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Modification of polyamide reverse osmosis membranes seeking for better resistance to oxidizing agents

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Abstract. One of the major limitations in the use of commercial aromatic polyamide thin film composite (TFC) reverse osmosis (RO) membranes is to maintain high performance over a long period of operation, due to the sensitivity of polyamide (PA) skin layer to oxidizing agents, such as chlorine, even at very low concentrations in feed water. This article reports surface modification of a commercial TFC RO membrane (BW30-Dow Filmtec) by covering it with a thin film of poly(vinyl alcohol) (PVA) crosslinked with glutaraldehyde (GA) to improve its resistance to chlorine. Crosslinking reaction was carried out at 25 and 40°C by using PVA 1.0 wt.% solutions at different GA/PVA mass ratio, namely 0.0022, 0.0043 and 0.013. Water swelling measurements indicated a maximum crosslinking density for PVA films prepared at 40°C and GA/PVA 0.0043. ATR-FTIR and TGA analysis confirmed the reaction between GA and PVA. SEM images of the original and modified membranes were used to evaluate the surface coating. Chlorine resistance of original and modified membranes was evaluated by exposing it to an oxidant solution (NaClO 300 mg/L, NaCl 2,000 mg/L, pH 9.5) and measuring water permeability and salt rejection during more than 100 h period. The surface modification effectively was demonstrated by increasing the chlorine resistance of PA commercial membrane from 1,000 ppm.h to more than 15.000 ppm.h.

Keywords: reverse osmosis; polyamide active layer; surface modification; chlorine resistance; poly(vinyl alcohol)

1. Introduction

Reverse osmosis (RO) process is recognized as the main option to obtain fresh water, and it is largely applied for ultrapure water production, and wastewater treatment due to the excellent quality of the permeated water, besides the feasibility to be easily coupled with other desalination processes (Baker 2004, Fritzmann e*t al*. 2007). The development of the asymmetric cellulose acetate (CA) membrane by Loeb and Sourirajan in the 1960s was the first breakthrough in the RO separation technology (Loeb and Sourirajan 1964). The second one was achieved by Cadotte and co-worker through the development of thin-film-composite (TFC) membrane with high flux and selectivity, using the interfacial polymerization concept in membrane preparation (Cadotte and Rozelle 1972, Cadotte 1981). TFC membranes usually contain a thin active skin of aromatic polyamide (PA), responsible for the membrane separation properties, and a polysulfone or polyethersulfone porous support, used to provide the mechanical stability (Petersen 1993). Cellulose acetate and TFC membranes differ in

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transport properties, and mainly in chlorine resistance. CA membranes have better resistance to chlorine, but inferior performance than composite PA membranes. However, PA membranes have propensity to organic fouling, owing to their hydrophobicity. Biological fouling, caused by microorganisms, usually is prevented by chlorination in pre-treatment stage, and the presence of free chlorine in the feed stream can lead to reactions with the PA skin layer, converting it to N-chloro derivative, that results in drastic decrease in the composite membranes performance (Glater *et al.* 1994, Buch *et al.* 2008).

In order to understand the chemical changes of the PA membranes upon exposure to free chlorine, several authors have suggested that the chlorine reaction with the polyamide may be includes: (1) N-chlorination of the amide N-H group, followed by ring-chlorination via an intermolecular rearrangement, called Orton-rearrangement or, (2) direct chlorination of the aromatic ring of the diamine unit forming various aromatic substitution products. Literature suggests that the chlorine resistance of these membranes depends on the chemical structures of the polyamides, mainly the nature of the amine used in the interfacial polymerization (Avlonits *et al.* 1992, Kim *et al.* 2000, Kang *et al.* 2007, Yu *et al.* 2009).

Studies have been carried out in searching for chlorine resistant polymers to produce RO membranes. Due to the well known properties like high hydrophilicity, good film-forming, anti-fouling characteristics besides good chemical, thermal and mechanical stability, poly(vinyl alcohol) (PVA) has been investigated extensively for desalination, pervaporation, biomedical separations and others applications. PVA membranes are especially suitable to dehydration of organic solvents by pervaporation (Li *et al.* 2006, Majumdar and Adhikari 2006, Hyder *et al.* 2009, An *et al.* 2011).

