Chlorine Resistant Membrane and The Mechanism of Membrane Degradation by Chlorine

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ABSTRACT

Polyamide reverse osmosis membrane used successfully for water desalination is made from the interfacial reaction of meta-phenylenediamine (MPD) with trimesoyl chloride. One problem with the membrane is that its performance is deteriorated upon prolonged exposure to chlorine often used for disinfecting feed water. ATR-FTIR and XPS analysis show chlorine reacts with the amide hydrogen and is attached to the polyamide membrane. A chlorine resistant membrane has been made using a non-MPD amine and appears to be five times as chlorine-resistant as the MPD-based membrane. ATR-FTIR and XPS analysis also show the chlorine-resistant membrane picks up chlorine much less than the MPD-based membrane upon exposure to chlorine. Monochloramine does not appear to affect adversely polyamide membranes.

KEYWORDS

Polyamide, reverse osmosis, membrane, chlorine degradation, chlorine-resistant, monochloarmine

INTRODUCTION

Polyamide reverse osmosis membranes have been used successfully for seawater desalination, purifying brackish water and recycling waste water. During the process, the membranes are often exposed to chlorine in feed water due to malfunction of dosing equipment of sodium bisulfite reducing chlorine to harmless chloride anion. Chlorine attacks the polyamide membranes to cause membrane failure as measured by enhanced passage of both salt and water. In this respect, a chlorine-resistant membrane is highly desirable not only for an accidental exposure to chlorine, but also long term exposure to chlorine in the feed water to inhibit microbial activities on the membrane.

It is well known that meta-phenylenediamine (MPD) moiety of the commercial polyamide membrane made from the interfacial reaction of MPD and trimesoyl chloride is the site of chlorine attack, suggesting that MPD with electron withdrawing group or non-MPD diamines may give more chlorine-resistant polyamide membranes (Kawaguchi, 1984). Accordingly, a new chlorine-resistant polyamide membrane (CRM) has been manufactured using a non-

MPD diamine. Chlorine resistance test on the commercial polyamide membrane and the CRM has been carried out using sodium hypochlorite and chloramines, respectively. It has been reported that commercial polyamide membranes showed fairly strong resistance to chloramine in the absence of ferric or aluminum ion, but they did not last long in the presence of both chloramines and the metal ions (Gabelich, 2002). The damaged membranes were characterized employing XPS (X-ray photoelectron spectroscopy) and ATR-FTIR.

METHODOLOGY

Materials

BE, a brackish water reverse osmosis membrane, manufactured by Woongjin Chemical Inc. (formerly Saehan Industries Inc) was used for chlorine resistance test. The chlorine resistant membrane (CRM) was made using a proprietary diamine and trimesoyl chloride (TMC), which was purchased from Aldrich Chemical, following the previously known procedure (Cadotte, 1981). Sodium hypochlorite as 12% aqueous solution was obtained from DC Chemical Co. Ltd., Seoul, Korea. Chloramine was generated in situ using sodium hypochlorite and ammonium chloride in a 4:1 ratio of Cl_2 and N by weight.

Static chlorine resistance test was carried out by soaking membranes in an aqueous solution of 500 ppm sodium hypochlorite at pH 6 for 14 days. Fresh hypochlorite solution was used everyday. The salt rejection and flux of the membranes exposed to chlorine were measured using a bench scale test system in a cross-flow mode at 225 psi. The cell size is 15 cm in length, 10 cm in width and 0.25 cm in height.

Long term chlorine resistance test on the membranes was performed using 4"x 40" elements in a pilot system set for 15 % recovery to give about 15 gfd flux for both BE and CRM from a feed water containing 10 ppm sodium hypochlorite at pH 7 at a pressure of 100 psi. The initial salt rejection and flux of BE and CRM were 99.1% and 30 gfd, and 99.2% and 27 gfd, respectively at 225 psi using 2000 ppm NaCl. The feed water was city tap water of Seoul containing about 200 ppm total dissolved solid (TDS). Aqueous solution of sodium hypochlorite was added to the feed water periodically to maintain 10 ppm residual chlorine concentration.

