The Chlorination and Chlorine Resistance Modification of Composite Polyamide Membrane

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ABSTRACT: Membrane-based separation technology is one of the most active separation technologies being employed in water treatment. Polyamides (PA) are widely used membrane materials because they exhibit excellent performance, such as high flux with high salt rejection, and enhanced stability against wide range of pH and temperature. Unfortunately, PA membranes exhibit extremely poor resistance to chlorine leading to increased operation costs and decreased membrane lifetime. In this study, we find new ways for prolonging membrane lifetime and reducing the operating costs by investigating the chlorination and modification of PA membranes. Varying concentrations of hypochlorite were used to chlorinate a commercial reverse osmosis membrane (BW-30, DOW). The results showed that short-time exposure to high concentrations of hypochlorite could cause more serious problems to membranes than long-time exposure to low concentrations under the similar total exposure. The performance of the chlorinated membranes was recovered to some extent after treatment with NaOH solution (pH 10), indicating that the alkali treatment could initiate the reversible regeneration of chlorinated membranes. Furthermore, an industrial grade epoxy resin was used to modify the membranes to enhance the chlorine resistance via the reaction between the amide nitrogen and epoxy bond. The successful modifications were confirmed by attenuated total reflectance Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy. Moreover, the chlorination tests showed that the modifications performed in these experiments enhanced the chlorine resistance of the membranes, especially for the membranes exposed to low concentration of chlorine. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41584.

INTRODUCTION

Reverse osmosis (RO) as one of the most advanced separation technologies has been widely used for seawater desalination,[1] treatment of industrial effluents,[2] and reclaimed water reuse.[3] Nevertheless, these applications severely suffer from membrane fouling (especially bio-fouling), which results in higher driving force and lower water flux.[4] Continual efforts have been made to overcome these obstacles, including surface modification of commercial RO membranes, pretreatment with feed water, periodical physiochemical cleaning after filtration, and optimal design and operation of membrane process.[5–8] Among these approaches, pretreatment by chlorine is widely used in RO applications. Unfortunately, composite PA membranes as the most commercially successful RO membranes are very sensitive to chlorine.[9,10] Attempts to dechlorinate the RO feed water are not completely successful; therefore, residual free chlorine inevitably causes irreversible deterioration of PA membranes, ultimately making the entire membrane useless.

Extensive research efforts have been devoted to understand and investigate the poor chlorine tolerance of PA membranes. In general, the poor chlorine resistance of PA membranes is due to the sensitivity of amide nitrogen to free chlorine.[9,11] Orton and Kwon et al. investigated the mechanism of chlorination,[11,12] but more researchers focused on the influence of chlorination on membrane performance.[13–16] In this study, when membranes were exposed to varying concentrations of hypochlorite and sodium hydroxide solutions, some new performances were observed, which provide some suggestions for applications of membranes.

Numerous methods have been advised to prepare PA membranes with enhanced chlorine resistance.[17–19] Based on the degradation mechanisms of PA membranes, the effective approaches include elimination of chlorine-sensitive sites in membranes and coating a protective layer on the membrane surface, which can retard or prevent the hydrogen on the amide nitrogen from being attacked by free chlorine. In this study, epoxide was used to modify the membranes via the reaction
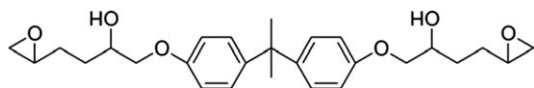
Figure 1. Chemical structure of epoxy resin E-40.

between the amide nitrogen and epoxy bond. The modification resulted in the consumption of the chlorine-sensitive sites and the cross-linking between epoxide and membrane formed a protective layer, which led to better chlorine resistance.

The objective of this study was to find ways to prolong the membrane lifetime. Evidently, membranes treated with different concentrations of hypochlorite showed different performances after the similar total exposure to chlorine; and alkali treatment could initiate the reversible regeneration of chlorinated membranes. Moreover, epoxy resin E-40 (industrial grade) was used to modify the membranes. The results showed that the modification retarded the decline of membrane flux during chlorination, and consequently enhanced the membrane chlorine resistance.