Poly(vinyl alcohol), a water soluble polymer, available with different degrees of hydrolysis must be modified by crosslinking for aqueous applications. To enhance the stability of the polymer, a variety of techniques based on physical, heat and chemical treatments are employed. Physical methods by cycles of freezing/thawing may introduce crystalline regions in PVA chains that act as crosslink bonds. Heat treatment of PVA also increases the crystallinity degree of the polymer. PVA may be chemically crosslinked by using multifunctional compounds, such as dialdehydes, dicarboxylic acids and anhydrides (Svang-Ariyaskul *et al.* 2006, Bolto *et al.* 2009).

Among the crosslinking agents, glutaraldehyde (GA) has been used frequently due to its property to react under mild conditions of temperature. Glutaraldehyde consists of two aldehyde groups (CHO), which can be attached to hydroxyl groups (OH) in PVA. There is an optimal ratio between the crosslinker and the polymer, low quantity of the aldehyde does not allow its use in aqueous solutions, whereas a large amount of the aldehyde can leads to unreacted pendant aldehyde groups in the PVA chains. The crosslinking reaction mechanism between PVA and GA is shown in Fig. 1 (Yeom and Lee 1996, Mansur *et al.* 2008, Figueiredo *et al.* 2008).

Surface coating method has been widely used to modify the surface properties of the aromatic polyamide TFC membranes (Kim *et al.* 2004, Yu *et al.* 2011). In this article we reported the surface modification of the commercial RO membranes by thin films of PVA crosslinked with GA for improved chlorine resistance. The crosslinking reaction was evaluated by measuring the water swelling degree and through the chemical and thermal changes of the PVA films observed by the attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and thermogravimetric (TGA) analysis.

The performances of the original and modified commercial membranes were investigated before, during and after hypochlorite exposure. The total chorine exposure was expressed as ppm.h. It has been known from literature that the short exposures time of membranes to high concentrations of free chlorine are equivalent to the long exposures time of membranes to low concentrations of free

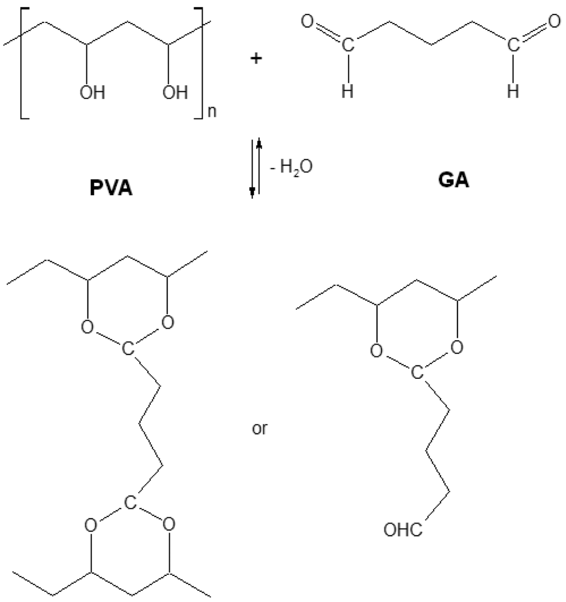

Fig. 1 Crosslinking reation between PVA and GA

chlorine (Kwon and Leckie 2006, Liu *et al.* 2011). The chemical composition and morphology of the original and chlorinated membranes surfaces were investigated by using ATR-FTIR and scanning electron microscopy (SEM) analysis, respectively.

2. Experimental

2.1 Membranes and chemicals

A flat-sheet commercial polyamide RO membrane (BW30, Dow Filmtec) was used in this study. The manufacturer reports an operation pH range between 2 and 11 and a maximum temperature and free chlorine tolerance of 45ºC and < 0.1 mg/L, respectively.

Poly(vinyl alcohol) (PVA, 99.5% hydrolyzed, MW 85,000-146,000) and glutaraldehyde (GA, 25% content in water) were purchased from Aldrich Chem. Co. Sodium chloride (NaCl) and sodium hypochlorite (NaClO, effective chlorine content: 5%) were purchased from Vetec Chem. Ltda. All the solutions were prepared with deionized water.