The effect of chloramines on BE and CRM membranes were conducted using 1.8"x12" element in a circulating system set for 15 % recovery. A feed water containing 10 ppm chloramines and 2 ppm ferric chloride in deionized water at pH 7 was circulated through the elements at 225 psi. The feed water was freshly prepared every other day.

Analytical Equipment

ATR-FTIR spectra were obtained using IlluminatIR (SensIR, Inc, CT, USA). Survey XPS (X-ray photoelectron spectroscopy, Sigma Probe, ThermoVG, U.K.) spectra were obtained by scanning over 0-1000 eV electron binding energy with a resolution of 1 eV. High resolution spectra (multiflex) were obtained by averaging 100 scans for each element with a resolution of 0.1 eV and peak deconvolution was performed to estimate the binding energy shift of each element.

RESULTS

XPS Analysis

Both CRM and BE soaked in 500 ppm sodium hypochlorite at pH 6 were analyzed using XPS and ATR-FTIR. XPS analysis of BE exposed to chlorine for one day and 14 days in Fig. 1 shows peaks due to oxygen at 530 eV, nitrogen at 400 eV and carbon at 285 eV, and also new peaks at 200 and 270 due to chlorine atom attached to the polyamide membrane.
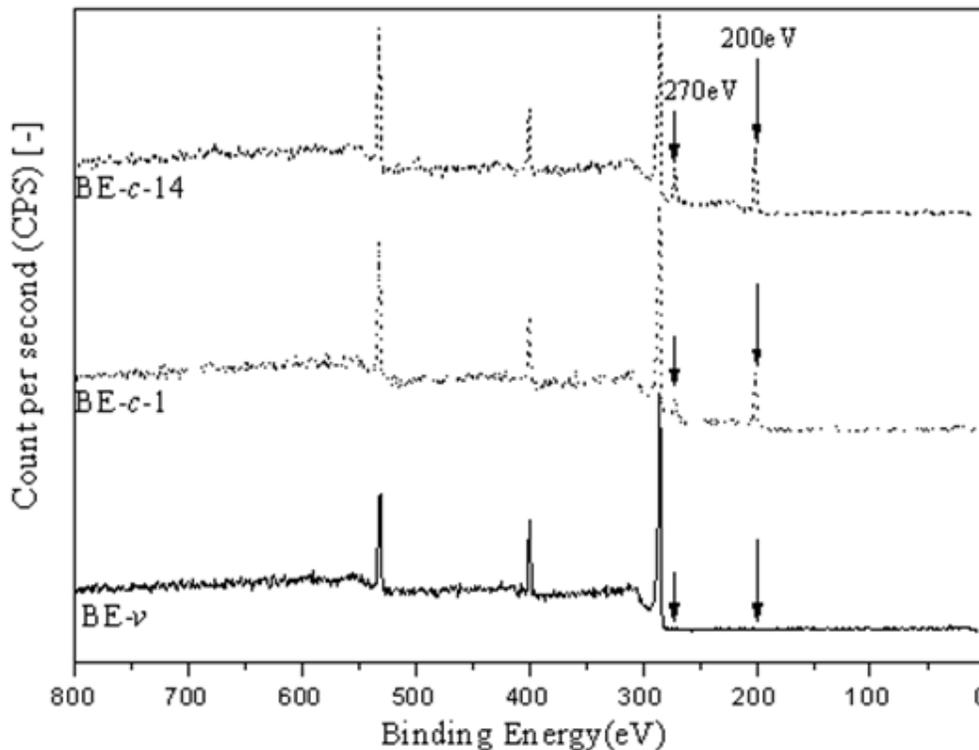
Figure 1. XPS of chlorine damaged BE (BE-*v* and BE-c denotes virgin and chlorine-exposed BE membrane, respectively).