MATERIALS AND METHODS

Chemicals and Reagents

Commercial polyamide RO membrane BW-30 (DOW) was used as the original membrane, owing to its wide applications in water treatment. The membrane surface was coated with polyvinyl alcohol, but the coating layer was highly non-uniform and non-continuous.[20] Therefore, the coating did not much affect the modification[21] or chlorination.[16] Epoxy Resin E-40 (Yueyang Petrochemical Industrial Company, industrial grade) was used without further purification as modification reagent (chemical structure shown in Figure 1). Ethyl ether and isopropanol (both AR, Shanghai Sinopharm Chemical Reagent Co., Ltd.) were used as solvents in the modification. Sodium chloride (NaCl, Sinopharm Chemical Reagent Co., Ltd, AR) was used to test the salt rejection of RO membranes. Sodium hypochlorite (6–14% effective components, stored in a fridge, recalibrated before use) purchased from Shanghai Aladdin Reagent Co. Ltd. was used to evaluate the chlorine resistance of the membranes. The deionized water and ultrapure water used in this study were produced in our laboratory.

Modification of PA Membranes

Flat sheet membranes were cut down from a BW-30 membrane module and stored in a lucifagal desiccator before use. To remove the residuum on the membrane surfaces, the membrane sheets were soaked in 30% (v/v) aqueous isopropanol solutions for 30 min, then washed several times with ultrapure water, and stored in ultrapure water overnight at 4°C with regular water replacement.

A self-made apparatus (Figure 2) was designed to ensure the modified reagent to only react with active polyamide surface and to avoid other unnecessary reactions during the modification. The pretreated membranes were dried with absorbent paper and sandwiched between the apparatus. Different concentrations of E-40 were dissolved in ethyl ether/isopropanol (1.5% V/W) solution and dispersed under ultrasonic concussion for 10 min. Then 15 g of the solution was poured into the appara-

tus. After reaction at 60°C for 20 min, the membranes were removed, washed several times with ultrapure water, and finally stored in ultrapure water at 4°C prior to the test and characterization.

Surface Characterization

The membranes surface characterizations were carried out with several analytical instruments to confirm the chlorination and modification. All the membranes used in this part were vacuum-dried at 50°C for 2 h before characterization.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy Analysis (ATR-FTIR). ATR-FTIR was used to analyze the chemical changes of the membranes in this study. A Nicolet AVATAR 360 FTIR spectrophotometer with an ATR accessory (ZnSe crystal) was used to collect the spectra. The incidence angle was 45° and each spectrum was recorded using 32 scans at a resolution of 4 cm^{-1} in the region between 400 and 4000 cm^{-1}.

X-ray Photoelectron Spectroscopy (XPS). XPS was applied to measure the atomic concentration on membrane surface. An XSAM800 analyzer from Kratos Analytics with a monochromatic MgKα radiation (7×10^{-7} Pa chamber pressure, hv = 1253.6 eV, 11.5 kV, 195.5 W) was used to analyze the membranes surface.

Scanning Electron Microscopy (SEM). SEM (FEI Quanta 200, Holland) was used to photograph the surface morphology of the membranes. The membranes were coated with gold before imaging and the images magnified by 10,000 times were obtained.

Atomic Force Microscopy (AFM). AFM was used to determine the surface roughness of the membranes. The experiments were performed in non-contact mode on an SPM-9500J3 AFM analyzer (SHIMADZU, Kyoto, Japan) and 5 μm × 5 μm images were obtained with a scan rate of 0.5 Hz.