2.2 Preparation of PVA and GA/PVA dense films

PVA solution was prepared by dissolving 1.0 wt. % of polymer in deionized water at 90ºC. After dissolution the solution was kept at room temperature for 3h in order to remove air bubbles. For the crosslinking reaction, GA 0.1 wt. % and PVA 1.0 wt. % solutions were mixed in different proportions under stirring for 30 min. The mass ratio of GA/PVA of 0.0022, 0.0043 and 0.013, was evaluated at 25 and 40ºC, following the procedure described by Figueiredo *et al*. The resulting solutions were then cast onto a PTFE Petry dishes and dried to obtain dense films and to investigate the crosslinking reaction between PVA and GA.

2.3 Swelling measurements

Swelling was determined by immersing 3 × 3 (cm) strips of PVA dense films in water at 25ºC and 40ºC until sorption equilibrium was reached (approximately 48 h). The swelling degree (S) was calculated by the relationship between swollen *(l_s)* and dried *(l_d)* strip length (Eq. (1)).

$$S\,(\%) = \left(\frac{I_s - I_d}{I_d}\right) \times 100 \tag{1}$$

2.4 Membrane surface coating

Membrane surface coating experiments were conducted by using a dip-coating method. The commercial membrane (BW30, Dow Filmtec) used in our work was obtained by taking a 5.5 × 11 (cm) samples from a spiral wound module. Before any modification, the samples were maintained in water bath for, at least, 24 hours. During the dip-coating procedure only the PA layer was in contact with GA/PVA solution. The contact of the membrane sample with coating solution was kept as short as possible, and has a little influence on the final PVA layer properties. The temperature during the coating procedures was ca. 23°C. After that, the coated membrane was dried for 24 h at a selected temperature for the crosslinking reaction (40ºC) in an oven (Nova Ética Ltda), or at room temperature (25°C).

2.5 Membranes performance

Reverse osmosis performance of all membranes was evaluated in terms of water flux and salt rejection employing a laboratory cross flow unit. The tests were carried out at pH 9.5 with a 2,000 mg/L sodium chloride (NaCl) and 300 mg/L sodium hypochlorite (NaClO) aqueous solutions. The chlorine resistance was evaluated through long term tests and the total exposure expressed as ppm.h. The chlorine concentrations were periodically determined by iodometric titration (Harris 1991).

The RO tests were operated at 3.0 Mpa, 25ºC and constant flow rate of 0.7 L/min. The flux and salt rejection were monitored in order to evaluate the performance after chlorine exposure. The water flux (L/m^2.h) was determined by direct measurement of the permeate flow. The salt concentrations in permeate and feed solutions were determined by measuring the ionic conductivity (Digimed Instruments Ltda). The salt rejection was calculated by Eq. (2)

$$R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_f and C_p were salt concentrations in the feed and permeate, respectively.

2.6 Membranes characterization

ATR-FTIR (Perkin Elmer, Spectrum 100) and TGA (Perkin Elmer, Pyris 1) were employed to characterize the chemical composition and the thermal properties of the PVA films, respectively. Infrared spectra of the films were obtained by scanning each sample 32 times at a resolution of 4 cm^{-1}.

For the TGA tests, 8 mg of each sample was heated from 50 to 600ºC at 10ºC/min. Furthermore, the surface chemical composition and the morphology of the original and modified RO membranes were analyzed by using ATR-FTIR and scanning electron microscopy (SEM, FEI Quanta 200). Before characterization by ATR-FTIR analysis, the original and modified membranes were dried carefully in order to eliminate the peaks due to water/moisture, which normally overlap with some of the peaks due to PVA. Samples for SEM analysis were dried in vacuum at room temperature for 12 h and then coated with a thin gold layer.

3. Results and discussion

3.1 GA/PVA dense films

3.1.1 Swelling behavior

Water swelling experiments were used to estimate the crosslinking effectiveness of GA/PVA films. The results are presented in Table 1. All the tests were performed in triplicate and the membrane mean thickness was around 150 µm. PVA crosslinked at 40ºC showed the lowest swelling degree, what confirmed the effect of the temperature on the crosslinking rate of PVA. Moreover, it seems to have an optimal GA content in this reaction, initially an increase in the crosslinker reduces the swelling degree, but further increases in its concentration leads to a water soluble film. As pointed out by Figueiredo *et al*. 2008, high GA concentration favors PVA branching instead of crosslinking. The lowest swelling degree was achieved with a GA/PVA molar mass ratio of 0.0043 at 40ºC.

