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Experimental study of the effects of hypochlorite on polysulfone membrane properties

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Abstract

Although chemical solutions are widely employed to clean membranes, they can also be responsible for changes in membrane properties. The two major drawbacks are then either the functional properties of the membrane gradually change, so the production can no longer meet requirements in terms of volume or quality, or the membrane simply breaks up (hollow fibers), and the system has to be shut down during maintenance. The aim of this experimental study was to gain a better understanding of the effect of hypochlorite cleaning solutions in different conditions (various pHs and temperatures) on the changes observed on an ultrafiltration hollow fiber membrane made from polysulfone (PSf) and polyvinylpyrrolidone (PVP). A wide range of methods characterizing the material have been used, from the atomic scale (ESCA) up to the module scale by force measurements on fibers. Exposure to sodium hypochlorite at rather high concentration seems to lead to chain breaking in the PSf molecules (gel permeation chromatography results). The consequences are changes in the membrane texture (scanning electron microscopy images), which are closely related to changes in the mechanical properties of the membrane. Membrane permeability appears to be poorly sensitive to such changes, which can be related to the fact that the permeability relies on the skin properties mainly.

Keywords: Characterization; Polysulfone; Ageing; Cleaning; Ultrafiltration; Hypochlorite

1. Introduction

Numerous strategies to alleviate membrane fouling have been searched for, including non-fouling membrane materials, improved hydrodynamics (turbulent, non-steady, secondary flows, multiphase flow), and enormous progress has been made in the past decade in process control which allows the frequency of in-place membrane chemical cleaning procedures to be reduced. However, these are still required whatever the type of application. In the drinking water industry, they occur at a pace of once in a week to once in a month. However, frequent chemical cleaning can give way to an increased risk of bacterial growth in the systems, so, in between chemical cleanings, short but frequent bio-sanitation procedures must be applied, to maintain a healthy system, and satisfy regulations.

Thus, the use of membrane processes requires the use of chemicals, selected for their oxidative, acido basic, or even bac-

teriostatic properties. Their frequent use, all along the lifetime of a membrane, and even in conditions chosen as mild as possible, has an impact on the membrane properties, on the economics of the process and on the environment. There are two ways in which the impact is felt: either the functional properties of the membrane gradually change, so production no longer comes up to requirement in terms of volume or quality, or the membrane simply breaks up (hollow fibers), and the system has to be shut down for the whole duration of maintenance, which is expensive.

These effects are especially noticed with polymer membranes, and for plants working over long periods of time: drinking water production by membrane is certainly one good example of this type of situation today. Engineers would like to anticipate such changes in membrane properties (also called ageing), and at least understand the mechanisms behind the changes, so as to be able to account for them in optimizing cleaning procedures.

It has been the aim of this experimental study to better understand the effect of some of the chemicals used to maintain membrane plants on the changes observed on an ultrafiltration

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membrane. For this, an “on-site” real-time analysis would probably last for several months or years, before one obtains the very first results, and this is the reason for us to choose the option of dipping the membranes in various solutions in a continuous manner (whereas in a plant, membranes are in contact with water most of the time and with cleaning agents for short, periodic times). From the few studies published so far, we have analyzed that membrane ageing can be due to both mechanical and chemical effects, and preferred to start studying the effect of only one of those parameters: the chemical one. In order to consider the two major drawbacks of membrane ageing, namely changes in functional properties and mechanical failure, we used a wide range of methods characterizing the material, from the atomic scale, up to the module scale by force measurements on membrane bundles. This paper reports the results we found and the conclusions drawn from them.

2. Background

There is abundant literature on membrane cleaning, especially in the fields of ultrafiltration and microfiltration, where fouling is most crucial, but also in reverse osmosis: there are numerous desalination plants in operation around the world, but few report on damage to the membrane properties and the consequences on the lifetime of the membrane.

The paper published by Zhu and Nyström [1] aimed at understanding the way in which cleaning agents react with the membrane and whether they actually modify the membrane in such a way to prevent fouling. To reach a reference state before studying fouling and cleaning efficiency, Zhu and Nyström [1] pre-treated polysulfone (PSf) and modified-PSf UF membranes with various cleaning agents in particular NaOH. After pre-treatment, membranes made of modified PSf exhibited the same surface charge as the untreated membrane and a strong increase in permeability. Different cleaning agents at various concentrations and pH were tested by Liikanen et al. [2] on a water treatment nanofiltration membrane. Their conclusions were that alkaline chelating cleaning agents are the most efficient in cleaning the membrane and that they led to a doubling of untreated membrane permeability. This result was attributed to membrane charge modifications in an alkaline environment and its ability to remove constituents from the membrane structure, making the membrane more open. But, according to the authors, even though the long-term effects of the cleaning methods tested were not generally evaluated, membrane characteristics (they did not mention which) were not degraded in a 13-week study. Benavente and Vasquez [3] studied the impact of hydrochloric acid, nitric acid and sodium hydroxide (1 mol L^{-1}) on polyamide/PSf reverse osmosis membranes. This study shows that both skin and support are affected by the treatment, leading to a permeability increase when the membrane is treated with HCl or HNO_3 and decrease when treated with NaOH. Slight modifications in the chemical composition of the surface of the polyamide active layer were observed after membrane treatment, which were attributed to polyamide oxidation. The authors ascribe the changes in membrane transport properties to a modification in polyamide skin structure (pore size/length, morphology).

Few papers address the question of the action of hypochlorite on the properties of porous membranes. Sayed Razavi et al. [4] investigated different cleaning procedures on PSf UF membrane fouled by extracts of soy flour. One of these procedures consisted in successive applications of cleaning agents among which sodium hypochlorite (150 ppm). The use of NaOCl increased the flow by about 20%. The considerable contribution of hypochlorite was attributed by the authors to its effect as a “membrane swelling agent” which enabled the foulant lodged within the pores to be flushed out. Mohammadi et al. [5] showed that the best combination to clean a PSf UF membrane fouled by microorganisms, proteins, fats, or minerals is sodium dodecyl sulfate and sodium hydroxide but a mixture of sodium hypochlorite and sodium hydroxide is also acceptable. They note that flux recovery is more than 100% if sodium hypochlorite is used at a concentration above 0.4 wt%. The authors proposed two explanations. Either the structure of the membrane is damaged and partially destroyed due to the contact with the NaOCl at high concentrations or sodium hypochlorite causes the membrane to be more hydrophilic and in addition to membrane cleaning, it makes the permeation flux increase. Damage of polyamide reverse osmosis membranes exposed to hypochlorous acid (HClO) have also been demonstrated by several authors including Gabelich et al. [6]. The mechanism of degradation is chlorination of polyamides through reaction of HClO with the nitrogen of the secondary-substituted amide group, which then results in ring chlorination.

