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Effective interface of a composite membrane serving as an ideally ultrathin barrier layer

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A novel idea relating to the selective barrier layer of a composite membrane is described. The effective interface of the composite membrane could act as a barrier layer which could be controlled to an ideally ultrathin thickness. A new type of polyamide composite membrane was prepared according to this idea, which possessed permeability and chemical resistance more than one magnitude greater than those of ordinary polyamide composite membranes. Copyright © 1996 Elsevier Science Ltd.

(Keywords: composite membrane interface; ultrathin barrier layer; crosslinking)

Introduction

Because of its superior performance in separation, the composite membrane has undergone rapid development since the concept was introduced[1]. The composite membrane is made by depositing an ultrathin barrier layer onto the surface of a suitable microporous substrate layer[2]. This approach has some key advantages over that of the integral asymmetric membrane approach. It offers the possibility of each layer being tailor-made for maximum performance[3]. In the reverse osmosis membrane, the ability to generate an ultrathin layer *in situ* on a microporous substrate allows the use of a variety of crosslinked polymeric composition, which will exhibit high water permeability and chemical resistance as well as high salt rejection[3,4]. However, due to the limitations of material and composite, the performance of composite membranes has not yet reached the ideal maximum, especially as regards permeability and chemical stability[5,6]. Scientists have invented various methods of improving the performance of composite membranes[7–11] but, because of their overemphasis on the thin film itself, they have not obtained satisfactory results[12]. To our knowledge, a potential ideally ultrathin barrier layer, which should be the effective interface of the composite membrane, has been neglected.

This work deals with the role of the effective interface of a composite membrane on the permeability and chemical resistance of the membrane. The results obtained show that the permeability and chemical resistance of the composite membrane are more than one magnitude greater than those of ordinary composite membranes if the effective interface is suitably controlled.

Experimental

The polysulfone–polyamide composite membrane was chosen as a typical composite membrane because of its present leading commercial position as an ultrathin film composite membrane.

A polysulfone substrate membrane with pore diameter about 20 nm was prepared by the phase inversion process[13]. Reactive groups were introduced to its surface by chemical or physical methods.

A poly(phenylene-trimesoylamide) thin film composite membrane was deposited onto the polysulfone surface by interfacial polycondensation[14]. A post-treatment was required to crosslink the molecules of polyamide and polysulfone in the interface through the reactive groups.

Figure 1 is a schematic diagram of this composite membrane. This interface-crosslinked structure possesses high chemical resistance; in addition, its stable interface can act as barrier layer whose thickness can be controlled to within a few nanometres, much less than that of the thin film itself[15,16]. Thus the permeability of the membrane can be greatly increased.

The surface of composite membrane was treated by 0.5% H_2O_2 (aq.) to make the thin layer lose its barrier function. Thus only the effective interface acts as the barrier layer.

The chlorine resistance of the composite membrane was tested in 50 ppm NaClO (aq.) for a certain period, after which its rejection and water flux were tested

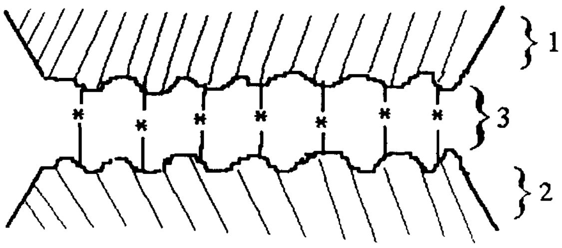

Figure 1 Schematic diagram of crosslinked interface composite membrane. 1: Polyamide ultrathin layer. 2: Polysulfone substrate layer. 3: Effective interface in which the polyamide and polysulfone are linked by reactive groups

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under conditions of 5000 ppm NaCl (aq.) at 1.5 MPa pressure.

To characterize the degree of crosslinking in the interface, the O/C ratio was measured by X.p.s. with VG ESCA-LAB MK-II, using a pass energy of 10 kV, 20 mA with an MgKα X-ray source.

Results and discussion

Figure 2 shows the effect of peroxide post-treatment time and degree of crosslinking on water flux and salt rejection of the composite membrane. Comparing curve C with curve A, we see that although post-treatment could enhance the water flux of the uncrosslinked interface composite membrane (curve C), its salt rejection decreased from 98.7% to about 80%, which meant that its barrier layer was damaged by peroxide. However, the flux of the crosslinked interface composite membrane (curve A) increased 10 times after 50 h peroxide post-treatment and retained a high salt rejection. In curve A, although the surface of the membrane was damaged by peroxide treatment and led to an increase in flux, the stable effective interface, which is a new barrier layer, still retains its barrier function to keep the salt rejection high. However, if the treatment is continued the rejection begins to decrease, which means that the extent of treatment must be carefully controlled; otherwise peroxide will not only damage the thin film but will also slightly damage the interface. On the other hand, the rejection can be kept constant if the extent of treatment is controlled to ensure that it is free of defect. Moreover, a long-term operating test has indicated that the effective interface possesses enough strength because of the sandwich structure of this composite membrane. These results mean that the interface is capable of serving as a selective barrier layer. Another result obtained is that the more reactive groups that are introduced, the less is the effect of post-treatment on rejection; this means that the more reactive groups introduced, the higher is the performance of the composite membrane.