RO Membrane Performance

The laboratory-scale cross-flow test unit used in this experiment consisted of a round membrane cell, a high-pressure pump, a temperature control system, a feed reservoir and an electromagnetic mixer. Its schematic and relevant parameters were published in our previous study.[22] The membrane performance was
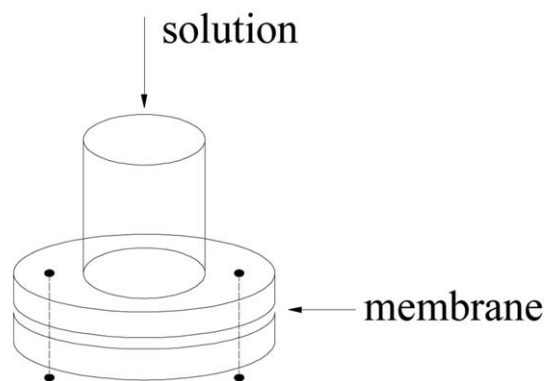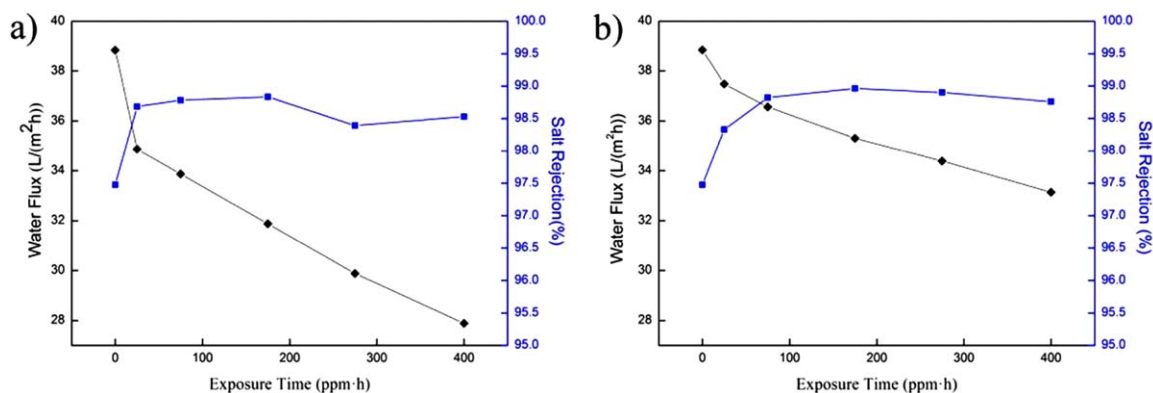

Figure 2. Illustration of self-made apparatus used for membrane modification and chlorination.

Figure 3. Performances of the original membranes: (a) 100 ppm hypochlorite solution exposure,(b) 10 ppm hypochlorite solution exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tested using 1000 mg/L NaCl solution at pressure of 1 MPa and temperature of 25°C. Concentrations of Cl$^-$ in the feed and the permeation water were detected by ion chromatography (Dionex ISC-900). The rejection and water flux were both measured at least 3 times (10 min/time) and then averaged. The salt rejection and water flux were calculated as follows:

$$\text{Salt rejection } (\%) = \left(1 - \frac{\text{concentration of permeation}}{\text{concentration of feed solution}}\right) \times 100 \quad (1)$$

$$\text{Water flux } (L/m^2h) = \frac{\text{permeate volume (L)}}{\text{membrane area}(m^2) \times \text{time (hours)}} \quad (2)$$

Evaluation of Chlorine Resistance
The membranes were sandwiched between our self-made apparatus. Then 100 mL of standardized NaClO solution (pH 7) was added into the apparatus and changed every 5 h. The apparatus was wrapped in aluminum foil and put into a shaker (25°C, 150 r/min), to eliminate the impacts of NaClO photolysis and concentration polarization. After the chlorination, the membranes were washed several times with ultrapure water and then the salt rejection and water flux were tested. Since the membrane performance depended on hypochlorite concentration (ppm) and contact time (h) during chlorination, the total exposure of the membrane to chlorine was expressed as ppm·h.

RESULTS AND DISCUSSION

Chlorination of Original Membranes
Salt Rejection and Water Flux. The salt rejection and water flux changes of the original membranes during chlorination at 400 ppm·h are given in Figure 3. The membranes were exposed to 10 and 100 ppm NaClO solution for different durations. The same results were observed as reported in other research,[13–16] i.e. the water flux declined and the salt rejections were improved.