In the present work, the membranes used were made of PSf modified by PVP and we comment on papers devoted to the action of hypochlorite on the properties of polymer membrane containing PVP (to confer a hydrophilic character). The most significant studies found in the literature are summarized in Table 1.

Except in the study reported by Wolff and Zydney [14], hypochlorite is used as part of a pre treatment to improve (or stabilize) membrane permeability prior to further studies. Hypochlorite pre-treatment is reported to enhance the flux of MF/UF membranes made of a blend of PVP and hydrophobic polymer. All studies refer to permeability and retention changes to assess the effects of chemical treatment on membrane properties. In each case, two to four additional characterization techniques were used but not all the scales from elementary to macroscopic have been reported in the same study.

Wienk et al. [7] were the first to report on an increase in permeability, ascribed to an elimination of PVP from the membrane matrix. This conclusion was confirmed by others. Wienk et al. [7] postulate that the selective PVP elimination could be due to the opening of a ring in the PVP molecules or to chain scission of PVP by hypochlorite. They quantify the contribution of both mechanisms to PVP degradation and conclude that the second mechanism seems to be the most important. These authors also studied the molecular mass of PES (material of the membrane matrix) treated with hypochlorite at different pHs and concluded that there was no reaction between PES and hypochlorite at pH 6.9–11.5. They completed this part of the study by showing that BSA retention was constant although the membrane water flux increased linearly with an increase in treatment time. Xu et al.

Table 1
Summary of published works on the action of hypochlorite on UF membranes containing PVP

Author	Membranes	PVP composition	[NaOCl] (ppm)	pH	Techniques	Tracers used for retention tests	$R_{\text{final}}/R_{\text{initial}}$
Wienk et al. [7]	PES/PVP	4.6 wt%	3000	3.9, 6.9, 11.5	Lp, R, IR, GPC	BSA	1
Qin et al. [8]	PES/PVP	5 wt%	4000	Not specified	Lp, R, SEM	PVP 40 kDa BSA	0.24 1
Xu et al. [9]	PEI/PVP	Different weight ratio	4000	Not specified	Lp, R, Ts, El, Tg, SEM	PEG 35 kDa	From 0.85 to 0.99
Qin et al. [10]	CA/PVP	5 wt%	200	7	Lp, R, SEM	PVP 24 kDa BSA	0 0.78
Jung et al. [11]	PAN/PVP	12 wt%	5000	Not specified	Lp, R, SEM, IR-ATR	Dextran 160 kDa	0.5
Qin et al. [12]	PAN/PVP	3 wt%	500–1000	7	Lp, R, SEM	PEG 35 kDa PVP 360 kDa	0.01 0.98
Qin et al. [13]	PSf/PVP	5 wt%	2000–6000	11.5	Lp, R, SEM	PVP 10–40 kDa BSA	From 0.13 to 0.33 1
Wolff and Zydney [14]	PSf/PVP	5 wt%	2400	7.4	Lp, R, ESCA, ζ	Dextrans 5–100 kDa	From 0.25 to 0.46

SEM: scanning electron microscopy, R: retention coefficient, El: elongation, Ts: tensile strength, Tg: glass transition temperature IR-ATR: infrared-attenuation total reflexion; ESCA: elementary spectroscopy for chemical analysis; ζ : zeta potential; PES: polyethersulfone; PEI: polyetherimide; CA: cellulose acetate; PAN: polyacrylonitrile; BSA: bovine serum albumin; PEG: polyethylene glycol.

[9] report a decrease in PEG 35 kg mol⁻¹ retention and a change in elongation at break point after immersion of the membrane in hypochlorite solutions at varying pH and duration. The first observation was attributed to the presence of bigger pores sizes because of the removal of PVP from the membrane matrix. No explanation was proposed for the modification of mechanical properties.

The effect of hypochlorite has also been investigated by Qin et al. [10] on CA/PVP hollow fiber UF membranes. SEM images show that the inner surface of the fibers appears to become smooth and the pores seem to be larger after the hypochlorite treatment. The porosity on the outer surface of the treated membrane appears to be higher than that of the untreated membrane. The authors mention that these changes in morphology can be attributed to the removal of PVP from the blended polymers. As a result, fluxes through hypochlorite treated membranes are three times higher than through untreated membranes and retentions (PVP 24 kg mol⁻¹ and BSA) are much lower. Similar experiments have been conducted by the same group of researchers on hollow fiber UF membranes made from various materials: PES/PVP [8], PAN/PVP [12], and PSf/PVP [13]. In reference [13] PVPs of different molecular masses were used as tracers in retention tests. The retention curves obtained with untreated and treated membranes are compared. According to the authors, the change in the shape of these curves implies that the pore size distribution of the treated membrane is narrower after soaking in 4000 ppm aqueous hypochlorite solutions for over 48 h at pH 11.5. Qin et al. [13] conclude that hypochlorite treatment appeared not only to remove residual PVP from the membranes, which reduced swelling of PVP in the pores, but also changed the membrane pore size or pore size distribution. They mention that this is an additional conclusion to the results obtained by Wienk et al. [7] who reported that hypochlorite treatment did not sub-

stantially alter the membrane pore structure because membrane retention measured using BSA was found to be constant. We assume this discrepancy between the conclusions drawn by the different authors can be due to the fact that BSA molecules are too large for the pore size of the membranes studied by Wienk et al. [7] and that BSA may foul the membrane and therefore interfere with the studied mechanism, resulting in no change in retention. Qin et al. [13] argue that if solutes of smaller molecular size than the membrane pores were used to measure the retentions, a significant change in retentions between a treated membrane and an untreated membrane might be observed pointing to a change in pore size.

A direct relationship between the membrane pore size and the duration of the bleach treatment is shown by Wolff and Zydney [14] who study the effect of hypochlorite on the transport characteristics of PSf/PVP hemodialyzers. Their results indicate that it would be possible to produce membranes with the desired permeability and sieving characteristics by properly controlling the time (and possibly the temperature and concentration) of the bleach treatment. According to the authors, their results also suggest that these membranes remain defect-free, i.e. there are no large non-retentive pores. Finally they underline the fact that bleach causes significant changes in the membrane properties beyond those associated directly to the removal of PVP. The origin of these changes is currently unknown, although they could be due to: the redistribution of PVP within the membrane structure, the chemical modification of the PSF itself, and/or a conformational change in the membrane polymer.