The main disadvantage of the polyamide membrane is its low chlorine resistance, which means that after even a short time of use in seawater its performance will deteriorate. Evidently, this will limit its application[3]. Hence many efforts have been made to improve its chlorine resistance, including changing the chemical structure of the main chain, but these have not really solved this problem[17,18]. The chlorine resistance of our composite membrane has also been examined. *Figure 3* shows the effect of chlorine on the salt rejection of our composite membrane. This membrane possesses very high resistance to free chlorine, up to that of a true chlorine resistant membrane which must possess more than 20 000 ppm.h according to the present standard[3]. By suitable control of the interface we can obtain a membrane possessing a chlorine resistance of 35 000 ppm.h, that is more than one order of magnitude above that of an ordinary polyamide membrane.

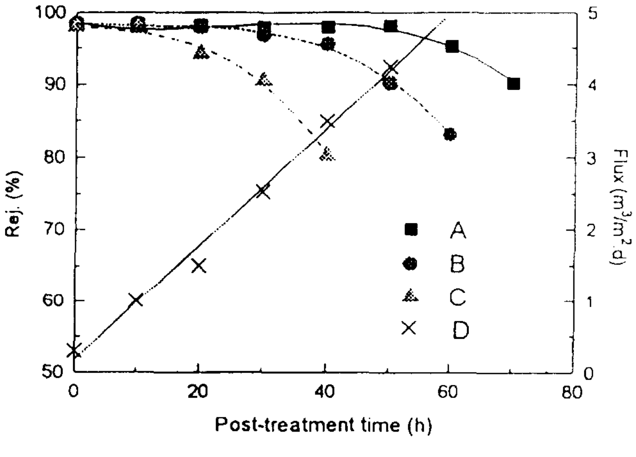

Figure 2 Effect of post-treatment and amount of reactive groups on performance of the membrane. The O/C ratio in the interface is used to characterize the amount of reactive groups introduced. A: O/C = 0.85. B: O/C = 0.53. C: O/C = 0.32. D: Effect of post-treatment on flux. Test conditions: 5000 ppm NaCl, 1.5 MPa, 20°C

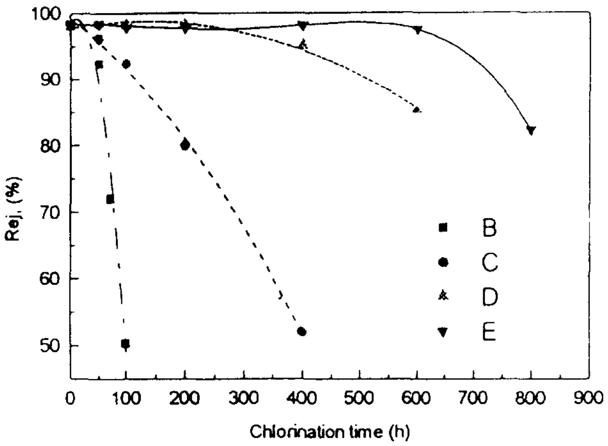

Figure 3 Effect of chlorination on performance of polyamide composite membrane. B: Without introducing reactive groups, 1 ppm Mn^{2+}. C: Without introducing reactive groups. D: Introducing reactive groups, 1 ppm Mn^{2+}. E: Introducing reactive groups. Test conditions: 50 ppm free chlorine, pH = 11, 5000 ppm NaCl, 1.5 MPa, 20°C

Table 1 Effect of introducing different amounts of reactive groups on the chlorine resistance of the membrane (amount expressed as O/C ratio in the interface). Test conditions: 50 ppm [Cl], pH = 11, 20°C

O/C	Chlorine resistance (ppm.h)
0.25	500
0.43	5 000
0.66	15 000
0.82	35 000

The effect of the Mn^{2+} ion on chlorine resistance was also examined. It was found that our membrane still exhibited a chlorine resistance of 15 000 ppm.h. In contrast, the salt rejection of ordinary polyamide composite membranes rapidly decreases after chlorination treatment in the presence of Mn^{2+} ions. The Mn^{2+} acts as a catalyst to speed up the chlorine attack on the polyamide and damages its structure[3], resulting in a decrease in the salt rejection of the membrane. An oxidation experiment also showed that our membrane possessed high tolerance to oxygen. This means that crosslinking the molecules between polyamide and polysulfone in the interface greatly enhanced its resistance to free chlorine and other chemicals, but crosslinking the polyamide molecules in the thin film did not enhance the chlorine resistance as much[3].

Table 1 shows the effect of different degrees of introduction of reactive groups on the chlorine resistance of the membrane. Because the degree of crosslinking in the interface is difficult to characterize, we have chosen the amount of introduced reactive groups to represent the degree of crosslinking. It is found that the chlorine resistance of our membrane increases with increasing degree of crosslinking, which illustrates that crosslinking the interface is the most effective method to enhance the chemical resistance.

From the above results we may conclude that the effective interface of a composite membrane can serve as a barrier layer. This ideally ultrathin selective barrier layer could enhance the permeability and chemical resistance of the composite membrane.

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