



Ageing of polyethersulfone/polyvinylpyrrolidone blends in contact with bleach water

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ARTICLE INFO

Article history:

Received 21 February 2013

Received in revised form

14 March 2013

Accepted 18 March 2013

Available online 26 March 2013

Keywords:

Polyethersulfone

Polyvinylpyrrolidone

Ageing

Bleach water

Hypochlorite

Radical oxidation

ABSTRACT

Polyethersulfone/polyvinylpyrrolidone (PES/PVP) ultrafiltration membranes are widely used to produce safe drinking water. Chemicals such as bleach are necessary to clean membranes; however, they are suspected of playing an important role in membrane ageing. To improve our understanding of how hypochlorite cleaning solutions affect filtration membranes, PES, PVP and thin films of PES/PVP blends have been aged by soaking in bleach water. This study was performed using 4000 ppm of free chlorine with a controlled pH of 8 and 12. Any modifications of the chemical structure of the thin films ($\sim 40 \mu\text{m}$) were analysed using infrared spectroscopy and any modifications to the molecular weight of the polymers were determined via size-exclusion chromatography. In addition, the involvement of a radical oxidation process was investigated by contacting the materials with $\cdot\text{OH}$ radicals generated by the irradiation of a titanium dioxide suspension. The results demonstrated that the degradation of PES/PVP blends in bleach water (sodium hypochlorite solution) involved radical oxidation of the PVP component, which promoted oxidation of the PES component.

This work allowed a mechanism for the degradation of hollow fibre ultrafiltration membranes based on PES (95%) and PVP (5%) in contact with hypochlorite cleaning solutions to be proposed.

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1. Introduction

When producing safe drinking water, the process of ultrafiltration enjoys a certain popularity which is mainly due to its highly efficient removal of particulates, viruses and bacteria. To optimise the performance and minimise costs, the effective cleaning of filtration membranes is necessary. The most frequent procedure for cleaning the membranes used for water production is a quick back flushing with detergents or chlorine at low concentration (2–10 ppm, basic pH) for a short time. Longer cleaning with higher concentrations of chlorine, or either alkaline or acidic solutions can be necessary to remove particles and fouling. Contact with these chemicals is suspected to play an important role in the ageing of these membranes, and it was proposed that the polymers constituting the membranes are oxidised by the hypochlorite [1–5]. The consequences of this oxidation are a decrease in the filtration properties of the membrane, which can suddenly collapse,

reducing its lifetime. It is therefore necessary to understand the mechanisms responsible for such degradation.

To the best of our knowledge, the mechanism for the degradation of PES/PVP membranes is unknown. Yadav et al. [5] and Arkhangelsky et al. [6] focused their attention on the oxidative action of hypochlorite on PES. However, most papers, such as those published by Gaudichet-Maurin et al. [7], have focused on the action of hypochlorite on the properties of polysulfone (PSU) or PSU/PVP membranes. Based on evidence, such as infrared spectroscopy (IR), size-exclusion chromatography (SEC) and proton NMR spectroscopy, a possible chain scission degradation process had been proposed for PSU, which suggests that this degradation involves an attack on the sulphone and isopropylidene bridge and the formation of sulphonic acid end-chains [7]. More recently, Causserand et al. [8] suggested that the mechanism of the degradation of PSU/PVP membranes involved radical oxidation by $\cdot\text{OH}$ radicals.

Wienk et al. [9] studied the oxidative effect of hypochlorite on PVP. Based on SEC experiments, these authors proposed both a chain scission mechanism and that the decrease in the PVP molar weight (M_w) was strongly dependent upon the pH of the hypochlorite solution. These authors also suggested that PVP degradation involves a radical oxidation mechanism based on the work of Holst and al. [10] who suggested the presence of radicals in bleach

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water (sodium hypochlorite). The work of Rouaix et al. [11] was devoted to the degradation of PSU hollow fibres (very porous structure, low PVP content ($\sim 5\%$)); the importance of the pH of the bleach solution to the fibres lifetime was also indicated because the loss of mechanical properties was shown to be more severe at pH 8 than pH 12.

Finally, one could mention studies on the oxidative effects of chlorine species on polyethylene pipes [12–16]. The degradation kinetic was shown to depend on the chlorine concentration and long induction periods were observed at low concentrations.

The aim of the present study was to obtain a better understanding of the effects of hypochlorite cleaning solutions on ultrafiltration hollow fibre membranes made of PES and PVP. To elucidate the PES/PVP filtration membrane degradation mechanism, we first studied the impact of sodium hypochlorite on PES thin films and dissolved PVP, and secondly on PES/PVP blended films with the PVP ratio varying between 5 and 50%. PVP is a water soluble polymer, whereas PES is quite hydrophobic. To differentiate the role the chemical structure of the polymer plays on the degradation mechanism versus that of its hydrophobicity, other hydrophobic polymers (polyethylene, polystyrene and polypropylene) were also immersed in sodium hypochlorite.

To perform these accelerated ageing experiments, samples were immersed in a bleach solution with 4000 ppm of free chlorine and a pH of 8. This pH was chosen because it corresponded to the higher degradation rate for PSU membranes according to Rouaix et al. [11].