In the present work we investigated the action of hypochlorite used during cleaning-in-place procedures in water production plants. In such applications, hypochlorite is used during two steps: one back flushing of ca. 1 min at 10 ppm of NaOCl not more frequently than every 30 min (the concentration varies

between 2 and 10 ppm and the pH is that of the water source); one cleaning procedure with NaOCl once a week (or even less frequently) for 1 h (total free chlorine concentration varies between 20 and 400 ppm and the pH is 12). In a preliminary paper [15], we reported the results obtained with PSf/PVP hollow fiber UF membranes soaked in hypochlorite solutions at pH 8 and 12 and 400 ppm of total free chlorine (TFC) (TFC corresponds to the sum of the concentration of hypochlorous acid and hypochlorite ions). Whatever the pH of the hypochlorite solution, we observed an increase in permeability with a decrease in retention. Analysis of the atomic composition of the membrane surface by ESCA revealed a simultaneous decrease in nitrogen percentage that can correspond to the removal of PVP from the surface. These results are in agreement with those reported by the authors mentioned above [7–14].

On the other hand, changes in mechanical properties of the membranes were observed only at pH 8. As the polymer matrix (PSf in this study) confers the membrane's mechanical properties, we assumed that PSf chains are damaged. Moreover, if we consider the diagram of predominance of HClO and ClO⁻ forms of chlorine in NaOCl solutions versus pH at 25 °C (Fig. 1 and data in the following in the case of 400 ppm TFC), it results that hypochlorous acid (HClO) is the form of chlorine responsible for mechanical degradation of the PSf membrane.

- pH 8: [HClO] = 100 ppm, [ClO⁻] = 300 ppm.
- pH 12: [HClO] = 0.2 ppm, [ClO⁻] = 399.8 ppm.

Similar observations were reported by Gabelich et al. [6] who mention that chlorination reactions with polyamide membranes have been shown to be pH dependent, with greater chlorine sensitivity observed at lower pH. Therefore, they assumed that HClO is the active species in polyamide chlorination.

To validate the previous assumption regarding the effect of HClO, experiments were conducted with the same HClO concentration over a range of pH values (5, 7, 8, and 10). Various membrane properties were monitored as a function of contact time: hydraulic permeability, tracer retention, mechanical properties, distribution of molar masses of the membrane material, SEM images, atomic composition, and swelling.

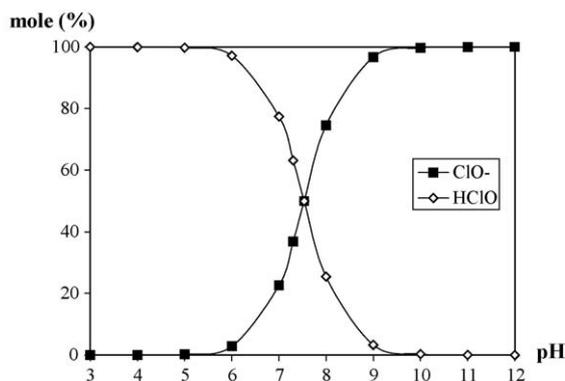


Fig. 1. Diagram of predominance of HClO and ClO⁻ forms of chlorine in aqueous solutions vs. pH at 25 °C.

3. Materials and methods

3.1. Membranes, modules, and procedure

The membranes studied were inner skinned hollow fibers ($D_{\text{int}} = 0.96$ mm and $D_{\text{ext}} = 1.70$ mm) and flat sheets made of a blend of PSf and polyvinylpyrrolidone (PVP), the latter being added to make the final material more hydrophilic. Flat sheet is the geometry necessary for ESCA analysis whereas all other experiments were conducted on hollow fibers. The PVP content is less than 5% (w/w). The nominal cut-off deduced from filtration of dextrans, as provided by the manufacturer, is 40 kg mol^{-1} .

The membranes were soaked in hypochlorite solutions containing a constant HClO concentration (100 ppm) at various pHs: 5, 7, 8, and 10 and at 25 °C. Fibers were sampled after 1, 2, 4, 8, and 16 days, from the tank, and modules were fabricated using 16 fibers of 30 cm in length. Modules are “home-made” by potting the fibers in a PVC shell, with “epoxy” glue. Contact times correspond to 0.5, 0.9, 1.8, 3.7, and 7.3 equivalent years on site for the unfavorable conditions (one back flushing step of 1 min at 10 ppm of TFC every 30 min plus one cleaning step of 1 h at 400 ppm of TFC once a week) and 5.9, 11.8, 23.6, 47.3, and 94.7 equivalent years on site for the most favorable conditions (one back flushing step of 1 min at 2 ppm of TFC every 30 min plus one cleaning step of 1 h at 20 ppm of TFC once a week). The equivalent exposure time was simply calculated via the product time \times concentration. For the bath at pH 8, the experiment was continued over 128 days.

Experiments at 6 and 40 °C have also been carried out at pH 7 and 100 ppm of HClO (6 °C is the minimum water temperature on a water production plant in winter, and 40 °C is the maximum water temperature in summer).

3.2. Solutions and analysis

Solutions were prepared from sodium hypochlorite concentrates (Oxena, 36° in chlorine) diluted in RO-treated water. The chlorine concentration was followed by a spectrophotometer at 530 nm (HACH 2400) using a specific reagent (DPD Free Chlorine Reagent HACH 14070-99 Pk/100) and standard samples for the calibration. The solutions were replenished every other day, so as to maintain a constant chlorine concentration. pH was adjusted with sodium hydroxide and hydrochloric acid (1 mol L^{-1}) supplied by Acros Organics. As previously mentioned, the solutions contained a constant concentration of HClO (100 ppm) at various pHs: 5, 7, 8, and 10. According to equilibrium (1) the TFC (defined in Eq. (2) in which the dissolved Cl₂ is neglected because very low at pH > 5) and ClO⁻ concentrations differ with pH (see Table 2):



$$[\text{TFC}] = [\text{HClO}] + [\text{ClO}^-] \quad (2)$$

with $\text{p}K_a(\text{HClO}/\text{ClO}^-) = 7.53$ at $T = 25$ °C.

Retention tests were conducted with a solution of PEG 10 kg mol^{-1} (Fluka) at a concentration of 1.0 g L^{-1} . This

Table 2
TFC, HClO, and ClO⁻ concentrations in hypochlorite solutions vs. pH

	pH 5	pH 7	pH 8	pH 10
[TFC] (ppm)	100	130	400	29914
[HClO] (ppm)	100	100	100	100
[ClO ⁻] (ppm)	0	30	300	29814

PEG was chosen at the beginning of the study, because its intrinsic retention [16] by the clean membrane was 90%. The hydrodynamic conditions correspond to laminar flow: $Re = 1800$. Tracer solution has been filtered at a constant pressure 0.5×10^5 Pa (0.5 bar) corresponding to a permeation flux of 2.2×10^{-5} m s⁻¹. The permeate was recycled to maintain a constant volume (and concentration) in the tank. Once the flux had stabilized (after a filtration period of 20 min), 10 mL filtrate and retentate samples were collected for subsequent Total Organic Carbon analysis (TOC-5050A, Shimadzu, Japan).