3.1.2 ATR-FTIR analysis

Fig. 2 shows the ATR-FTIR spectra of the original and crosslinked PVA dense films prepared at 40ºC using different GA contents. The main absorbance bands are related to hydroxyl and acetate groups of PVA. The broad band occurring at around 3315 cm^{-1} is related to the asymmetric stretching of the hydroxyl (O–H) groups; two sharp bands at 2940 and 2890 cm^{-1} corresponding to asymmetric and symmetric stretching of the methylene (C–H) groups, besides another band at 1090 cm^{-1} due to acetal (C–O) groups. Many studies have already shown that the absorbance ratios of functional groups to a reference peak can quantitatively analyze the IR spectra changes related to the crosslinking reaction (Yeom and Lee 1996, Figueiredo *et al.* 2008). Table 2 shows the absorbance ratios of the hydroxyl groups at 3315 cm^{-1} and the methylene reference bands at 2940 cm^{-1}, both for the original and crosslinked PVA dense films at 40ºC. The results showed a relative decrease in the absorbance ratios for the crosslinked PVA films, indicating the effectiveness for the crooslinking reaction.

Table 1 Water Swelling Measurement of GA/PVA dense films

Temperature (ºC)	GA/PVA (mass ratio)	Water Swelling Degree (%)
25	0.0022	>100
	0.0043	80 ± 3
	0.013	soluble
40	0.0022	85 ± 5
	0.0043	55 ± 4
	0.013	soluble

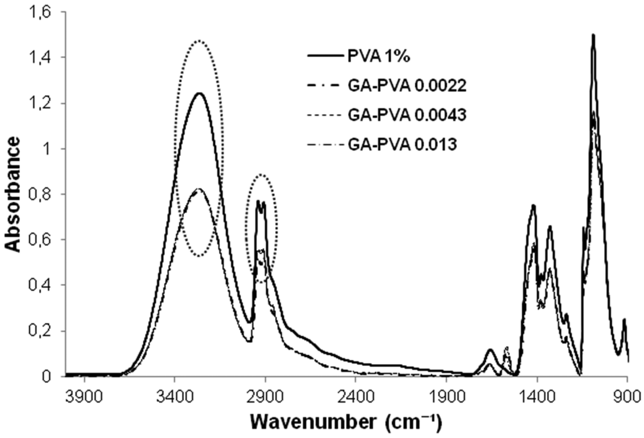

Fig. 2 ATR-FTIR spectra of the PVA dense films before and after crosslinking with GA at 40°C

Table 2 Absorbance ratios of the hydroxyl groups at 3315 cm^{-1} and methylene reference bands at 2940 cm^{-1} from PVA films crosslinked at 40°C

PVA Films	A_1 (3315 cm^{-1})	A_2 (2940 cm^{-1})	A_1/A_2
PVA 1%	1.244106	0.770775	1.6141
GA/PVA(0.0022)	0.814767	0.523143	1.5574
GA/PVA(0.0043)	0.821334	0.551571	1.4766
GA/PVA(0.013)	0.823178	0.548899	1.4997

Furthermore, the analysis of ATR-FTIR spectra for the crosslinked PVA films confirmed the water swelling results, showing a more effective polymer crosslinking with GA/PVA mass ratio of 0.0043.

3.1.3 Thermal gravimetric analysis (TGA)

TGA was used to evaluate the thermal stability of the crosslinked PVA prepared at 40ºC. Fig. 3 shows the mass variation of PVA and GA/PVA dense films with temperature increase. TGA curve of PVA dense film revealed three main mass loss regions: the first one, around 100ºC, related to the evaporation of physical and chemical bond water, characteristic of the hydrophilic polymers; the second stage, at 270ºC, is regarded to the disruption of the polymer structure with polyene formation, whereas the third stage, around 400ºC, may be ascribed to the polymer backbone decomposition. TGA curves of GA/PVA dense films with mass ratios of 0.0022, 0.0043 and 0.013 also showed three main degradations steps. Comparing to PVA, the first stage of mass loss is reduced, which indicates a reduction in the water uptake of crosslinked films. The second stage onset is shifted to higher temperatures, denoting an increase in the thermal stability as a result of the crosslinking reaction between PVA and GA. For unmodified or modified polymers the third step remains around 400ºC.