In addition, thermal ageing, which is well known to provoke polymers degradation through a chain radical oxidation mechanism, was performed at 140 °C. Moreover, the specific role of the $\cdot\text{OH}$ radicals for degrading both PES and PVP was studied using the photocatalytic activity of titanium dioxide (TiO_2) in an aqueous suspension.

Any changes in the chemical structure of the polymers were monitored using a combination of different analytical techniques, including spectroscopic characterisation based on infrared (IR) and UV–visible analysis and the determination of the molecular weight via size exclusion chromatography (SEC).

2. Experimental

2.1. Materials and processing

Poly (oxy-1,4-phenylenesulfonyl-1,4-phenylene), usually called polyethersulfone (PES) ($M_w \approx 35\,000\text{ g mol}^{-1}$), high density poly(ethylene) (PE) ($d = 0.950\text{ g cm}^{-3}$) and poly(styrene) (PS) ($M_w \approx 280\,000\text{ g mol}^{-1}$) were purchased from Sigma Aldrich. Isotactic polypropylene (PP), (HP500 N) was purchased from Basell S.p.A. Polyvinylpyrrolidone (PVP) ($M_w = 360\,000\text{ g mol}^{-1}$) was purchased from Scientific Polymer Products (SP²). The chemical structures of PVP and PES are presented in Fig. 1.

PES (80 μm), PE (85 μm), PP (80 μm), and PS (40 μm) thin films, were obtained via compression moulding between PTFE-coated glass cloth at 200 bars for 1 min at 250 °C, 100 °C, 150 °C and 200 °C respectively.

The PES/PVP blends were prepared by dissolving these two polymers (PES and PVP) in dimethylformamide (DMF) at different

concentrations (95/5, 50/50 in weight). DMF (ACS reagent, $>99.8\%$) was purchased from Sigma Aldrich. Two grams of the polymers were dissolved in 10 mL of the solvent under strong magnetic stirring over 2 h at room temperature. When the mixture was completely dissolved, the solution was deposited onto an aluminium sheet using an Erichsen Coatmaster 809 MC, and dried overnight at room temperature to form free-standing films (thickness $\sim 30\text{ }\mu\text{m}$).

PVP films were prepared by dissolving PVP powder in water at 20 g L^{-1} . The solution was deposited onto an aluminium sheet using an Erichsen Coatmaster 809 MC and dried at room temperature under vacuum.

Commercial bleach water was used (2.6% free chlorine).

2.2. Characterisation techniques

2.2.1. Spectroscopic analysis

Changes in the UV–visible spectra were followed using a Shimadzu UV-2550 PC spectrophotometer equipped with an integrating sphere.

Infrared (IR) spectra were recorded in transmission mode using a Nicolet 760-FTIR spectrophotometer (nominal resolution of 4 cm^{-1} , 32 scan summations) and in reflection mode with a Nicolet 380-FTIR spectrophotometer equipped with a Thunderdome-ATR accessory with a diamond crystal (4 cm^{-1} , 32 scans).

The FTIR-transmission of aged PVP samples were analysed after its deposition onto ZnS or ZnSe plates via the evaporation of aliquots of an aqueous aged PVP solution (hypochlorite and TiO_2 suspension). The FTIR transmission spectra and ATR-IR spectra were recorded for the aged thin film samples (PES and PES/PVP blends). Because PVP is a highly hygroscopic polymer, the samples were stored for 45 min on the IR spectrometer bench, which was purged with dry air, before the analysis.

2.2.2. Chemical derivatisation treatments

Most of the oxidation products were identified using chemical derivatisations that selectively convert the oxidation products into groups with different IR characteristics [17]. Sulphur tetrafluoride (SF_4), ammonia (NH_3) and HCl treatments were all conducted using a previously described procedure [18,19].

2.2.3. Size exclusion chromatography

The average molecular weight (M_w) of the polymeric samples was obtained by size exclusion chromatography (SEC) using an universal tri-detectors calibration. Triple detection employs a concentration detector (Refractive index detector, RI), a viscometer (DP) and a light scattering detector. (VISCOTEK Trisec 270). The mobile phase was N-methyl pyrrolidone (NMP) (HPLC grade). Two mix-organic columns (LT4000 and T6000) were used at a flow rate of 0.6 ml min^{-1} and a temperature of 45 °C. The calibration was performed using 98 kDa and 236 kDa polystyrene standards purchased from the Malvern Company.

2.3. Ageing protocols

2.3.1. Hypochlorite immersion

PES and PES/PVP blends in the solid state were aged by soaking in an aqueous hypochlorite solution containing 4000 ppm of free chlorine (37.12 mL of 2.6% free chlorine solution in 1 L of water) at both pH 8 and 12. PVP, which is a water soluble polymer, was dissolved in the hypochlorite aqueous solutions at both pH 8 and 12. No mechanical stirring was used to avoid any loss in the physical integrity of the thin polymer films. The pH was controlled using a Jenway 3310 pH metre and adjusted using sulphuric acid (0.5 M) and sodium hydroxide solutions (0.1 M). Before each analysis, the

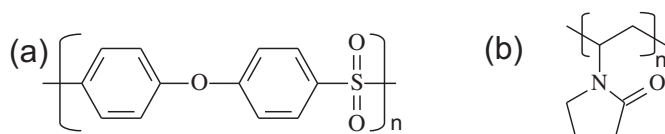


Fig. 1. Chemical structures of PES (a) and PVP (b).

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