XPS analysis of CRM exposed to chlorine for 1 day and 14 days in Fig. 2 shows new peaks at 200 and 270 eV assigned to chlorine atom attached to the membrane in addition to oxygen at 530 eV, nitrogen at 400 eV and carbon at 285 eV. The new peaks in Fig. 2 are much smaller than those in Figure 1.
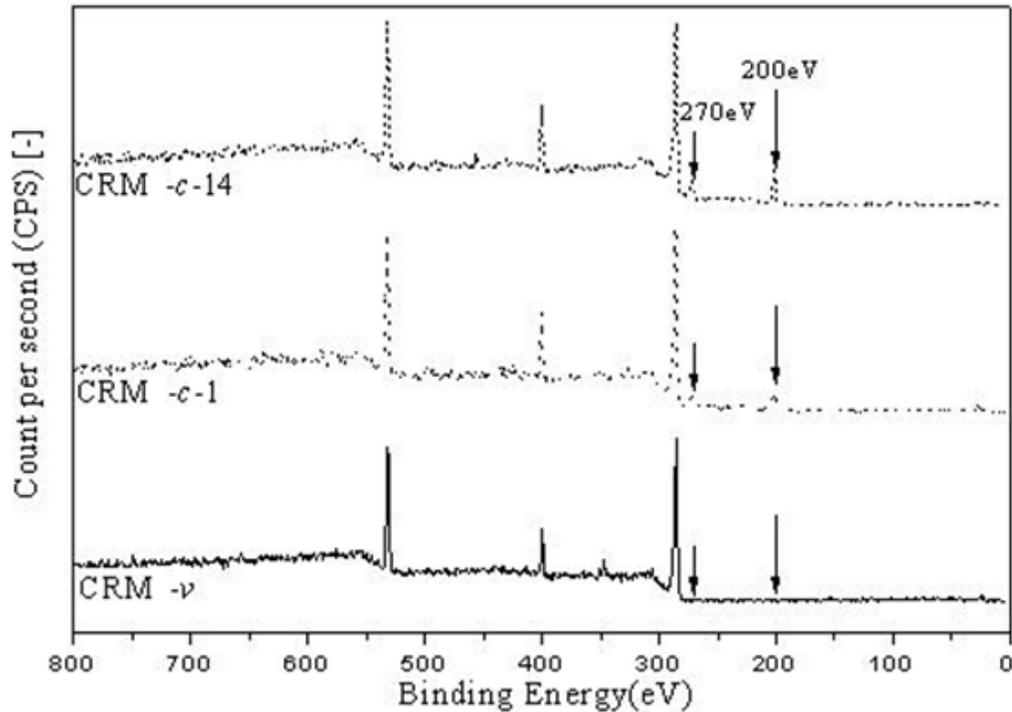
Figure 2. XPS of chlorine damaged CRM (CRM-*v* and CRM-c denote virgin and CRM membrane exposed to chlorine, respectively).

Fig. 3 shows the atomic concentration ratio of chlorine to nitrogen (Cl/N) of BE and CRM upon exposure to chlorine as shown in Figures 1 and 2.
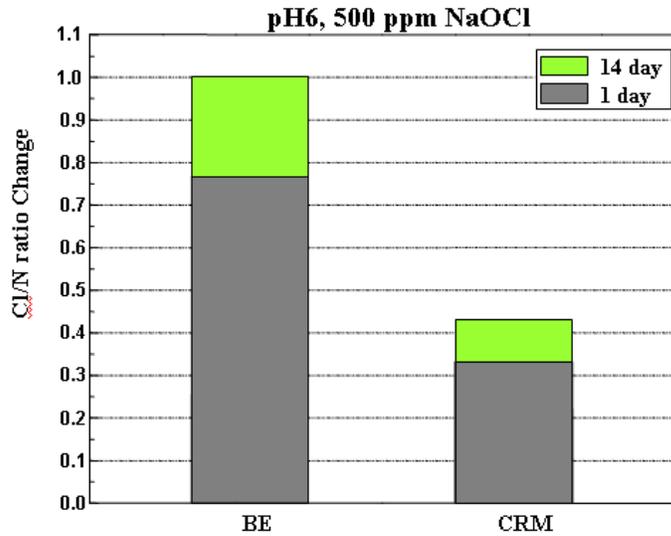
Figure 3. Cl/N ratio of chlorine damaged BE and CRM