Interestingly, some new performances were observed after exposure to different concentrations of hypochlorite. At the high exposure concentration (100 ppm), the water flux decreased rapidly from 39 (0 ppm·h) to 35 L/m^{2}h (25 ppm·h) in the early stage. Then the flux decline was slowed down, in an approximately linear way to 28 L/m^{2}h (400 ppm·h). By contrast, water flux decreased from 39 (0 ppm·h) to 33.5 L/m^{2}h (400 ppm·h)

during the low exposure concentration [Figure 3(b), 10 ppm], which was much slower than that after high concentration exposure. Moreover, the rapid decline in the early stage was also not observed at the low exposure concentration. Meanwhile, the salt rejection changes were also different. Those different changes in both salt rejection and water flux clearly demonstrated that although ppm·h was equal, short-time high-concentration exposure caused more serious chlorination to the membranes than long-time low-concentration exposure. These results also suggest that the pretreatment of RO feed should be conducted at low-dose continuous disinfection, rather than high-dose intermittent disinfection as much as possible in industrial applications.

In addition, in the previous research,[11,23] the chlorination of PA was achieved in two steps: the reversible N-chlorination and the subsequent irreversible ring-chlorination via Orton Rearrangement. Therefore, to investigate the irreversible condition under different chlorination concentrations, the reversible regeneration processes were adopted. In this section, we found that when a chlorinated membranes were treated with NaOH solution (pH 10), the membrane flux recovered modestly. In addition, the chlorinated membrane treated with pure water (b, d) and the original membrane treated with NaOH (e) were investigated as contrast tests, to find out the reason of recovered membrane flux. The results were shown in Table I. As a result, the membrane flux of contrast tests (b, d and e) did not much change after treatment with pure water or NaOH solution. Thus, the recovered flux of NaOH-treated chlorinated membranes clearly evidenced that the treatment of NaOH caused the reversible regeneration of chlorinated amide. However, under both conditions, the fluxes of the NaOH-treated chlorinated membrane were less than the original membrane, indicating that irreversible chlorination happened under both conditions. Meanwhile, after high concentration chlorination, the irreversible chlorination was much greater than that after the low concentration chlorination, which was also consistent with the earlier conclusion that the short-time high-concentration exposure could cause more serious chlorination than the long-time low-concentration exposure.

ATR-FTIR. ATR-FTIR which is effective to characterize the functional groups on RO membrane surface was used to analyze

Table I. The Normalized Flux of Different Treated Membranes

| Chlorination concentration	→	Chlorinated normalized flux	→	NaOH treated normalized flux	→	Water treated normalized flux
a 10 ppm		0.86		0.93		–
b 10 ppm		0.86		–		0.86
c 100 ppm		0.74		0.85		–
d 100 ppm		0.74		–		0.74
e 0 ppm		–		1.02		–

the surface chemical changes of RO membranes after different treatments and thereby to explain the different changes of salt rejection and water flux.

The ATR-FTIR spectra (1350–$1750 cm^{-1}$) of the membranes were shown in Figure 4 and normalized at the peak of $1487 cm^{-1}$ ($v_{c=c}$ of benzene). Several peaks were observed in this region, including the peak at 1543 cm^{-1} (region I) associated with N–H bending, the one at 1609 cm^{-1} (region II) attributed to the hydrogen-bonded carbonyl of amide, and the one at 1662 cm^{-1} (region III) attributed to C=O stretching. They are the characteristic functional groups of polyamide.[24,25] Compared with the original membrane (line a), remarkable spectral changes were observed after high concentration chlorination (line c). The peak at 1662 cm^{-1} (region III) shifted to higher wavenumber (1666 cm^{-1}). The peaks at 1543 (region I) and 1609 cm^{-1} (region II) decreased remarkably in intensity. All these results confirmed that hydrogen bonds between C=O and N–H were destroyed or weakened seriously under high concentration chlorination. However, after the similar total exposure of the membrane to chlorine, the spectra changed less significantly after low concentration chlorination (line b) than after high concentration chlorination. The peaks associated with the N–H in plane bending and the hydrogen-bond only decreased a little in peak intensity. Moreover, the C=O stretching peak did not shift much (only from 1662.3 to $1662.4$ cm^{-1}). These results all indicated that there was abundant N–H in the polyamide layer after low concentration chlorination. On the other hand, the spectra of NaOH treated high concentration chlorinated (100 ppm·5 h) membranes were shown in line d. The peaks position of these membranes partially shifted to the original membrane, and their intensities were recovered modestly. This result also proved that exposure to NaOH solution can partially and reversibly regenerate the chlorinated amide to the initial amide. Therefore, together with the performances of the NaOH-treated chlorinated membranes discussed above, we could conclude that the regular alkali washing could retard the chlorination of membranes in industrial applications.