3.2 Surface modification of commercial RO membranes (BW30 Dow Filmtec)

3.2.1 ATR-FTIR analysis

Fig. 4 presents the ATR-FTIR spectra of uncoated and coated commercial RO membranes. The

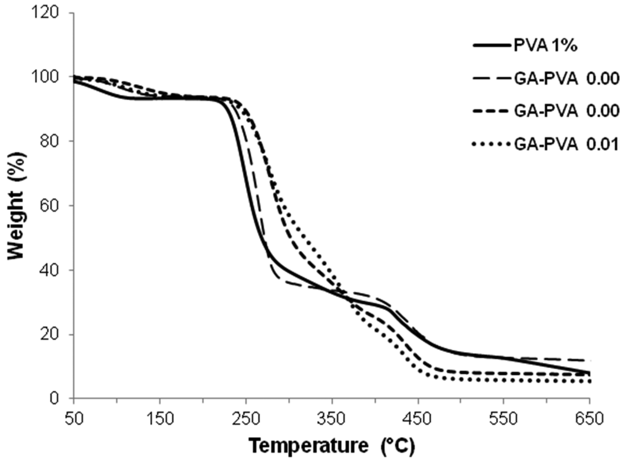

Fig. 3 TGA curves of PVA dense films prepared at 40°C and crosslinked with different GA contents

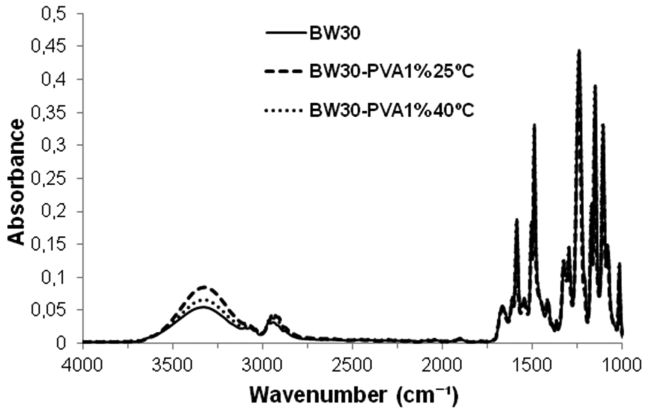

Fig. 4 ATR-FTIR spectra of uncoated commericial RO membrane (BW30) and coated ones with PVA 1% (GA/PVA=0.0043) prepared at 25 and 40°C

RO membranes were modified by coating them with GA/PVA solution, with further thermal treatment for PVA crosslinking. It can be clearly seen an increase in the main absorption peaks related to the PVA top layer, a broad absorption band at 3315 cm^{-1} (hydroxyl groups) and the two bands at 2940 and 2890 cm^{-1} (methylene groups), for both modified membranes evaluated at two temperatures, 25 and 40°C, respectively. This result confirms the presence of an extra layer of PVA on the commercial polyamide RO membrane. The increase in the absorption bands at 3315 cm^{-1} (O-H groups) was more intense when the membrane was treated at 25°C, indicating the presence of more O-H groups, which means a lower PVA crosslinking density. Moreover, the results are in agreement with the water swelling measurements (Table 1). It is interesting to observe that the unmodified membrane also presents the same absorption bands expected for PVA. According to Tang *et al,* 2008, the existence of this absorption bands in the commercial membrane suggests the presence of a coating or a modifying agent on the commercial RO membrane surface.