Effect of pH on Chlorination of Polyamide Membranes

Fig. 4 exhibits the effect of pH on chlorination of BE membrane, which is exposed to 1000 ppm chlorine at pH 4 for 10 min. and at pH 10 for 1200 min. At pH 4, BE is chlorinated much faster than pH 10.
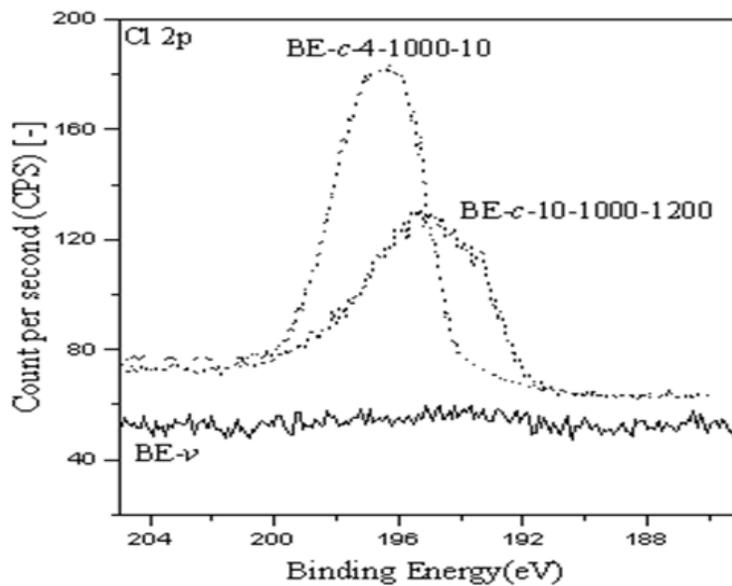

Figure 4. Effect of pH on the degree of chlorination of BE membrane. *v* and c denote

**virgin and chlorine-exposed, respectively. The first numerals represent pH, 1000 is
the concentration of chlorine in ppm and the last numerals are exposed time in min.**

ATR-FTIR Analysis

Fig. 5 shows ATR-FTIR spectra of BE membranes before and after exposure to chlorine.
It is noticeable that virgin BE membrane displays a peak at 3326 cm^{-1} due to N-H stretching,
a peak at 1603 cm^{-1} due to an aromatic ring stretching and a peak at 1543 cm^{-1} due to in-plane
N-H bending (amide II peak) and those peaks disappeared in the case of BE exposed to
chlorine.
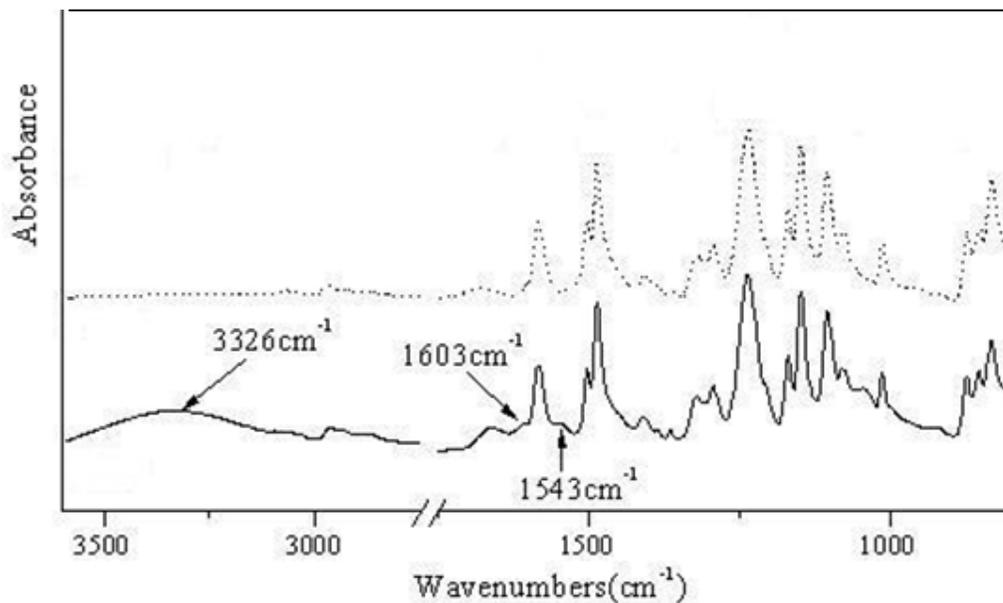
**Figure 5. ATR-FTIR of virgin (lower spectrum) and chlorine damaged BE membrane
(upper spectrum).**