3.3. Other methods

Mechanical properties (elongation and tensile strength at break point) were measured on fibers under wet conditions with an Instron 4301 (speed of stretching = 200 mm min⁻¹ for a sample of 200 mm).

The distribution of the molar masses of the membrane material was measured by gel permeation chromatography (GPC) after dissolving a membrane sample (4 mg) in THF. Only PSf was analyzed then, since PVP is insoluble in THF and was removed from the analyzed samples by filtration through 0.45 μm discs. Three styragel columns (Waters Styragel HR, Milford, USA) were used in series to cover the range of molar masses from 1 to 200 kg mol⁻¹. Flow of eluant was 1.9 mL min⁻¹ and the temperature of the column was 25 °C. Detection was based on a differential refractometer (Waters 410, Milford, USA) and a light scattering detector at three angles: 44.7°, 90°, and 135.3° (Mini Dawn, Wyatt Technology Corporation, Santa Barbara, CA, USA).

Scanning electron microscopy (SEM) pictures were obtained with a LEO 435 VP instrument (Carl Zeiss NTS GmbH, Oberkochen, Germany) after cutting the membrane in the axial direction with a scalpel and metallization of the sample surface (see Fig. 2).

The atomic composition of the membrane surface was obtained by ESCA (Escalab Mk II (VG)). Four elements were analyzed: sulfur (that represents polysulfone); nitrogen (that represents PVP); sodium and chlorine that are present in ageing solutions. These analyses were conducted only on flat sheets. The sample size was 2 mm × 2 mm, and it was taken from the skin previously dried.

Swelling was determined from measurements under wet conditions of the fiber diameter under an optical microscope (Euromex, Netherlands). A swelling index, S , was calculated as follows:

$$S = \frac{D_{\text{ext}} - D_{\text{int}}}{D_{\text{ext},0} - D_{\text{int},0}} \times 100 \quad (3)$$

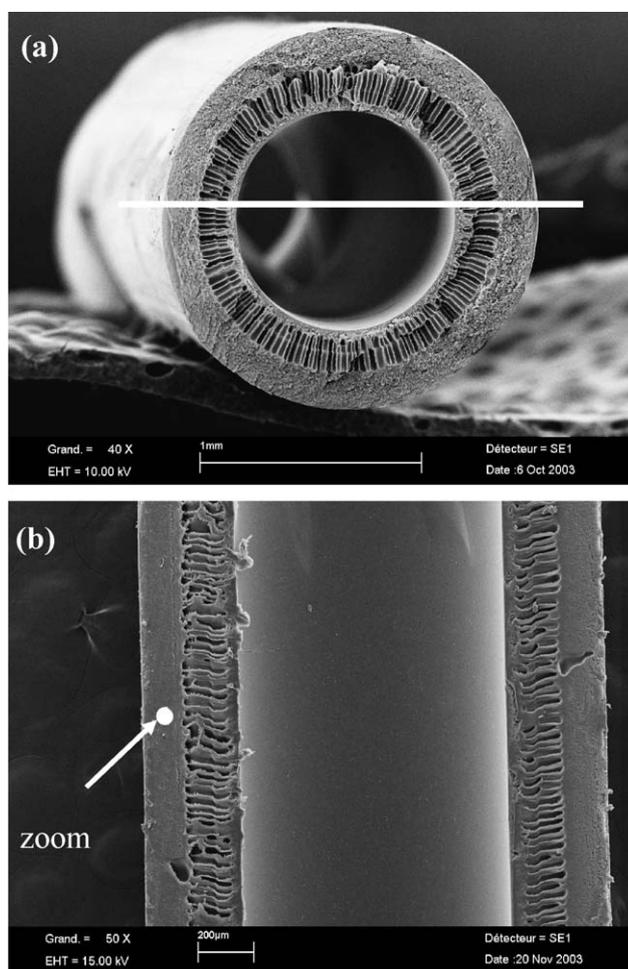


Fig. 2. SEM pictures of a new hollow fiber membrane (a) cross-section and (b) sample cuts in the axial direction and area that has been zoomed in Figs. 7, 8, 13 and 14.

where $D_{\text{int},0}$ and D_{int} are the internal diameter of the new and aged hollow fiber, respectively; $D_{\text{ext},0}$ and D_{ext} are the external diameter of the new and aged hollow fiber.

When $S \approx 1$, the membrane has conserved its geometrical properties. $S > 1$ indicates a swelling of the membrane structure.

4. Results

4.1. Effect of total free chlorine concentration

As already mentioned the objective of this set of experiments was to verify if hypochlorous acid (HClO) is the chlorine form which is mainly responsible for the degradation of the mechanical properties of the PSf membrane. In this aim, HClO concentration was maintained constant in solutions at various pH values (5, 7, 8, and 10) corresponding to different TFC and ClO⁻ concentrations (Table 2).

Results obtained are shown in Tables 3 and 4 and Figs. 3–10. Permeability L_p and mechanical properties E_l and T_s (elongation and tensile strength at break point) are reported as a function of contact time in relative values, compared to the initial membrane characteristics $L_{p0} = 7.9 \times$

Table 3

Evolution of elementary composition (at.%) during contact time at the membrane surface soaked in the solution at 400 ppm TFC, pH 8 (ESCA)

Atom	S	N	S/N	Na	Cl
New membrane	42.2	52.9	0.80	4.91	0
1 Day	57.0	37.9	1.50	2.7	2.4
2 Days	39.0	25.6	1.52	4.9	30.5
16 Days	52.9	30.3	1.75	8.7	8.1

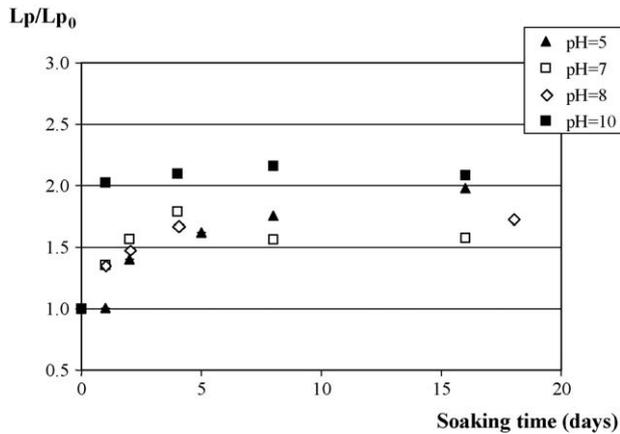


Fig. 3. Evolution of permeability of membranes soaked in the baths at 100 ppm HClO, different pHs.