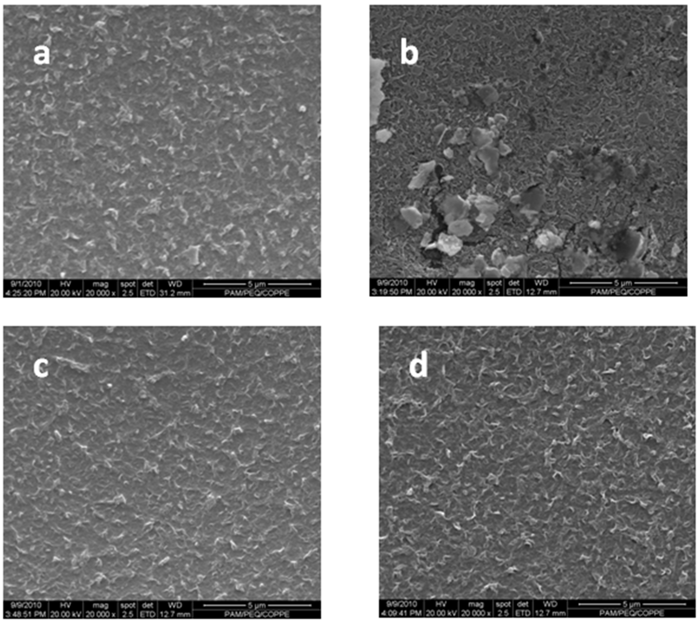

Fig. 5 SEM images (20,000×) of uncoated commercial RO membranes (BW30) (a) before and (b) after chlorine exposure (15,000 ppm.h) and coated ones with PVA wt.1% (GA/PVA=0.0043; T=25°C) (c) before and (d) after chlorine exposure (15,000 ppm.h)

3.2.2 SEM analysis

The surfaces of uncoated and modified commercial RO membranes were characterized by using SEM analysis. Fig. 5 compares SEM microphotographs of uncoated and coated membranes before and after chlorine exposure. It can be seen clearly from Fig. 5(a-b) changes on the unmodified membrane surface after chlorine exposure (15,000 ppm.h), probably by the removal of polyamide layer. However, almost no changes were observed on the modified membrane surface (Fig. 5(c-d)), indicating that PVA extra layer improves the resistance of PA membrane in oxidizing medium.

3.3 Membrane performance

The permeation tests for original and modified membranes were carried out at pressure of 3.0 MPa, pH 9.5 and 25°C, using 2,000 mg/L NaCl and 300 mg/L NaClO aqueous solutions. The membrane chlorine resistance was evaluated by measuring the water permeability and salt rejection (NaCl). The results are shown in Figs. 6 and 7.

As can be seen in Fig. 6, the membranes permeability increase with chlorine exposure (ppm.h) and this behavior is more pronounced for the uncoated membrane. For instance, after 10,000 ppm.h of chlorine exposure the unmodified membrane exhibited a 10-fold increase in the permeability while the membranes with an extra layer of PVA around 3.0% of increase.

The increase in the water permeability might be caused by the conformational deformations of polyamide chains due to N-chlorination and concomitant ring-chlorination reactions through Orton-rearrangement, disrupting the intermolecular hydrogen bonds and destroying the symmetry of polyamide network, resulting in a transformation from crystalline regions to an amorphous state (Kwon and

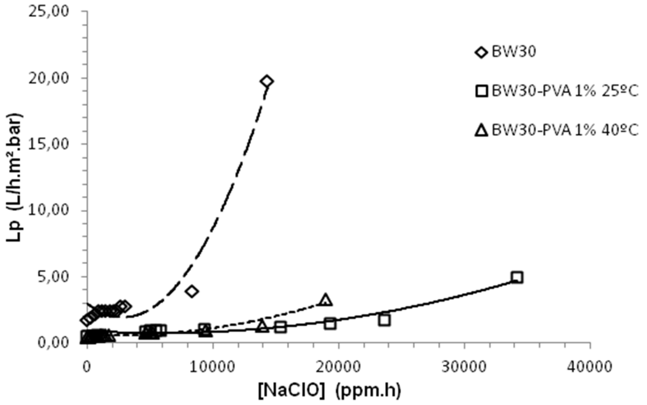

Fig. 6 Water permeability (Lp, L/h.m^2.bar) evolution of uncoated commercial RO membrane (BW30) and coated ones with PVAwt. 1% (GA/PVA=0.0043) prepared at 25 and 40°C, with oxidizing feed solution (NaCl 2,000 mg/L; NaClO 300 mg/L; pH 9.5, 25°C, 3.0 Mpa)

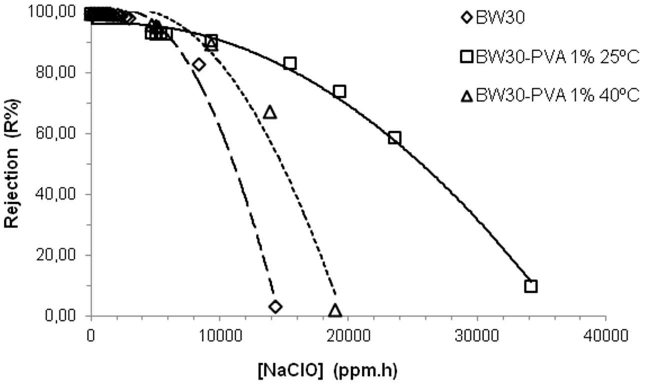

Fig. 7 Salt rejection (NaCl, R%) evolution of original commercial RO membrane (BW30) and modified ones with PVAwt. 1% (GA/PVA=0.0043) prepared at 25 and 40°C, with oxidizing feed solution (NaCl 2,000 mg/L; NaClO 300 mg/L; pH 9.5, 25°C, 3.0 Mpa)

