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Ageing of hollow fiber membranes in polyvinylidene fluoride (PVDF) used in water treatment

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Introduction

Membrane technologies are integrated in all sectors for the production of drinking water, process water in industry, as well as for the wastewater treatment. The selection of membranes is mainly driven by their quality and their durability in order to guarantee as long as possible the sanitary safety of the produced water.

Filtration membranes are elaborated from different materials depending on their applications. They could be made of polysulfone[1-3], or cellulose acetate[4], or polyacrylonitrile[5], as well as polyvinylidene fluoride. Despite the fact that the PVDF material is the market leader for these membranes, very few works[6,7] deal with the study of the ageing of PVDF membranes.

The aim of this work is to understand the degradation mechanisms of PVDF membranes. In order to assess the contribution of the hollow fiber geometry as well as the impact of the additives used in membrane fabrication onto the membrane ageing, a film of pure PVDF is compared to two porous membranes, one composed of PVDF only and another PVDF membrane with additive.

The objective was to establish the relationship between changes in mechanical properties and evolution of the chemical structure according to the operating conditions, an approach that has never been proposed in the literature up to now.

Methods

Samples

A commercial film of PVDF (Kynar 740*, Goodfellow*) of 50 µm thickness was used. Both commercial membranes are made of PVDF. The first (named PVDF/0) do not contain any additive whereas the second one (named PVDF/PVP) has poly(N-vinyl pyrrolidone) (PVP) as an additive. Both membranes have similar inner and outer diameters.

Ageing experiments

Samples were put in contact with chemical solutions at a temperature of 40°C. The chemical baths were containing solutions of sodium hypochlorite (NaOCl) at a concentration of 4000 ppm

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and at different pHs: pHs 6 and 7.5 were achieved by adding HCl and pH 11.5 was achieved naturally (no pH adjustment). A solution of sodium hydroxide (NaOH) at pH 12 without any NaOCl was also tested.

The impact of each solution was studied at different contact times of several days. The intrinsic properties of the membranes were measured by means of tensile tests for mechanical wear of the membrane and by means of dynamic vapour sorption for its hydrophilicity. The results were correlated to the analysis of the membrane chemical structure by using FTIR-ATR spectroscopy as well as ^{1}H and ^{13}C nuclear magnetic resonance (NMR).

Results

The membrane materials were characterized at their initial state in terms of chemical structure and properties (mechanical and hydrophilic). Thus, the analyses of the chemical structure confirmed the presence of PVP in the second commercial membrane (named PVDF/PVP).

DVS analyses led to determine the hydrophilicity of the selected materials (*Fig. 1*). The results showed that both PVDF samples (film and membrane) were hydrophobic whereas the PVDF/PVP membrane had a relatively high hydrophilicity.

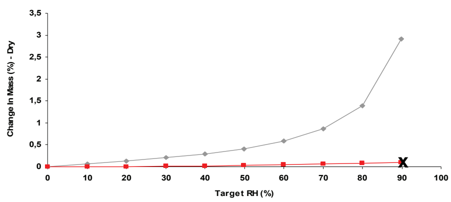

Fig. 1. Sorption isotherms of PVDF film (x), PVDF/0 membrane (red) and PVDF/PVP membrane (grey)

The ageing experiment demonstrated that the hydrophilic agent in the PVDF/PVP membrane had disappeared after soaking in NaOCl solution at pH 11.5 whereas it was still present after soaking in sodium hydroxide. The FTIR analysis of the membrane material also pointed out the intensity drop of the peak at 1670 cm^{-1} wavelength (corresponding to the C=O bond of PVP) after sodium hypochlorite exposure but no decrease of this peak after soaking in sodium hydroxide. No change in mechanical properties was detected though for both experiments.

A discoloration was observed on the PVDF/PVP membrane after exposure to sodium hydroxide whereas the PVDF film and the PVDF/0 membrane kept their initial color. The discoloration of PVDF/PVP membrane did not impact its mechanical properties. The additive could be involved in this modification either through its direct degradation or by accelerating the possible degradation of the PVDF.

Further experiments using sodium hypochlorite at lower pHs are currently conducted in order to estimate the impact of HClO and ClO^- species on material ageing.

Discussion

The comparison of the ageing of PVDF film and the PVDF/0 membrane allows estimating the impact of the porous structure. Similarly, the impact of membrane's additive is evaluated by comparing the chemical and mechanical behaviours of both PVDF/0 and PVDF/PVP membranes.

The analysis by dynamic vapour adsorption confirmed that the addition of PVP in the PVDF membrane increases its hydrophilic feature : the water adsorption of PVDF/PVP membrane is 2.9% against 0.09% for the PVDF/0 membrane.

Only the PVDF/PVP membrane has undergone a modification of its chemical structure after exposure to sodium hypochlorite at pH 11.5 and composed of 99.9% of ClO^-, due to the complete disappearance of PVP. The membrane mechanical properties were not affected though.

In order to deepen the degradation mechanisms of the membrane, the research works have then been oriented to the study of the role of the chlorinated species.

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