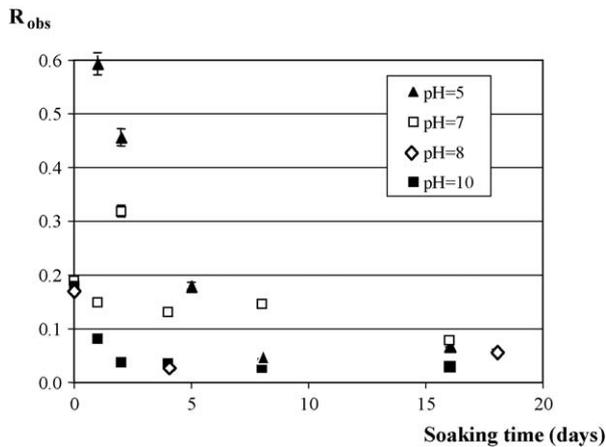


Fig. 4. Evolution of observed retention of PEG 10 kg mol^{-1} of membranes immersed in baths at 100 ppm HClO, at different pHs.

Table 4

Swelling index S , polydispersity index PI , and average molar masses in number M_n and in weight M_w of new membrane and membranes immersed for 16 days at pH 5, 7, 8, and 10 at 25°C

	New membrane	pH 5	pH 7	pH 8	pH 10
Swelling index, S	–	1.07 ± 0.02	1.09 ± 0.02	1.12 ± 0.02	1.10 ± 0.02
M_n (kg mol^{-1})	31	31	35	31	21
M_w (kg mol^{-1})	51	45	51	48	44
PI	1.6	1.5	1.5	1.5	2.1

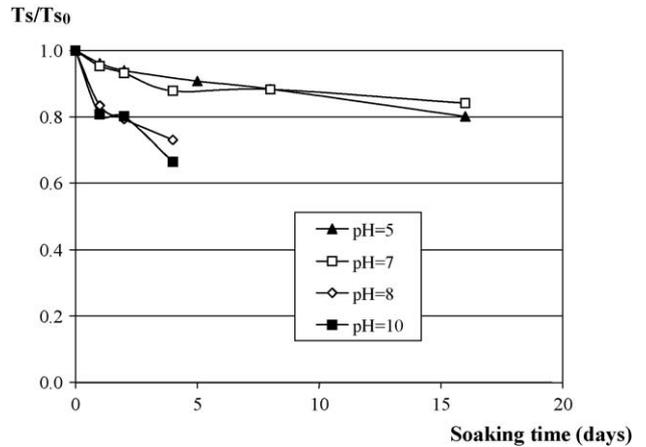


Fig. 5. Relative tensile strength at break point of membranes soaked in the baths at 100 ppm HClO, at different pHs.

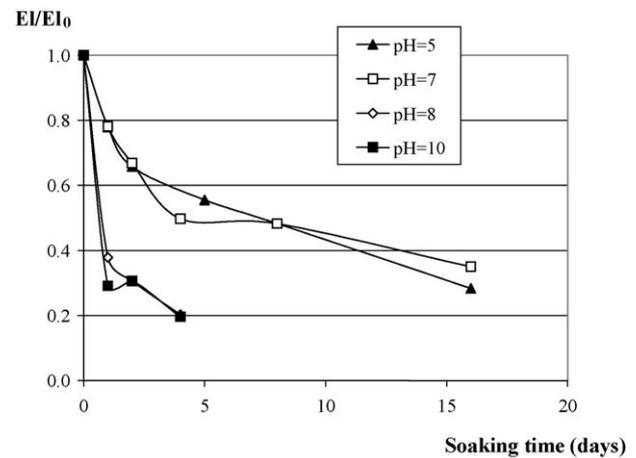


Fig. 6. Relative elongation at break point of membranes soaked in different baths at 100 ppm HClO, at different pHs.

$10^{-13} \pm 0.2 \times 10^{-13} \text{ m}$ ($100\text{L/h/m}^2/\text{bar} = 2.3 \times 10^{-13} \text{ m}$ at 25°C), $El_0 = 37\%$ (El_{raw} polysulfone = 50–100% as provided by the manufacturer) and $T_{S0} = 7.3 \text{ N}$. The observed retention of PEG 10 kg mol^{-1} measured on a new membrane is 18%.

Whatever the pH, permeability increased with contact time and then leveled off (Fig. 3). At pH 10, permeability was 2.1 times higher than the initial permeability for a residence time in hypochlorite solution of only 1 day.

In Fig. 4, we observe that, except for a few experimental points that we cannot explain (pH 7 after 2 and 8 days), the observed retention of PEG 10 kg mol^{-1} decreased with time

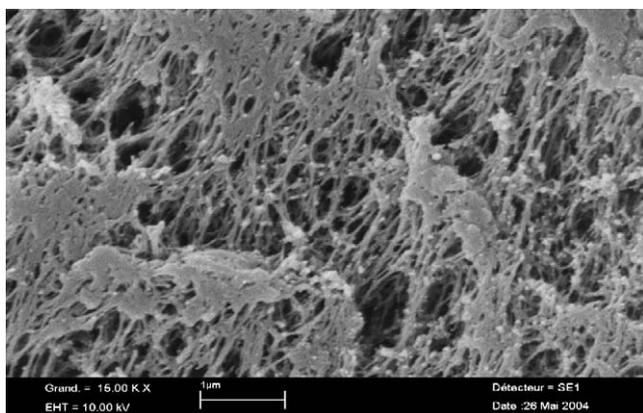


Fig. 7. SEM picture of a new membrane.

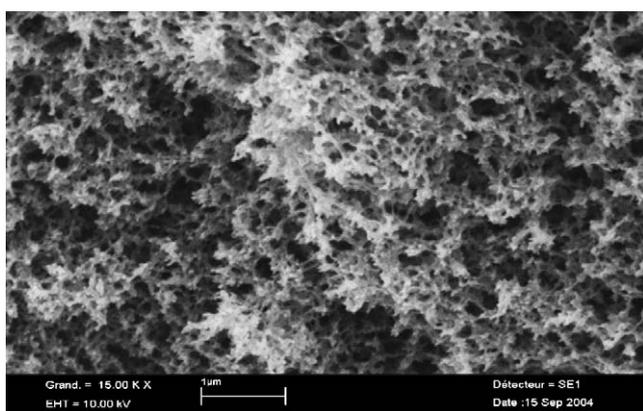


Fig. 8. SEM picture of a membrane immersed for 16 days at 100 ppm in HClO, 25 °C.

all pHs, especially at high pH. For long residence times in hypochlorite solutions all retentions tended to zero. For pH 10, this low value is even reached after 2 days of residence time.