Leckie 2006, Kang *et al.* 2007). Although, this effect is also observed for coated membranes, the extra layer of PVA reduces its intensity, acting as a protective layer for PA. The membrane with PVA crosslinked at 25°C presented higher resistance to oxidant medium. This result could be attributed to the temperature restriction for the commercial RO BW30 membrane (45°C).

Fig. 7 shows the NaCl rejection as a function of NaClO exposure time (ppm.h) for all membranes, uncoated and modified ones. It is observed a reduction in NaCl rejection for all membranes, which may also be related to changes in PA morphology due the chlorination of amide N-H group to N-Cl group, resulting in higher salt passage through the membranes.

As shown by Figs. 6 and 7, it might be observed an improvement in the chlorine resistance for the modified membranes. For instance, when the oxidant exposure was around 15,000 ppm.h, the water permeability of the uncoated commercial membrane was 20 (L/h.m^2.bar), while for the modified membrane with an extra layer of PVA, crosslinked at 25°C, was 1.2 (L/h.m^2.bar). The same behavior is observed for the salt rejection. Once again, when the chlorine exposure was around

15,000 ppm.h the salt rejection of the uncoated commercial membrane was 3.0%, while for the modified membrane was as high as 90.0%.

4. Conclusions

Commercial RO membrane was modified by coating with an extra layer of PVA crosslinked with GA. The crosslinking reaction was investigated by swelling measurements, ATR-FTIR spectra and TGA. It was found that GA/PVA mass ratio equal to 0.0043 and 40°C are suitable conditions for the crosslinking reaction. The chlorine resistance of original and modified TFC commercial RO membrane was evaluated through the water permeability and salt rejections measurements during 113 h testing period with an oxidant solution (NaClO 300 mg/L, pH 9.5). The best performance, i.e., higher improvement in chlorine resistance, was observed by coating the membranes with GA/PVA, mass ratio equal to 0.0043 and temperature of crosslinking 25°C.

It can be concluded that PVA layer was successfully crosslinked with GA and it is an excellent material to be used in surface coating methods in order to modify the surface properties of the commercial RO TFC membrane, especially to improve its chlorine resistance.

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References

An, Q., Li, F., Ji, Y. and Chen, H. (2011), "Influence of polyvinyl alcohol on the surface morphology, separation and anti-fouling performance of the composite polyamide nanofiltration membranes", *J. Membrane Sci.*, **367**(1-2), 158-165.

Avlonits, S., Hanbury, W.T. and Hodgkiess, T. (1992), "Chlorine degradation of aromatic polyamide", *Desalination*, **85**(3), 321-334.

Baker, R.W. (2004), *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons, Ltd., Chichester.

Bolto, B., Tran, T., Hoang, M. and Xie, Z. (2009), "Crosslinked poly(vinyl alcohol) membranes", *Progress in Polymer Science*, **34**(9), 969-981.

Buch, P.R., Mohan, D.J. and Reddy, A.V.R. (2008), "Preparation, characterization and chlorine stability of aromatic-cycloaliphatic polyamide thin film composite membranes", *J. Membrane Sci.*, **309**(1-2), 36-44.

Cadotte, J.E. (1981), "Interfacially synthesized reverse osmosis membrane", *US Patent* 4,277,344.

Cadotte, J.E. and Rozelle, L.T. (1972), "In situ formed condensation of polymers for reverse osmosis membranes", *OSW PB-Report*, No. 927.

Figueiredo, K.C.S., Alves, T.L.M. and Borges, C.P. (2009), "Poly(vinyl alcohol) Films Crosslinked by Glutaraldehyde Under Mild Conditions", *J. Appl. Polymer Sci.*, **111**(6), 3074-3080.

Fritzmann, C., Löwenberg, J., Wintgens, T. and Melin, T. (2007), "State-of-the-art of reverse osmosis desalination", *Desalination*, **216**(1-3), 1-76.