Fig. 6 exhibits ATR-FTIR spectra of CRM membranes before and after exposure to chlorine.
It is noticeable that virgin CRM membrane displays a peak at 3326 cm^{-1} due to N-H
stretching, a peak at 1603 cm^{-1} due to an aromatic ring stretching and a peak at 1543 cm^{-1} due
to in-plane N-H ending (amide II peak) and the three peaks disappeared in the case of CRM
exposed to chlorine.
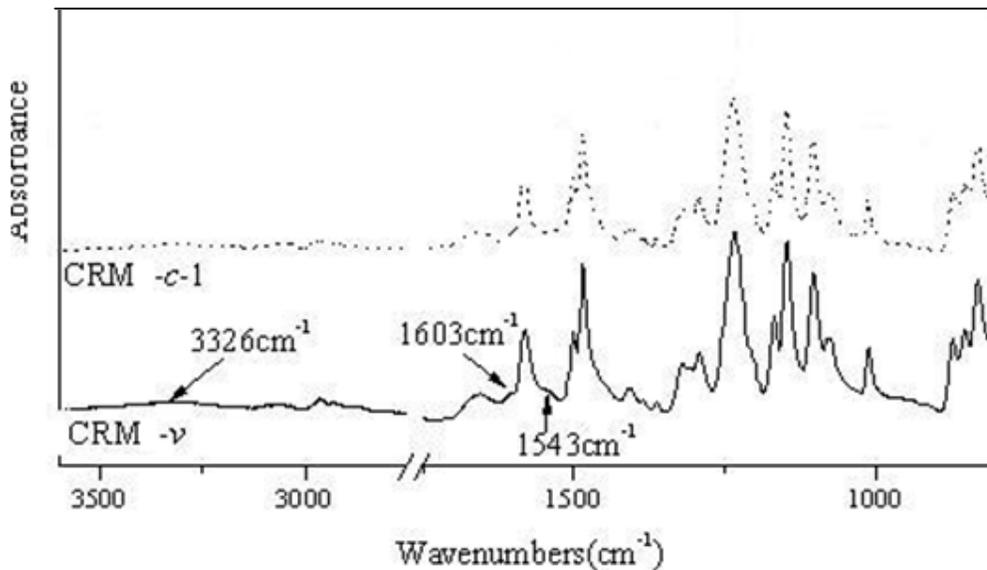
Figure 6. ATR-FTIR of virgin (lower spectrum) and chlorine damaged CRM membrane (upper spectrum).

Long term chlorine resistant test using pilot system

Fig. 7 shows a long term chlorine resistant test on BE and CRM membranes in a pilot system employing 4"x 40" elements. Initial salt rejection and flux of BE and CRM were 99.1% and 30 gfd, and 99.2% and 27 gfd, respectively at 225 psi using 2000 ppm NaCl.

The measured parameters are salt rejection and ppmhr, which is chlorine concentration (ppm) times time (hour). The ppmhr is often used to compare a chlorine resistance of one membrane with another membrane. One simple way is to select the ppmhr when salt rejection drops to about 90 %. The ppmhr of CRM is about 2500 at 90 % salt rejection whereas that of BE is about 500. The result shows CRM is at least 5 times as chlorine-resistant as BE. Another way is to calculate the slope of the curve of Fig. 7 as shown in Table 1, though the curves are not linear.