Modification of RO Membranes

Membrane Performance. Figure 5 presented the effects of E-40 modification on water flux and salt rejection. Modification of the original membrane with 0.5% (w/w) E-40 caused about a 23.5% decrease in water flux and about a 0.45% increase in salt rejection. Modification with 1% E-40 caused about a 37.6% decrease in water flux and about a 0.77% increase in salt rejection. However, when E-40 concentration increased to 2%, the changing rates of water flux and salt rejection were minimized. Thus, the similar performances between the membranes modified with 1% and 2% E-40 indicated that the graft of E-40 to the membrane surface might be nearly saturated after modification with 1% E-40.[26] Therefore, in the subsequent experiments, the modification concentration was set at 1%. Surface modifications always resulted in the decline of water flux. Some similar or even more obvious reductions were reported.[26–28] The
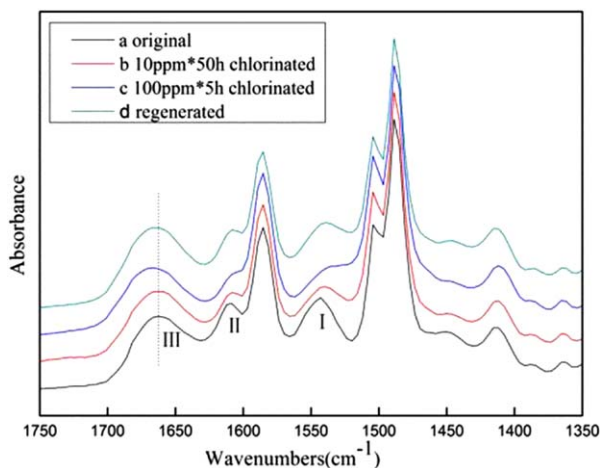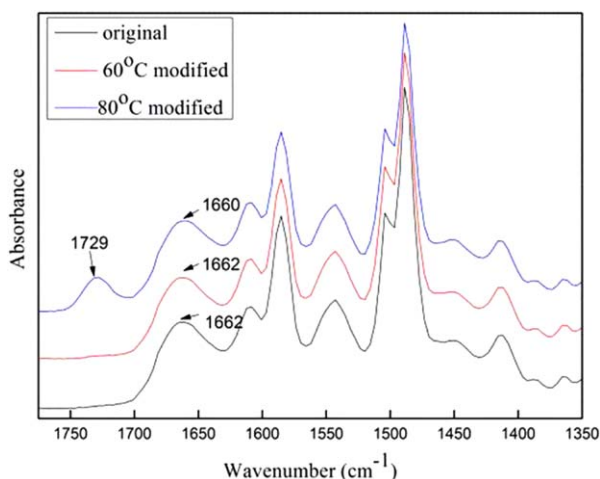