Glater, J., Hong, S. and Elimelech, M. (1994), "The search for a chorine-resistant reverse osmosis membrane", *Desalination,* **95**, 325-345.

Harris, D.C. (1991), *Quantitative Chemical Analysis*, W.H. Freeman & Co, New York.

Hyder, M.N., Huang, R.Y.M. and Chen, P. (2009), "Composite poly(vinyl alcohol)–poly(sulfone) membranes crosslinked by trimesoyl chloride: Characterization and dehydration of ethylene glycol–water mixtures", *J. Membrane Sci.*, **326**(2), 363-371.

Kang, G-D., Gao, C-J., Chen, W-D., Jie, X-M., Cao, Y-M. and Yuan, Q. (2007), "Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane", *J. Membrane Sci.*, **300**(1-2), 165-171.

Kim, C.K., Kim, J.H., Roh, I.J. and Kim, J.J. (2000), "The changes of membranes performance with polyamide molecular structure in the reverse osmosis process", *J. Membrane Sci.*, **165**(2), 189-199.

Kim, I.C., Ka, Y.H., Park, J.Y. and Lee, K.H. (2004), "Preparation of fouling resistant nanofiltration and reverse osmosis membranes and their use for dyeing wastewater effluent", *J. Ind. Eng. Chem.*, **10**, 115-121.

Kwon, Y-N. and Leckie, J.O. (2006), "Hypochlorite degradation of crosslinked polyamide membranes I. Changes in chemical/morphological properties", *J. Membrane Sci.*, **283**(1-2), 21-26.

Kwon, Y-N. and Leckie, J.O. (2006), "Hypochlorite degradation of crosslinked polyamide membranes II. Changes in hydrogen bonding behavior and performance", *J. Membrane Sci.*, **282**(1-2), 456-464.

Li, B-B., Xu, Z-L., Qusay, F.A. and Li, R. (2006), "Chitosan-poly (vinyl alcohol)/poly (acrylonitrile) (CS–PVA/PAN) composite pervaporation membranes for the separation of ethanol–water solutions", *Desalination*, **193**(1-3), 171-181.

Liu, M., Chen, Z., Yu, S., Wu, D. and Gao, C. (2011), "Thin-film composite polyamide reverse osmosis membranes with improved acid stability and chlorine resistance by coating N-isopropylacrylamide-co-acrylamide copolymers", *Desalination*, **270**(1-3), 248-257.

Loeb, S. and Sourirajan, S. (1964), *U.S. Patent* 3,133,132.

Majumdar, S. and Adhikari, B. (2006), "Polyvinyl alcohol: A taste sensing material", *Sensors and Actuators B*, **114**(2), 747-755.

Mansur, H.S., Sadahira, C.M., Souza, A.N. and Mansur, A.A.P. (2008), "FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde", *Mater. Sci. Eng.*, **28**(4), 539-548.

Petersen, R.J. (1993), "Composite reverse osmosis and nanofiltration membranes", *J. Membrane Sci.*, **83**(1), 81-150.

Svang-Ariyaskul, A., Huang, R.Y.M., Douglas, P.L., Pal, R., Feng, X., Chen, P. and Liu, L. (2006), "Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol", *J. Membrane Sci.*, **280**(1-2), 815-823.

Tang, C.Y., Kwon, Y-N. and Leckie, J.O. (2008), "Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes I. FTIR and XPS characterization of polyamide and coating layer chemistry", *Desalination,* **242**(1-3), 149-167.

Yeom, C.K. and Lee, K.H. (1996), "Pervaporation separation of water-acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde", *J. Membrane Sci.*, **109**(2), 257-265.

Yu, S., Liu, M., Lü, Z., Zhou, Y. and Gao, C. (2009), "Aromatic-cycloaliphatic polyamide thin-film composite membrane with improved chlorine resistance prepared from m-phenylenediamine-4-methyl and cyclohexane-1,3,5-tricarbonyl chloride", *J. Membrane Sci.*, **344**(1-2), 155-164.

Yu, S. Lü, Z., Chen, Z., Liu, X., Liu, M. and Gao, C. (2011), "Surface modification of thin-film composite polyamide reverse osmosis membranes by coating N-isopropylacrylamide-co-acrylic acid copolymers for improved membrane properties", *J. Membrane Sci.*, **371**(1-2), 293-306.

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