As shown in fig. 8, the flux of BE and CRM is increased upon exposure to chlorine as a sign of membrane degradation by chlorine. The flux of BE is increased 8 fold, while that of CRM only 2 fold after being exposed to 10 ppm chlorine for 800 hours, indicating again that CRM is much more chlorine-resistant than BE.
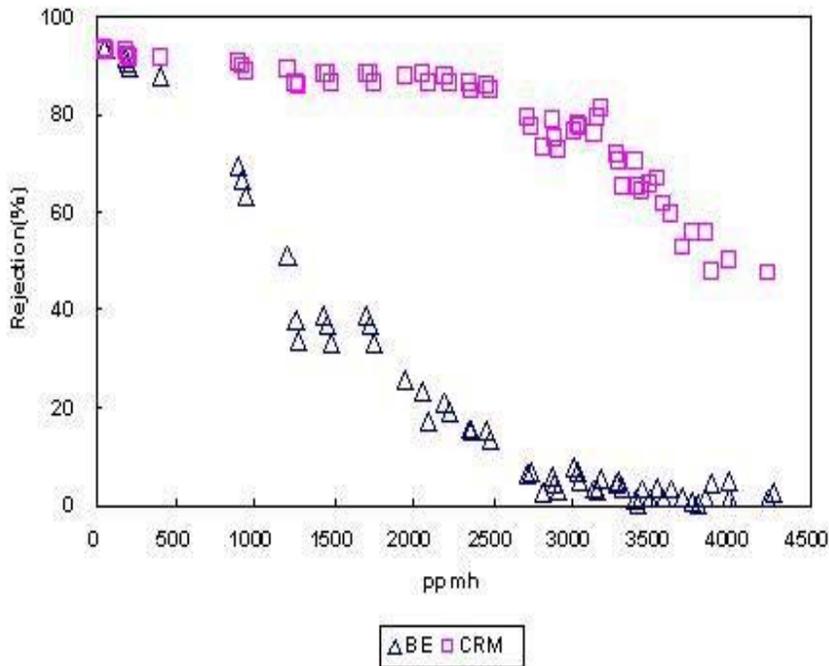
Figure 7. Chlorine resistance test of BE and CRM in a pilot system

Table 1. Comparison of Chlorine Resistance of BE to CRM

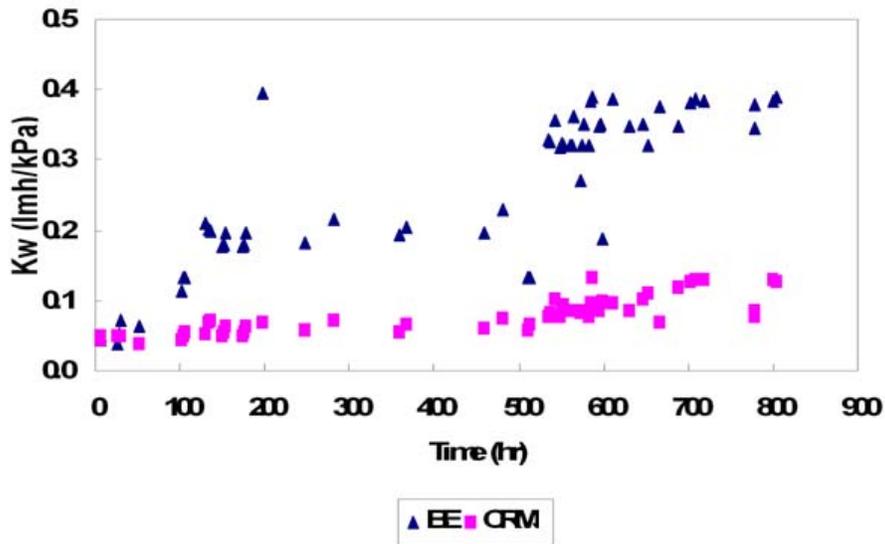| Chlorine Contact (ppm-h)	BE Regular membrane			CRM Chlorine resistant membrane			Ratio of Slope
	Initial Rejection R_i	Final Rejection R_f	Slope $\dfrac{R_i - R_f}{ppm\text{-}h}$	Initial Rejection R_i	Final Rejection R_f	Slope $\dfrac{R_i - R_f}{ppm\text{-}h}$	$\dfrac{Rt_{BE}}{Rt_{CRM}}$
1000		63.52	0.029		88.82	0.0044	6.77
2000	93.43	25.67	0.033	93.23	87.76	0.0027	12.37
3000		6.51	0.028		76.50	0.0055	5.19

$R_{t} = R_i - R_f / ppm\text{-}h$

Figure 8. Specific flux (Kw) of BE and CRM upon exposure to chlorine.