Figure 4. ATR-FTIR spectra of original, 500 ppm·h chlorinated and regenerated membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
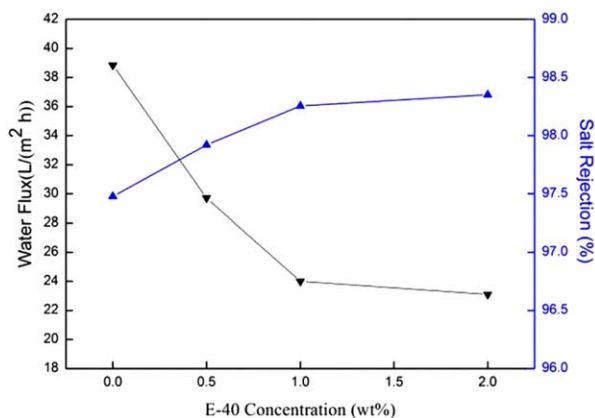
Figure 5. Water flux and salt rejection for different concentration of E-40 modified membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. ATR-FTIR spectra of original and modified membranes. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

decline could be explained by the fact that the E-40 plugged the surface defects of the PA membranes or that the transport ability of the PA membranes was influenced during the modification,[27,29] which also caused the increase in salt rejection.

Characterization of Modified Membranes via ATR-FTIR and XPS. Figure 6 showed the ATR-FTIR spectra (1350–1775 cm^{-1}) of the original and modified membranes. No remarkable difference was found between the original membrane and the 60°C modified membrane. This was because epoxy bond only reacted with primary amines on chain ends, but these primary amines accounted for a too small proportion to cause remarkable spectral changes in this condition.[30,31] However, this phenomenon also indicated that the coated layer was thinner than the penetration depth of ATR-FTIR (1 μm).[32] Some obvious spectral changes were observed after the higher activity modification (80°C, 40 min). In this condition, besides the primary amines, epoxy bond also reacted with some secondary amines in the chain. Those reactions caused the peak of C=O stretching to shift to lower frequency (Figure 6), indicating the occurrence of red shift. Besides, the peak at 1729 cm^{-1} was attributed to the isomerization of secondary alcohols coming from the epoxide ring-opening reaction.

Table II presented the atomic percentages of N, C, and O on the surface of an unmodified membrane and E-40 modified membranes (1% at 60 and 80°C) tested by XPS. The contents of N, C, and O in E-40 were also calculated and shown in

Table II. The relative high N/O ratio (N/O ratio = 1:1 in fully cross-linked PA membrane, N/O ratio = 2:1 in no cross-linked PA membrane) was due to the polyvinyl alcohol coating layers on membrane surface discussed before,[20] which did not affect the modification much. After modification at 60°C, C content rose from 75.2% to 75.8%, the content of O and N declined from 22.0% to 21.8% and from 2.8% to 2.4%, respectively. Since E-40 contained no nitrogen and had a higher C content and lower O content than the original membrane, the increase in C content and decreases in N and O contents after modification were reasonable and proved that E-40 was modified successfully to membrane surface. Additionally, the more significant changes of N, C and O contents on membrane surface after modification indicated a larger amount of E-40 on the membrane surface at 80°C, which was also consistent with the ATR-FTIR results.

Characterization of Modified Membranes via SEM and AFM. Surface morphology of the original and modified membranes was characterized by SEM and AFM. Slight changes were observed in SEM images (Figure 7) between the original and modified membranes. The SEM image of the original membrane showed an ordered peak-and-valley structure of aromatic polyamide [Figure 7(a)]. However, this structure became disordered and denser after modification at 60°C and then seemed to be relatively smoother after modification at 80°C. Those changes indicated that the membrane surface morphology was influenced by modification.

Further investigations were carried out by AFM. Three-dimensional 5 μm scan images for the unmodified and modified membranes were taken, and the root mean square roughness (Rms),[25] arithmetic mean roughness (Ra) and 10 point mean roughness (Rz) of the membrane surface was calculated and listed at the bottom table in Figure 7. After modification at 60°C, Rms increased from 51.7 to 62.7 nm, but after modification at 80°C, it decreased to 50.3 nm. AFM results also confirmed the observation in SEM images. The relatively smoother surface after modification at 80°C might be attributed to the fact that the valley structures were 'filled' with too much E-40 in this condition.

Effect of Modification on Chlorine-Resistance
Water Flux. Figure 8 presented the normalized water flux changes in the original and modified membranes during chlorination with 400 ppm·h hypochlorite. At the beginning of high-concentration exposure, water flux declined rapidly in the original membrane, but was stable in the modified membrane.

