

Syntheses of chlorine resistant reverse osmosis membranes

Nowon Kim, Yong-Taek Lee

Department of Environmental Engineering, Dongeui Univ., Busan, Korea

College of Environment and Applied Chemistry, Kyunghee Univ., Yongin, Gyounggido, Korea

Abstract

Most of thin film composite reverse osmosis membranes include amide linkages, which are susceptible to chlorine attack resulting in N-chloro derivatives. This study examined a new method based on post-treatment of reverse osmosis membrane with various silane derivatives to improve chlorine resistance. The silane derivatives contain one alkyl group and three alkoxy groups such as trifluoromethyltrimethoxysilane, 3-aminopropylmethoxydiethoxysilane and 3,3,3-trifluoropropyltrimethoxysilane. Compared to commercial membranes, silane derivatives coated membranes showed significantly enhanced chlorine durability.

Introduction

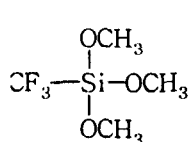
Reverse osmosis (RO) membrane processes are economical in removing a feed water into a purified permeate water. One of the most successful RO membranes is the aromatic polyamide thin film (TFC) composite membrane, which made from depositing the interfacial reaction product of the active layer. The aromatic polyamine having at least two primary amine substituents and the aromatic acyl halide has three acyl halide substituents on a porous polysulfone support[1]. RO membranes based on polyamide have excellent separation characteristics. However, two issues were brought up as major problems for RO membrane processes: (a) the risk of fouling, which may require extensive pretreatment or chemical cleaning of the membrane, (b) degradation of polyamide by chlorine results in a short lifetime of the membrane[2]. A number of research groups have been studied on fouling steps in systematic development and membrane development, because fouling is not only the problem of RO membrane processes but also all pressure-driven membrane processes[3]. In contrast, reports of chlorine resistant membranes are rarely found in the literature because degradation of membrane by residue chlorine is a unique problem for polyamide TFC RO membranes. Furthermore, the pre-treatment of activated carbon or reductant have been used widely for chlorine tolerance in the desalination process of seawater and brackish water. But a small amount of chlorine can reduce performances of polyamide membranes, degradation of RO membrane by chlorine is more or less a normal phenomenon of most RO systems. The amide linkage is easily susceptible to chlorine attack resulting in N-chloro derivatives[4]. In this study, we investigated a new

method for making a chlorine resistant composite membrane having high salt rejection. The essential step is sol-gel process on a conventional TFC RO membrane with silane coupling reagents[5-7].

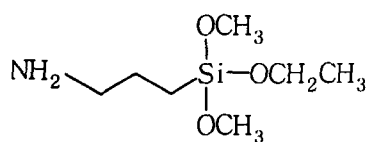
Experimental

Three commercial membranes were used as substrates for silane coating, SWC1 (Hydranautics, USA), and normally used after washed overnight with deionized water at room temperature. Then the membranes were soaked in an aqueous solution containing 5 wt/v % of propylene glycol (PG) for 30 minute followed by draining the excess solution off. Trifluoromethyltrimethoxysilane(TFMTMS),3-aminopropylmethoxydiethoxysilane(APMDES) and 3,3,3-Trifluoropropyltrimethoxysilane(TFPTMS) were used as silane coupling agents which obtained from Fluoka, Switerland.

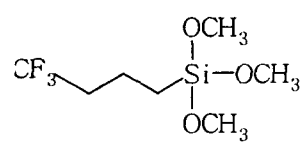
TFPTMS_n-SWC1 membranes were prepared according to following procedure. To an aqueous solution of TFMTMS (n wt/v%) was prepared to sol-gel process. To the resulting solution, PG treated substrate membrane (SWC1) taped on glass was dipped for 10 min, cured at 80 °C for 3 min. Then the synthesized composite membrane was rinsed in 0.2% Na₂CO₃ aqueous solution at room temperature. **APMDES_{0.5}-SWC1** was prepared according to the general procedure described above by using 0.5 wt/v% APMDES and SWC1. **TFMTMS_{0.5}-SWC1** was prepared according to the general procedure described above by using 0.5 wt/v% TFMTMS and SWC1.



TFMTMS



APMDES



TFPTMS

After the RO performance and chlorine resistance test, the membranes were washed with water and dried. The morphology of the active layer of RO membranes was studied with SEM and AFM. The hydrophobic change was investigated with contact angle analyzer. Si contents of the active layer complexes built on polyamide were determined by EDX. The performance of the commercial membranes and silane coating membranes were measured with a flat cell RO test unit. Membrane performances were investigated by the comparison of membrane permeation performance under the continuous and intermittent operation modes with mixed feed solution containing NaOCl and NaCl. The concentration of feed solution was 35000 ppm NaCl and 2000 ppm NaOCl at seawater desalination operating condition while 2000 ppm NaCl and 2000 ppm NaOCl at brackish water desalination operating condition. All tests were conducted at 25°C.