**Effect of Monochloramine on Polyamide membrane**

The salt rejection and flux of both BE and CRM did not change after the membranes were exposed to a feed water composed of 10 ppm monochloramine and 2 ppm ferric chloride at pH 7 for 1000 hours.

DISCUSSION

XPS study on BE and CRM membranes exposed to chlorine reveals the presence of new peaks at 200 eV and 270 eV due to chlorine atom in addition to oxygen, nitrogen and carbon as shown in Figures 1 and 2, indicating chlorine atom is attached to the polyamide membranes. One noticeable difference is that the intensity of chlorine peak of Fig. 1 (BE) is greater than that of Fig. 2 (CRM), suggesting that CRM is more chlorine-resistant (less reacting with chlorine) than BE. The difference in reactivity toward chlorine between BE and CRM is more graphically shown in Fig. 3, where a ratio of chlorine atom concentration to nitrogen atom concentration on BE and CRM membranes is depicted. The more is chlorine attached to the membranes, the higher is the ratio. The value of the ratio for CRM is less than half of that for BE, indicating again that BE is more reactive toward chlorine than CRM. The data in Fig. 3 also tells us a majority of chlorination is done in one day exposure to chlorine. Additional 13 days exposure only resulted in extra chlorination one third of the original chlorination (BE) and one fourth (CRM).

The effect of pH on chlorination of BE membrane is illustrated in Fig. 4 after being exposed to 1000 ppm chlorine at pH 4 for 10 min. and at pH 10 for 1200 min., respectively. The intensity of chlorine peak from chlorination at pH 4 for 10 min is greater than pH 10 for 1200 min., suggesting chlorination rate at pH 4 is approximately120 times as fast as pH 10. This finding is in line with the concentration of HOCl depending on pH. At pH 4, more than 99.5 % of chlorine exists as HOCl. At pH 10, more than 99.5 % of chlorine is ionized to become OCl⁻ and only less than 0.5 % exists as HOCL (Jenkins and Snoeyink, 1980), HOCl is known to be 100 times as reactive as OCl⁻.

ATR-FTIR analysis of both BE and CRM before and after exposure to chlorine shows N-H stretching peak (3326 cm^{-1}) and N-H bending peak (amide II peak) (1543 cm^{-1}) disappear as shown in Fig. 5 and 6, respectively, proving that chlorine reacts with the amide hydrogen to generate CON-Cl groups. Another interesting point is that a small peak at 1603 cm^{-1} due to an aromatic stretching disappears (this aromatic group is believed to belong to polyamide and the adjacent big peak belongs to polysulfone used as a support for the polyamide). This finding allows us to surmise that CON-Cl groups may affect the adjacent aromatic ring or the chlorine atom of CON-Cl rearranges itself to the adjacent aromatic ring (most likely MPD ring), known as Orton Rearrangement (Orton, 1928) as shown in the following diagram.
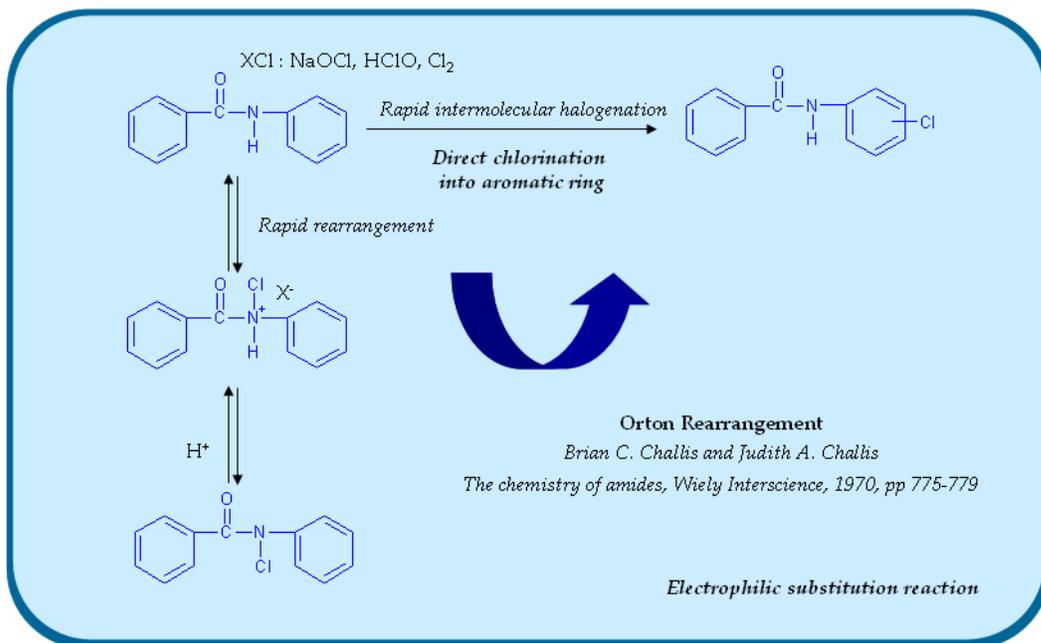
However, the possibility of direct aromatic ring chlorination cannot be ruled out completely.