From ESCA analyses (Table 3), we observed some chlorine absorption at the membrane surface. The proportion of nitrogen was lower than in a new membrane, which suggests that the PVP content decreases at the surface. It soon reached a plateau

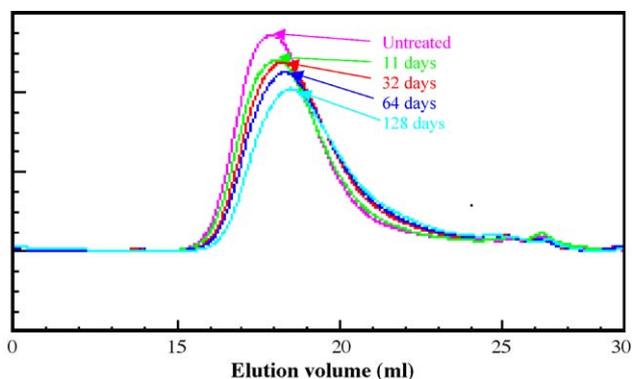


Fig. 9. Chromatograms for new membrane and membranes immersed in hypochlorite solution at 100 ppm HClO, pH 8 for different durations. The molar mass at the maximum of the distribution equals 78.3 kg mol^{-1} for the new membrane, 74 kg mol^{-1} after 11 days, then 60 kg mol^{-1} after 32 days, 59 kg mol^{-1} after 64 days, and 52 kg mol^{-1} after 128 days.

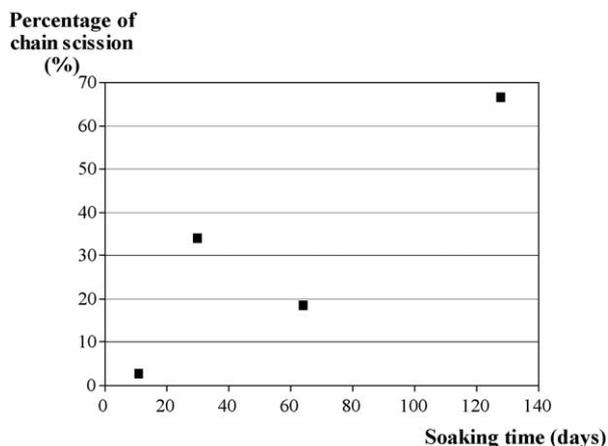


Fig. 10. Percentage of PSf chain scission vs. soaking time for membranes immersed in hypochlorite solution at 100 ppm HClO, pH 8.

so the value after 16 days was close to that after 1 day (see S/N values in Table 3). This can explain the change in permeability that increased during the first 4 days, and then reached a plateau (see Fig. 3).

The mechanical properties (Figs. 5 and 6) gradually decreased with residence time, but pH 8 and 10 provide much worse conditions than pH 7 or 5 at constant HClO concentration: the mechanical resistance of membrane samples dipped in solutions at pH 8 and 10 were too low to measure after 4 days. We noted that elongation at break point is more sensitive to degradation than tensile strength.

When some macroscopic properties of the membrane are altered, the microscopic morphology changes, the membrane becoming spongy whereas the morphology of a new membrane is filamentous. This is illustrated for certain conditions in Figs. 7 and 8, but was observed systematically. Concerning the swelling index (Table 4), the error prevents us to definitely conclude if the fiber swells at the same time.

Chromatograms obtained by GPC were used to calculate the average molar mass in number M_n ($\pm 10\%$) and in weight M_w ($\pm 10\%$) of the PSf chains in membrane samples. The average molar masses after 16 days under various pHs are reported in Table 4. The results suggest a molecular degradation of PSf in membranes soaked at pH 10 while at pH 5 and 7 M_n and M_w remained very similar to those of the untreated membrane. The polydispersity index $PI (=M_w/M_n)$ remained lower than 2 (Table 4), which suggests that molecular chain scission took place in the bulk of the membrane material. That means that there is no preferential location (at the surface for example) for this mechanism to take place.

We report in Fig. 9 the chromatograms obtained after various contact times between the membrane and the hypochlorite solution at pH 8. We observe a drift towards lower molar masses with time.

The mole number of chain scissions (n) per unit mass of sample after a contact time t can be determined using the following equation [17] with an accuracy of $\pm 20\%$:

$$n = \frac{1}{M_{nt}} - \frac{1}{M_{n0}} \quad (4)$$

Table 5

Swelling index S , polydispersity index PI , and average molar masses in number M_n and in weight M_w of membranes immersed 16 days in baths at pH 7 and various temperatures

	Temperature ($^{\circ}C$)		
	6	25	40
Swelling index, S	0.99 ± 0.02	1.09 ± 0.02	1.12 ± 0.02
M_n ($kg\ mol^{-1}$)	27	35	20
M_w ($kg\ mol^{-1}$)	46	51	33
PI	1.7	1.5	1.7

where M_{nt} is the average molar mass in number after ageing ($kg\ mol^{-1}$); M_{n0} is the average molar mass in number of new membrane ($kg\ mol^{-1}$).

As shown in Fig. 10, the proportion of chain scissions for membrane samples immersed in hypochlorite solution at pH 8 increased versus soaking time. If we consider the results obtained after 11 days soaking, n was equal to 8.8×10^{-4} moles of chain scission per kg of analyzed sample. We determine the percentage of chain scission by the calculation: $nM_{n0} \times 100$ ($M_{n0} = 31.2\ kg\ mol^{-1}$) which led to a figure of 2.8%. As previously mentioned, the mechanical properties of membrane samples immersed in solutions at pH 8 cannot be measured after 4 days because the membrane is too fragile and elongation loss of fiber soaked in the bath at pH 8 for 4 days was 80% (Fig. 6). It appears that the chain scissions occur at the same time as the dramatic change in mechanical properties. If the latter is the consequence of the former, this would mean that a few chain scissions (less than 2.8%) can have a high impact on the elongation and tensile strength at break point of the whole membrane material.

Overall, these results and those published in Ref. [15] suggest that the presence of $HClO$ is necessary for fiber degradation to take place but it is not the only parameter that has to be taken into account since at constant $HClO$ concentration, the higher the pH, the higher the levels of ClO^- and the greater the degradation of the fiber.

4.2. Effects of temperature

In addition to room temperature ($25\ ^{\circ}C$), two temperatures were studied (6 and $40\ ^{\circ}C$), for an $HClO$ concentration of 100 ppm and pH 7. Results are given in Table 5 and Figs. 11–14. These conditions were determined according to data taken over a year from a water production plant. pH 7 is the annual average pH of water at this site. Finally, an $HClO$ concentration was chosen high enough to generate fiber modifications, if indeed they do occur, after a contact time of 16 days (cf. pH 8 [15]).

At $40\ ^{\circ}C$, membranes became very brittle after 8 days, the permeability increased by a factor 2.6 and was larger than at 6 and $25\ ^{\circ}C$ (Fig. 11), in similar conditions. We can observe that the effect at $25\ ^{\circ}C$ is not consistent with that at 6 and $40\ ^{\circ}C$. This is not due to the experimental error, but to the lack of reproducibility of such experiments over a long period of time, given the variability of commercial membranes.

