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# Ageing of polysulfone ultrafiltration membranes in contact with bleach solutions

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**Abstract**

During disinfections, water ultrafiltration membranes are mechanically and chemically stressed. A previous study demonstrated (S. Rouaix, Characterisation and study of ageing of an ultrafiltration membrane, PhD thesis, Université Paul Sabatier, Toulouse, France, 2005) a drop of membranes mechanical properties in contact with bleach accompanied by a degradation of transport properties. It clearly appears fiber embrittlement is a determining criterium, specially for water treaters. It seems thus essential to study long term behavior of polysulfone membranes in focussing on chemical structure–mechanical properties relationships. In this article, polysulfone membranes were immersed in bleach solutions with various pH values. Their structural changes were monitored by mechanical testing, molar mass determination and spectrochemical measurements. The observed degradation, which generates an embrittlement of the fiber, occurs by chain scission (determined by Size Exclusion Chromatography) with the hydroxyl radical $OH^{\bullet}$ formed in the bleach solution. The lifetime of the fiber depends on the total chlorine concentration of the ageing solution but also on its pH which drives the formation of hypochlorous acid and hypochlorite ion in great proportion, essential condition for the formation of hydroxyl radicals.


*Keywords:* Ultrafiltration; Polysulfone; Bleach; Hypochlorous acid; Radical degradation

## 1. Introduction

In the water ultrafiltration plants, membrane disinfection is realized with bleach solutions. These latter react relatively rapidly and unselectively with a wide variety of organic substrates and as a consequence they could also attack the polymeric materials constitutive of the membrane.

The main component (matrix) of the membrane is often a thermoplastic polymer chosen for its processing and mechanical properties. Most frequently polymers are bisphenol A polysulfone (PSU) [1,2], polyethersulfone (PES) [3], polyetherimide (PEI) [4], polyacrylonitrile (PAN) [5] and cellulose triacetate (CA) [6]. These materials must be modified, generally by polymeric additive blending/grafting, in order to increase their hydrophilicity. The additive most frequently used is polyvinylpyrrolidone (PVP). The above mentioned matrices are usually considered stable in use and washing conditions, explaining the lack of scientific literature on their possible ageing processes. On the other hand, ageing of PVP in bleach solutions has been extensively studied. Wienk et al. [2] studied the behavior of PES/PVP membranes in sodium hypochlorite solutions at pH values ranging from 3.9 to 11.5, and observed PVP consumption. According to Roesink [7], two distinct processes could occur: (i) chain scission resulting from attack by hydroxyl radicals formed in acidic media, and (ii) pyrrolidone ring opening by an ionic process in alkaline media. Qin et al. confirmed Wienk's observations in various membranes such as PSU/PVP [2], CA/PVP [6] and PAN/PVP [5]. Both mechanisms were tentatively checked using, for instance, IR spectrophotometry [8] or XPS [9]. This latter method, applied to hollow fibers, allows distinguishing internal and external faces of the membranes.

The PVP consumption can also influence membrane transport properties and can generate for example a permeability increase inducing a drop of tracers retention [2,5,6]. From this observation, Qin et al., proposed an optimized method to control final porosity of (PSU/PVP) membrane by soaking in a bleach solution at given concentration [10]. Moreover, a PVP decrease induces, as expected, a decrease of membrane hydrophilicity leading to a fouling increase [2,5,6]. Bleach solutions play thus a significant role on the membrane porous structure as on its transport properties which can affect using properties of the membrane and can have serious consequences in filtration plants.

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In the case under study (PSU/PVP), poly(ethylene oxide) (PEG) was used as a pore former. It is generally assumed that this agent is extracted by the water during the wash following the coagulation phase but, as it will be seen later, non-negligible PEG fractions can remain trapped in the polysulfone matrix, which justifies the same investigation as for PVP. Inspired by works of Holst [11] and Epstein [12], Fukatsu and Kokot [13] have studied the PEG degradation in modelling bleach solution media. The PEG undergoes radical degradation, presumably induced by hydroxyl radicals, with formation of aldehydic chain ends. Thus, the residual PEG presence could prove to be, as PVP, a "weak point" of the membrane material in bleach solutions.

A non-negligible amount of scientific knowledge has been accumulated on the polymeric additives present in the membranes under study. Concerning matrices, it is generally accepted that the above quoted polymers are considerably more stable than their additives in bleach solutions, however it would be difficult to imagine that they are totally unreactive. On the other hand, linear polymers can be embrittlened by a very small number of chain scissions [1]. The problem can be formulated as follows: (i) Are repeated washing operations able to induce significant damage on matrix macromolecules? (ii) Is the damage induced by direct interaction between the polymer and the bleach solution or by reactive species resulting from the attack of additives? (iii) How can one determine quantitatively the extent of damage after exposure in bleach solutions?