Table II. Atomic Percentage of Elements in E-40, Original Membrane, and Modified Membranes

Sample	XPS surface elemental analysis			Relative ratio		
	C (%)	O (%)	N (%)	O/C	N/C	N/O
E-40	80.2	19.8	0	0.247	0	0
Original membrane	75.2	22.0	2.8	0.293	0.037	0.127
60°C modified membrane	75.8	21.8	2.4	0.289	0.032	0.11
80°C modified membrane	77.3	21.5	1.2	0.278	0.016	0.006
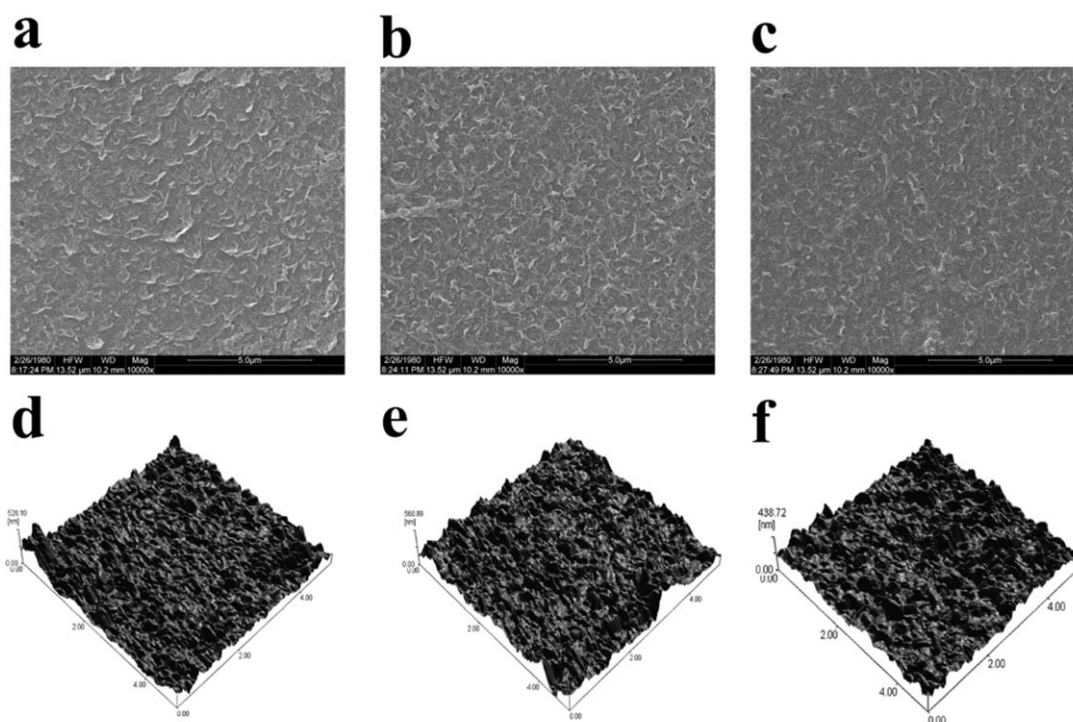
| sample	Rms(nm)	Ra (nm)	Rz(nm)	Prj. Area (µm2)
Original membrane	51.7	39.0	229.5	25
60 °C modified membrane	62.7	47.6	273.5	25
80 °C modified membrane	50.3	39.1	211.6	25

Figure 7. Scanning electron microscopy and atomic force microscopy images (including morphological statistics) of (a, d) original membrane, (b, e) 60°C modified membrane, and (c, f) 80°C modified membrane.

The reasons were that the modification consumed the primary amines on chain ends that prevent them from chlorination, and that a protecting layer might be formed, which prevented free chlorine from attacking the membrane surface. However, with further chlorination, the water flux of the modified membrane also started to decrease, indicating that the protecting layer could only inhibit the free chlorine from approaching the membrane surface at the early stage. After long time immersion, the membranes were also destroyed by the free chlorine, which penetrated through the protecting layer. Nevertheless, the changing rates and the general decline of water flux were less obvious in the modified membranes than the original membrane because of the modification.