Result and Discussion

Silane coating complexes prepared.

The silane complexes prepared by the condensation of polyamide with silane derivatives contain one alkyl group and three alkoxy groups. This study was measured by EDX, SEM and AFM to clarify the relationship between surface structures of silane complexes and their chlorine resistance. Fig. 1 shows the EDX and SEM of TFPTMS_n-SWC1. EDX spectrum indicates the residue contents of the Si and fluoride. SEM images show that the surface blending is proportional to Si content. Fig. 2 shows the surface roughness as function of the concentration of TFPTMS. The value of surface roughness decreased with increasing the concentration of TFPTMS.

RO performance

The initial flux and salt rejection of uncoated membrane and six silane-coated membranes are shown in Table 1. Silane-coated RO membranes had similar salt rejections compare to uncoated RO membranes, but fluxes varied in a range of 25 to 30% decreasing. Fig. 3 shows the salt rejection decline of TFPTMS-treated membranes after NaOCl being added to feed water. The salt rejection of coated membranes decreased less than that of the uncoated membrane. We also tried the chlorine resist test on APMDES-treated membranes and TFMTMS-treated membranes. The results of the initial flux and salt rejection were not as good as seawater desalination membranes. But chlorine resistance exhibits a similar trend as TFPTMS-treated membranes.

Table 1. Flux and salt rejection before and after exposure to NaOCl for 8.5 hr

	Before Chlorine addition ^(a)		After 2000 ppm NaOCl addition ^(b)	
	Rejection (%)	Flux (gfd)	Rejection (%)	Flux (gfd)
SWC1 (control)	99.2	15.4	94.2	40.1
TFPTMS _{0.2} -SWC1	99.2	12.1	96.4	34.1
TFPTMS _{0.5} -SWC1	99.1	11.4	97.6	27.4
TFPTMS _{1.0} -SWC1	99.1	11.2	98.2	21.6
TFPTMS _{2.0} -SWC1	99.1	10.8	98.1	20.2
APMDES _{0.5} -SWC1	90.4	12.3	88.2	16.8
TFMTMS _{0.5} -SWC1	99.4	6.3	98.3	6.5

^(a) Measuring condition: 35000 ppm NaCl solution, 25°C, 55Kgf/cm²

^(b) Measuring condition: 35000 ppm NaCl and 2000 ppm NaOCl addition, 25°C, 55Kgf/cm²

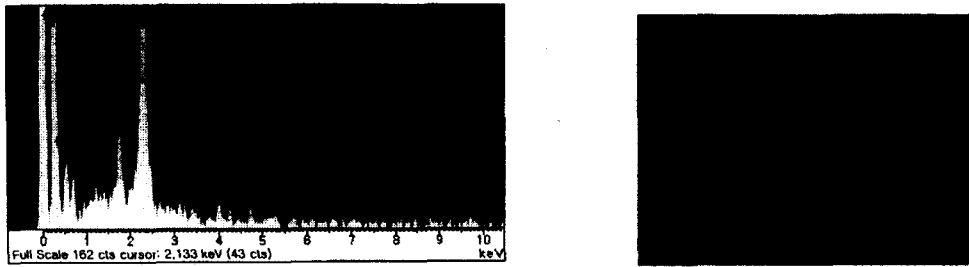


Fig. 1. The surface analysis of TFPTMS_{2.0} treated membrane with EDX and SEM (modified SWC1).

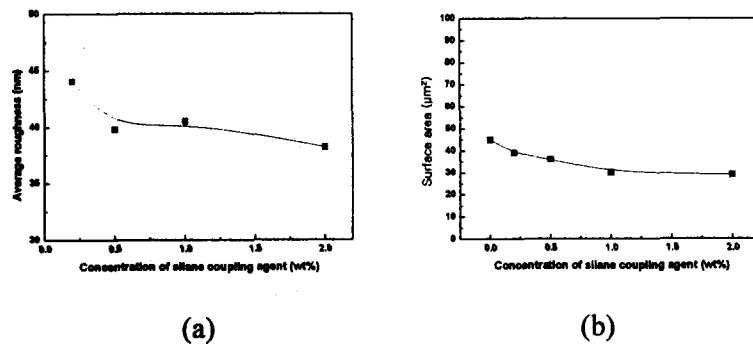


Fig. 2. Plot of surface parameter against concentrations of TFPTMS_n treated membranes (modified of SWC1); (a) average roughness, (b) surface area.

