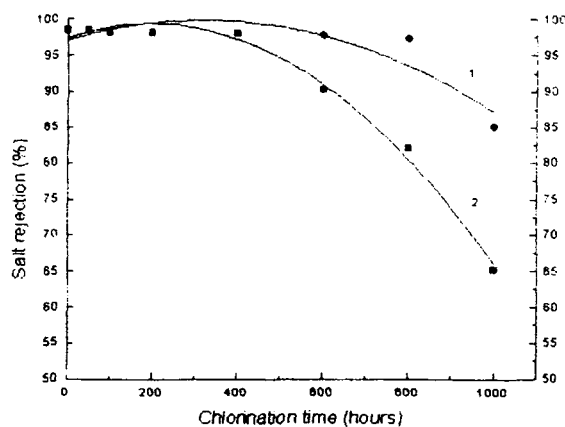


Figure 2 Effect of free chlorine on salt rejection polyamide composite membrane with cross-linking at interface: 1. Without Fe^{3+} ; 2. Fe^{3+} . Test conditions: 50 ppm NaClO (aq); pH = 11; 5000 ppm NaCl; 1.5 MPa; 20°C.

Table I Effect of Introducing Different Amount of Reactive Groups on Chlorine Resistance of Membrane^a

O/C	Chlorine Resistance ^b
0.25	500
0.43	5000
0.66	15000
0.82	35000

^a The amount was expressed by O/C at the interface.

^b The amount of chlorination (ppm·h) when the salt rejection decreased by 0.5%. Test conditions: 50 ppm [Cl]; 5000 ppm NaCl (aq); pH = 11; 20°C.

terface greatly enhanced the resistance to active chlorine, but crosslinking the polyamide molecules in the thin film did not enhance the chlorine resistance so much.² Table I shows the effect of different degrees of introduced reactive groups on the chlorine resistance of the membrane. Because the degree of cross-linking at the interface is difficult to characterize, we have chosen the amount of introduced reactive groups to represent the degree of cross-linking. It is found that the chlorine resistance of our membrane increases with the increase in degree of cross-linking, which illustrates that cross-linking the interface is the most effective methods to enhance chemical resistance.

CONCLUSIONS

Cross-linking the interface of these composite membranes can improve the chlorine resistance greatly. The more cross-linking bonds that are introduced, the more chlorine resistance the composite membrane possesses.

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