On the other hand, compared with the original membrane, the water flux of the modified membrane did not decline remarkably after exposure to 175 ppm·h hypochlorite at low concen-

tration chlorination, presenting an even better performance at this condition. Therefore, considering the aforementioned conclusion that low concentration with long time exposure could cause minor damage than high concentration with short time exposure, this phenomenon also suggested that modification could prolong membrane lifetime to a great extent in some real applications (very low exposure concentration for long time).

Salt Rejection. As shown in Figure 9, the normalized salt rejections of both the original and the modified membranes increased after exposure to the hypochlorite. But similar to the changing trends of water flux, the salt rejection of the modified membranes changed at a much slower rate than the original membrane both at the beginning and during the whole stage. These results also indicated that the original membrane was destroyed more seriously during the chlorination and that
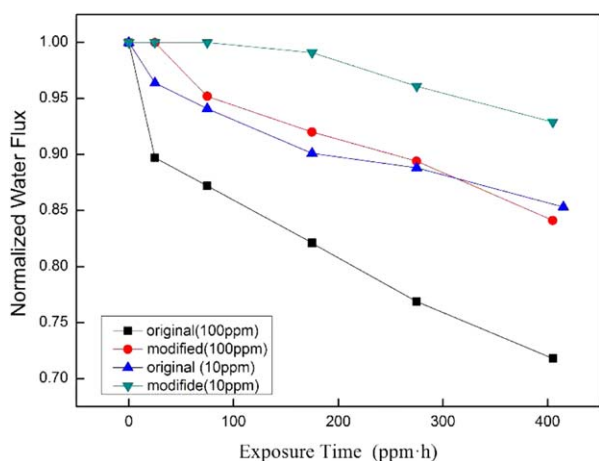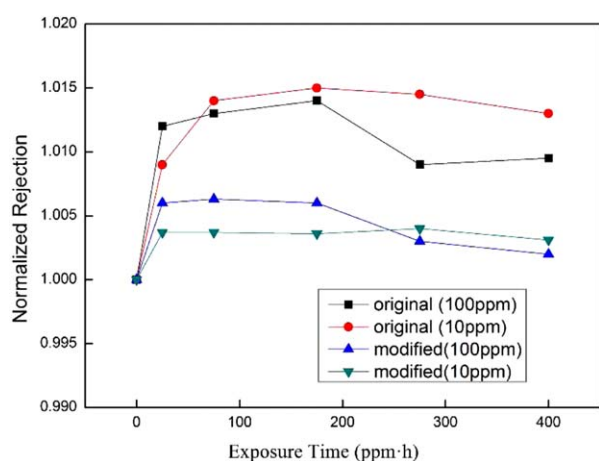
Figure 8. Normalized water flux of original and modified membranes under chlorine treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the modification improved the chlorine resistance of membranes.

CONCLUSIONS

Different concentrations of sodium hypochlorite were used to chlorinate RO membranes. The membrane performance and ATR-FTIR results clearly indicated that short-time exposure to high concentrations destroyed the membrane more seriously than long-time exposure to low concentrations, under the similar total exposure to chlorine. Moreover, alkali treatment could initiate the reversible regeneration of chlorinated membranes, partially recovering the membrane from chlorine poisoning. Furthermore, the membrane performance and results also indicated that the pretreatment with RO feed should be conducted as low-dose continuous disinfection rather than high-dose intermittent disinfection as much as possible, and that regular alkali washing could retard the chlorination of membranes.

Figure 9. Normalized rejection of original and modified membranes under chlorine treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

An industrial grade epoxy resin E-40 was used to modify RO membranes. XPS, SEM, AFM, and ATR-FTIR results confirmed the successful grafting of E-40 onto the membrane surface, and the modification significantly influenced the properties of membrane surface. The evaluation of chlorine resistance demonstrated that the modification could enhance the membrane chlorine resistance, and consequently prolong the lifetime of the membranes, in particular, at low chlorination concentration.

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