This article aim is to try to answer these questions in the case of hollow fibers made of PSU containing PVP and PEG.

## 2. Experimental

### 2.1. Materials

The studied membrane is commercialized into an hollow fiber with internal skin. It is mainly constituted of polysulfone (PSU) (Manufacturer's data: $M_n = 20\,kg\,mol^{-1}$, $M_w = 77\,kg\,mol^{-1}$). It also contains poly(*N*-vinyl-2-pyrrolidone) (PVP) $M_w = 29\,kg\,mol^{-1}$ and polyethylene glycol (PEG) $M_w = 1.5\,kg\,mol^{-1}$ as additives.

This membrane is elaborated by phase inversion and the fiber is processed by co-extrusion: the homogeneous solution of polymers is spun around a needle into which is passed the coagulation liquid. Precipitation occurs at the end of the spinneret by diffusion of the coagulating liquid into the polymer solution. Once processed, the fiber is rinsed with water. Geometric characteristics of the fiber are: internal diameter $(m) = 1 \times 10^{-3}$; external diameter $(m) = 1.8 \times 10^{-3}$; skin layer thickness $(m) < 1 \times 10^{-6}$.

The constitutive polymers of the membrane were also studied separately. Polysulfone used is called UDEL and supplied as films (thickness = 75 μm) by Lipp-Terler (Gaflenz, Austria). PVP and PEG are commercial products, purchased as powder.

### 2.2. Ageing conditions

These tests were performed in immersing fiber, film of polysulfone and powder of PVP and PEG into hypochlorite solutions. A complete description of the fiber soaking process is described by Rouaix [1]. In this part, we will focus on the description of the membrane's constitutive polymers ageing. Ageing baths concentration is 400 ppm total chlorine at a pH of 8. This pH corresponds to the industrial solution used for backwashes to clean and disinfect ultrafiltration modules. Backwash concentration is generally from 2 to 8 ppm, and it was here increased to observe more clearly the effects of ageing.

These ageing solutions were modified with a iodometric balance of the hypochlorite ions. This balance is performed from commercial bleach solutions in which the initial chlorometric degree was 9.2 °C. Once the solution is modified, the pH is controlled using a pH meter (Hanna, France), and adjusted by addition of chlorhydric acid 35% volume (VWR, France). The whole operation (balance and pH adjustment) is done every 2 days to guarantee a constant bleach concentration. The final solutions are kept away from natural light.

PSU films were taken from the ageing solution from 1 day of exposure to 115 days. Its initial state was obtained by soaking into distilled water. Samples dedicated to tensile tests were put into distilled water and the others were rinsed and vacuum dried at 50 °C over 24 h.

### 2.3. Characterization methods

#### 2.3.1. Fourier transform infrared spectrophotometry

IR spectra were recorded between 4000 and 400 $cm^{-1}$ with a 4 $cm^{-1}$ resolution using a Bruker IFS28 apparatus. PVP and PEG powders were analysed in attenuated total reflection (ATR) mode. PSU films were analysed in transmission mode.

#### 2.3.2. Nuclear magnetic resonance

Proton NMR spectra were recorded at 30 °C with a Bruker AVANCE spectrometer with a spectral width of 12 ppm. Sixty-four scans were accumulated with a delay of 2 s. As PVP and PEG were soluble in the ageing solution, it was necessary to lyophilise the solution and then to dissolve the resulting powder in deuterated chloroform.

#### 2.3.3. Tensile testing

Tensile tests in fibers were previously made and reported by Rouaix [1]. Tensile tests on PSU films were performed at 20 °C, 1 mm $min^{-1}$ strain rate using an INSTRON 4281 series 1× dynamometer. The sample geometry was chosen according to ISO 6239 standard [14]. From the stress–strain experimental curves, the engineering ultimate stress $\sigma_r$ and ultimate strain $\varepsilon_r$ were determined. Then, $\sigma_r$ was plotted against $\varepsilon_r$ to obtain the "rupture envelope". The comparison of the latter with the initial tensile curve $\sigma = f(\varepsilon)$ gives interesting information on the embrittlement mechanism [1].

#### 2.3.4. Steric exclusion chromatography

SEC chromatograms of tetrahydrofuran solutions of PSU were obtained using a Varian apparatus equipped with an injection flood gate VALCO. A dual detection system: UV absorption (Varian 9050) and refractometer (HP1046A) were used. The column system was constituted of a pre-column PL gel 5 μm