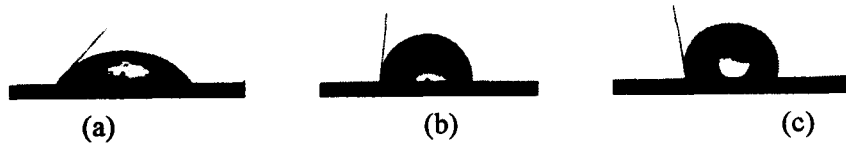


Fig. 3. Contact angle changes of TFPTMS_n treated membranes depending on concentration of silane coupling agent (modified SWC1); (a) untreated, (b) 0.2 wt%, (c) 2.0 wt%.

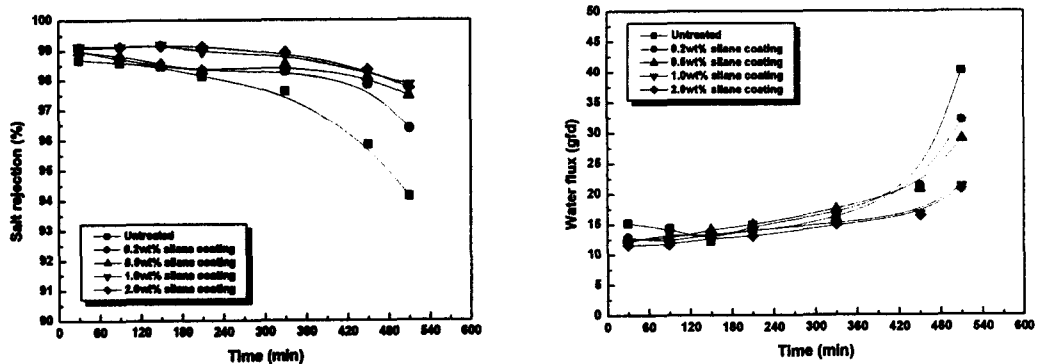


Fig. 4. Flux and Salt rejection changes of TFPTMS_n coated and uncoated membranes with 2000 ppm of NaOCl and 35000ppm of NaCl mixed water solution.

Conclusion

The purpose of the present work is to establish a new method to obtain the chlorine resistant membrane from the commercial RO membrane and to elucidate the relationship between surface properties and chlorine resistance of membranes. Chlorine resistant reverse osmosis membranes were coated with silane derivatives on commercial membranes. The resulting treated membrane has an improved resistance to chlorinated feed solutions containing 2000 ppm NaOCl and 35000 ppm NaCl, compared with uncoated membrane. The membrane rejection decline by NaOCl was supposed to be due to hydrophilic interaction between the membrane and residue chlorine. The experimental results from contacting angle analysis, SEM, AFM and EDX show that silane coated membranes have higher hydrophobic. As a result, it is expected that silane-coating method can be utilized for the preparation of chlorine resistant membranes. The treated membrane will therefore find considerable application for the treatment of chlorine disinfection water.

Acknowledgment

This research was supported by a grant (4-1-1) from *Sustainable Water Resources Research Center of 21st Century Frontier Research Program*.

Reference

1. John E. Cadotte, "Interfacially synthesized reverse osmosis membrane", *U.S. Patent 4,277,344* (1981).
2. Bart Van der Bruggen, Liesbeth Lejon and Carlo Vandecasteele, "Reuse, treatment and discharge of the concentrate of pressure-driven membrane processes", *Environmental Science and Technology*, **37**, 3733 (2003).
3. Michelle Champman Wilbert, "Enhancement of membrane fouling resistance through surface modification", *Water Treatment Technology Program Report No. 22, U.S. Department of the Interior*, Chap. 2-3, (1997)
4. M. Kurihara, T. Uemura, Y. Himeshima, K. Ueno, R. Bairinji, "Development of cross-linked aromatic polyamide composite reverse osmosis membrane", *J. Chem. Soc. Jpn.* **2**, 97, (1994).
5. E. P. Plueddemann, "Silane Coupling Agent", Plenum press, USA, (1991).
6. In Jun Park, Dong Kwon Kim, Soo Bok Lee, "Fluorine-Containing Modification Agents", *Prospectives of Industrial Chemistry*, **2**, (1999).
7. Yong Taek Lee, Kazutoshi Iwamoto, Hideyuki Sekimoto and Manbu Seno, "Pervaporation of water-dioxane mixtures with poly(dimethylsiloxane-co-siloxane) membranes prepared by sol-gel process", *J. Memb. Sci.*, **42**, 169 (1989)