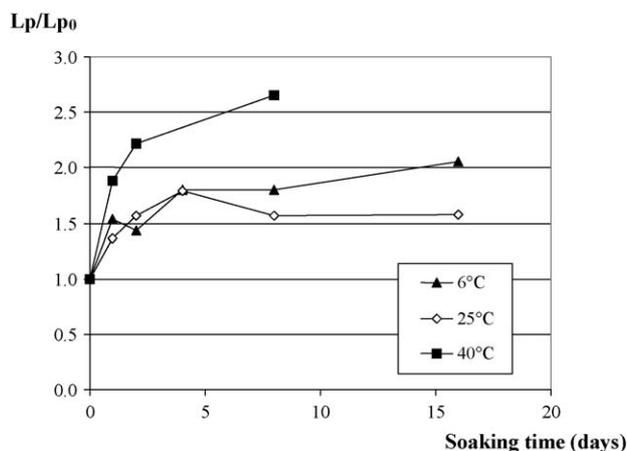


Fig. 11. Permeability evolution of membranes soaked in hypochlorite solutions at 100 ppm $HClO$, pH 7, at different temperatures.

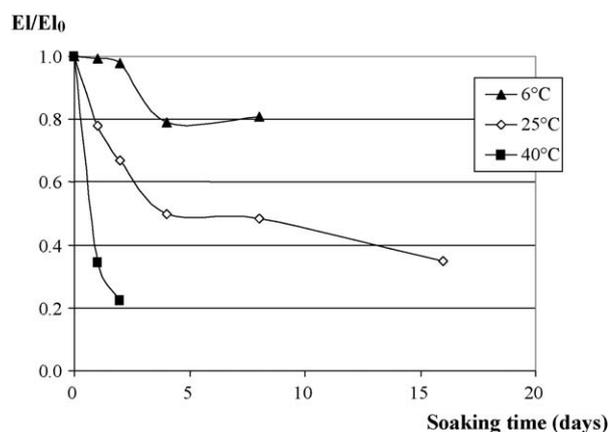


Fig. 12. Relative elongation at break point of membranes immersed in hypochlorite solutions at 100 ppm $HClO$, pH 7, and various temperatures.

At $6\ ^{\circ}C$, loss of tensile strength was negligible (results not shown here) whereas elongation loss (Fig. 12) was about 20% after 8 days of soaking. At $40\ ^{\circ}C$, tensile strength and elongation were only measurable for the two first days. Fiber weakening was thus activated by temperature: elongation loss of fiber soaked in the bath at pH 7 and $40\ ^{\circ}C$ for 2 days was 80%, i.e. the same

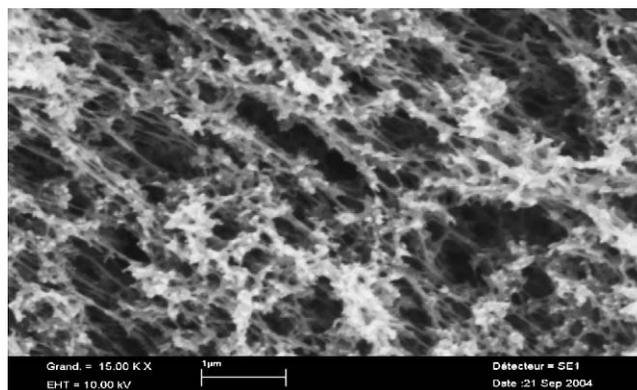


Fig. 13. SEM picture of membrane soaked for 16 days at 100 ppm $HClO$, pH 7, $6\ ^{\circ}C$.

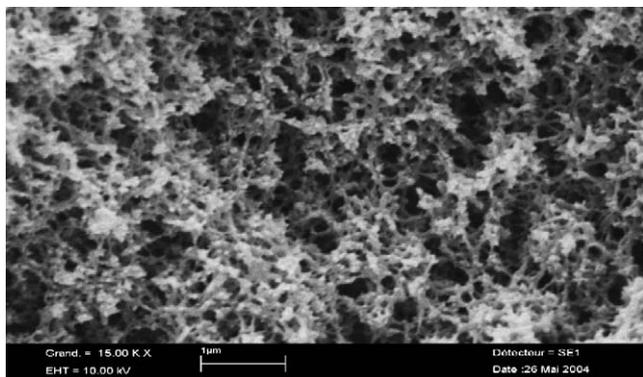


Fig. 14. SEM picture of membrane immersed 16 days at 100 ppm HClO, pH 7, 40 °C.

as that of a fiber soaked for 4 days in similar conditions but at 25 °C.

SEM pictures of membrane immersed 16 days at 40 °C (Fig. 14) show a spongy morphology. At 6 °C (Fig. 13) a slightly filamentous morphology is still visible after 16 days (see also Fig. 7). These results seem to show that, during ageing, the absence of modification of the membrane mechanical properties is correlated to an unchanged membrane morphology.

Average molar masses of membranes immersed for 16 days in solutions at pH 7 and different temperatures are reported in Table 5. The greatest decrease in average molar masses was observed in membrane treated at 40 °C. We also note that stronger fibers (experiment at 6 °C) did not swell (Table 5).

5. Discussion and others results

We have shown in a previous report [15] and discussed in Section 2 that when a membrane is in contact with hypochlorite solutions but not hypochlorous acid (pH higher than 11 and 400 ppm of total free chlorine) membrane mechanical properties and PSf molar mass do not vary significantly. The conclusion was that in the absence of the HClO form of chlorine, PSf is not damaged.

On the other hand in Section 4.1, we noted that, in the presence of a given concentration in hypochlorous acid (HClO), membrane properties are modified more at high pH (in the range 5–10). This shows that an increase in ClO^- (Table 2) and OH^- concentrations play a role in membrane degradation.

With the hollow fibers used in this study, the support is made up of a mixture of PSf/PVP with PSf as polymer matrix. As a consequence we assume that the decrease in mechanical properties observed is mainly attributed to PSf degradation, which occurs in the bulk of the membrane material.