The long term chlorine resistant test of BE and CRM membranes in a pilot system shown in Fig. 7 demonstrates that CRM is at least 5 times as chlorine-resistant as BE. The difference in chlorine resistance between BE and CRM could arise from the fact that MPD moiety of BE undergoes chlorination directly or indirectly as described above. The amide bond of the chlorinated MPD group may be more easily hydrolyzed than the virgin amide bond. In another aspect, the chlorinated MPD moiety may be converted to a quinoid derivative upon further chlorination. The quinoid derivative can be easily hydrolyzed to result in cleavage of the polyamide chain (Koo, 1986). Subsequently, the salt rejection of the membrane decreases and the flux increases. The literatures also suggest non-MPD amines for chlorine-resistant membranes (Kawaguchi, 1984, Glater, 1994 and Shintani, 2007). In this regard, a chlorine-resistant CRM membrane has been developed using a non-MPD amine.

On the contrary to chlorine, monochloramine has been found to cause no effect on the salt rejection and the flux of both BE and CRM, after being exposed to a feed water containing 10 ppm monochloramine and 2 ppm ferric chloride at pH 7 for 1000 hours. The literatures confirm that monochloramine itself does not harm MPD-based polyamide membranes, but in the presence of aluminum and ferric ions, monochloramine is reported to affect adversely the MPD-based polyamide membranes (Gabelich, 2002 and 2005). It is also reported that ferrous ion can react with monochloramine (NH_2Cl) to generate amine radical ($NH_2\cdot$), which may be responsible for attacking polyamide membrane (Vikesland, 2002) in a chain reaction as shown in the equation below.

$$Fe(II) + NH_2Cl \longrightarrow Fe(III) + NH_2\cdot + Cl^-$$

The literatures suggest that monochloramine can become reactive toward polyamide membranes in a right environment such as the presence of a reducing agents like ferrous ion or colloidal metal aggregates of aluminum and ferric ion. A further study is warranted to clarify this issue.

CONCLUSION

XPS analysis of a polyamide reverse osmosis membrane (BE) exposed to chlorine showed the presence of chlorine atom attached to the membrane. XPS study also showed non-MPD based chorine-resistant polyamide membrane (CRM) picked up chlorine less than half of chlorine contents of BE. ATR-FTIR analysis of the chlorine-damaged BE and CRM showed chlorine reacted with the amide hydrogen to produce CON-Cl. The chlorine atom of CON-Cl group rearranged itself to MPD ring. It could be directly chlorinated too. A long term chlorine resistant test on BE and CRM membranes in a pilot system for 450 hours in the presence of

10 ppm chlorine at pH 7 reveals that CRM is at least 5 times as chlorine-resistant as BE. This may not be sufficient to give 3 years warranty in a continuous use with a feed water having 1 ppm residual chlorine. More study is required to improve the chlorine resistance of CRM. Monochloramine does not seem to affect the polyamide membranes even in the presence of ferric ion, in contradiction to the results in the literatures. A further study seems to be necessary to clarify this issue.

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