An additional experiment was conducted to verify this assumption. We obtained from the manufacturer hollow fibers made of pure PSf according to the same protocol as for the PSf/PVP membrane. These membranes have an inner diameter of 9.4×10^{-4} m and an outer diameter of 1.62×10^{-3} m, i.e. a slightly thicker fiber than those made of PSf/PVP. Their permeability is 7.3×10^{-14} m, which is much lower than that of

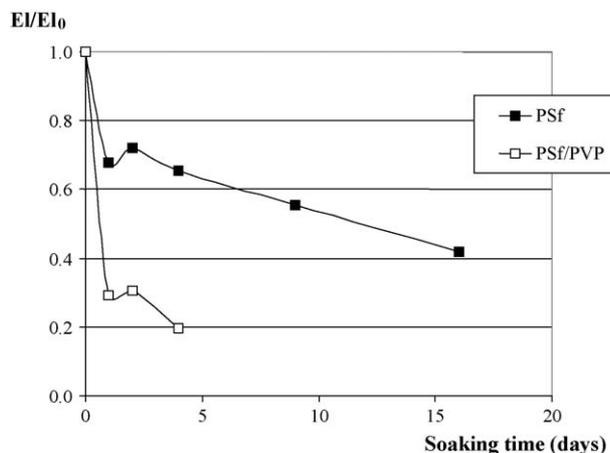


Fig. 15. Elongation at break point of PSf and PSf/PVP membranes vs. soaking time in solution at 100 ppm HClO, pH 10, 25 °C.

membranes containing PVP; retention of PEG 10 kg mol^{-1} is 20% in the same conditions of flux and cross flow velocity, so about the same as that of the PSf/PVP membrane. They have an elongation at break point of 56% and a tensile strength at break point of 10 N.

We carried out tests with this PSf membrane in a solution of 100 ppm HClO, pH 10, 25 °C. Results in terms of elongation versus contact time are presented in Fig. 15. Even in the absence of PVP, we note degradation after contact with hypochlorite solution which confirms that PSf can be altered in the presence of the bleaching agent. The loss of mechanical properties (35% after 4 days and 60% after 16 days) is not as great as for the PSf/PVP membranes immersed in the same solution (80% after 4 days of immersion). But, understanding the exact role of PVP in the mechanical strength of the membrane would need further investigation.

ESCA measurements revealed a decrease in the proportion of nitrogen at the membrane surface after immersion in baths at pH 8 and 12, 400 ppm total free chlorine [15]. At the same time, permeability increased and retention decreased, but only at pH 8 was mechanical degradation observed. In the conditions for which membrane permeability decreases without apparent degradation of the structure (immersion in water or in alkaline solution [15]), the nitrogen composition at the surface was unchanged versus new membrane. These results fit with those obtained by Wolff and Zydney [14] on PSf/PVP membranes. Then we conclude that there was partial elimination of PVP during fiber contact with hypochlorite solutions, whatever the pH and HClO concentration. However, results obtained at pH 12 and 400 ppm total free chlorine show that PVP elimination of the matrix is not sufficient to change membrane properties other than permeability and retention. PVP is thus not involved as a major component in the material strength.

Overall, it can therefore be concluded that deterioration of mechanical properties is essentially due to PSf degradation. Xu et al. [9] also obtained fiber weakening after contact with hypochlorite solution without however reaching a conclusion as to the mechanism of action of hypochlorite on the polymer matrix of the membrane (polyetherimide). Concerning the

mechanism of PSf degradation, chromatography revealed that it is a chain scission.

SEM pictures of a new membrane show a filamentous morphology. When membrane is degraded after contact with hypochlorite and mechanical properties are changed, the morphology becomes spongy from the first days of soaking ($5 \leq \text{pH} \leq 12$ for an HClO concentration of 100 ppm, $T > 6^\circ\text{C}$).

This evolution of membrane structure shown by SEM is only due to PSf chain scission and not to the removal of PVP, since, after soaking in conditions for which removal of PVP is still effective but without degradation of PSf (400 ppm TFC, pH 12) no change in membrane morphology and no swelling were observed. In fact, the removal of PVP only has an influence on permeability but not on membrane strength. This last result is not surprising considering that the PVP content is less than 5% (w/w) of the membrane material.

The SEM images point out that mechanical weakening is accompanied by polymer filament (PSf) relaxation leading to a change in the apparent morphology accompanied by chain length reduction (Tables 4 and 5).

Membrane structure evolution after PSf chain scission can be due to physico-chemical or structural phenomena. Among the physico-chemical phenomena, membrane hydration must play a critical role. Water sorption analyses on the same type of new and aged fibers [18] have not revealed more water adsorption in the case of aged than new membranes. More probable is then that a few chain ruptures lead to a re-organization on the microscopic scale, under the effect of mechanical stress that would explain that non-degraded membranes preserve their filamentous morphology, whereas degraded membranes lose it.

Comparing Figs. 3 and 6 shows that while the permeability stabilizes over dipping time, mechanical properties changes continue until the membrane is extremely fragile. Considering that the permeability is driven by the skin properties, whereas the mechanical strength relies on the whole membrane support, this observation suggests that the skin of the membrane is not very specifically damaged by the contact with the bleach solution, and therefore that the damage to the membrane by the cleaning solutions occurs throughout the whole structure of the latter.

From a practical point of view, our results suggests that cleaning steps combining bleaching agent and alkaline chemicals should definitely avoid the pH range between 8 and 10 (as can be seen in Figs. 5 and 6), and better be run at pHs either around 7 or 12, for a minimum of deterioration of the PSf membranes.

We have to underline that, because we decided to challenge the membranes with severe conditions, our results are obtained under the condition of 100 ppm HClO, which is higher than most of the practical conditions. Moreover, the chlorine in the cleaning solution first plays a role of disinfectant to react with/kill the microorganisms on the membrane, then the residual chlorine with much reduced concentration may have chance to attack the membrane material. On the other hand, the present study was run using clean membranes, whereas, some of the fouling materials can have a synergetic effect with bleach (either protective or catalytic), and this has to be further investigated for each type of processed water.

As a consequence, the conclusion that can be draw from these statements is that PSf membranes can stand normal cleaning conditions over several years.

6. Conclusions and perspectives

A long exposure to sodium hypochlorite produces chain breaking in the PSf molecules, which leads to changes to the membrane texture on the microscopic scale, and which is closely related to changes in the mechanical properties of the membrane. Few chain scissions have a very high impact on elongation and tensile strength at break point of the membrane material (loss of 80% in elongation at break point for a percentage of chain scissions lower than 2.8%). Membrane permeability seems to be poorly sensitive to such changes, and this can be related to the fact that the permeability relies on skin properties mainly.

Polysulfone membranes, modified by PVP withstand long contact with bleaching solutions. pHs between 8 and 10 should be avoided (this risk is low in normally conducted membrane plants), whereas pH 7 and 12 are quite safe. However, it seems that the process of PSf chain breakage is temperature activated, and that operating below 25°C is probably much safer than operating at higher temperatures.

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Nomenclature

El	elongation at break point (%)
Lp	permeability (m)
M_w	average molar mass in weight (kg mol^{-1})
M_n	average molar mass in number (kg mol^{-1})
n	number of moles of chain scissions per mass unit of sample
PI	polydispersity index
R_{obs}	observed retention (%)
S	swelling index
Ts	tensile strength at break point (N)

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