



1    **Abstract:**

2    An important setback for a wider use of membrane processes in industry is fouling,  
3    caused by aggregation of biomolecules at membrane surface and pores. Two  
4    important approaches to reduce this effect are the use of chemical cleaning procedures  
5    and the functionalisation of the membrane surface. However, both processes may lead  
6    to membrane degradation and structure alteration due to free radical formation or  
7    radical interaction with membrane polymer chains.

8    In this work, electron paramagnetic resonance (EPR) was used to evaluate and  
9    quantify radical formation in both chemical cleaning and membrane functionalisation by  
10   UV grafting, allowing for a better understanding of free radical formation processes and  
11   their influence on membrane characteristics. Studies under different cleaning and  
12   grafting conditions, such as, cleaning agent concentration and pH, light intensity and  
13   irradiation were also performed showing the potential of EPR as a technique for  
14   monitoring both procedures.

15   The information provided by EPR may contribute significantly to the development of  
16   new cleaning strategies which minimise the effect of membrane ageing and to the  
17   implementation of new and more efficient grafting procedures.

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19   **Keywords:** Membrane ageing; Membrane chemical cleaning; Membrane grafting;EPR;  
20   ESR.

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## 1        **1. Introduction**

2        Fouling of membranes caused by the adsorption and deposition of organic or/and  
3        inorganic material on the membrane surface and within the membrane porous structure  
4        is a major drawback of pressure-driven membrane processes, leading to the decrease  
5        of membrane flux and selectivity.

6        Chemical cleaning is used to remove organic and inorganic foulants from membrane  
7        surface and pores, being the most common procedure for fouling control in membrane  
8        processes. However, cleaning agents used to remove foulants are usually aggressive  
9        and their successive contact with membrane materials may lead to a decrease of  
10       membrane lifetime and, eventually, to membrane replacement [1-2].

11       Several solutions and protocols are used for membrane cleaning though, the most  
12       commonly used in reverse osmosis systems, consist in the usage of hypochlorite  
13       solutions [2]. These solutions are known to originate free radicals [3] that not only,  
14       oxidise the organic material present on the membrane surface, but may also interact  
15       with the membrane polymer affecting its structure and lifetime. This interaction between  
16       free radicals and membrane polymer may lead to the formation of free radicals in the  
17       membrane material [4-6] which causes scission of the membrane polymer chains and  
18       subsequent degradation of the membrane. In order to develop improved cleaning  
19       protocols, which are effective in fouling reduction but simultaneously minimise  
20       membrane ageing, it is necessary to understand the mechanisms behind the formation  
21       of the referred free radicals and their role in the oxidation of the membrane polymers.  
22       Most of the work reported in the literature on membrane ageing, is focused in studying  
23       the alterations induced in membrane performance and membrane morphology [7-9].  
24       Fewer studies focus their attention in the mechanisms responsible for the molecular  
25       alterations occurring in the membrane polymer.

1 Mitigation of the membrane fouling problems has been attempted through application  
2 of different strategies. In particular, membrane functionalisation has deserved a special  
3 attention during the last decade [10-13]. The objective of membrane functionalisation is  
4 to change the membrane surface chemistry without altering substantially the  
5 membrane bulk properties, guaranteeing high physical and fouling resistant  
6 membranes. Among membrane functionalisation techniques, graft techniques present  
7 themselves as an attractive surface modification method. In these techniques,  
8 membranes are exposed to an irradiation source which can be a low temperature  
9 plasma, electron-beam or UV irradiation, among others, in the presence of a selected  
10 monomer [10,14]. Due to various advantages, such as rapid reaction, simple operation  
11 and low cost, UV grafting procedures are one of the most used to selectively alter  
12 membrane surface characteristics [10,13]. When using this functionalisation technique,  
13 two main approaches can be taken. The first one consists in the use of photoinitiators  
14 or photosensitizers acting as connectors between the membrane polymer and the  
15 desired monomer. The second approach consists in the use of membranes composed  
16 of UV-light sensitive polymers. Commonly, in the second approach membranes are  
17 exposed to UV-light producing radical sites that act as polymerization initiators and  
18 onto which the desired monomer can graft [10-13]. Due to its easy applicability this was  
19 the technique employed in this study.

20 Current studies are focused on the selection of the most adequate initial conditions in  
21 order to obtain membranes with the final desired characteristics. Small attention has  
22 been given to the mechanisms involved in membrane grafting. Knowledge of the  
23 mechanisms involved in membrane functionalisation through UV grafting techniques is  
24 crucial for further optimisation of membrane grafting procedures. It is expected, that  
25 optimisation will lead to higher grafting degrees while causing minimum membrane  
26 degradation.

1 Understanding the molecular mechanisms responsible for membrane oxidation during,  
2 membrane cleaning and membrane grafting will lead to the development of  
3 methodologies capable of minimising membrane fouling and ageing, contributing to the  
4 optimisation of membrane processes. In order to achieve this understanding it is  
5 crucial to identify and characterise the formation and decay of free radicals in the  
6 membrane polymers and contacting media, during cleaning and grafting procedures.  
7 This fundamental information can be acquired with electron paramagnetic resonance  
8 (EPR).

9 EPR is a spectroscopic technique used in the detection of chemical species that have  
10 unpaired electrons, such as free radicals, inorganic complexes and transition metals,  
11 spin traps and spin labels. EPR has been the standard technique in quantification and  
12 characterisation of radical species, their stability and decay kinetics. For this reason, it  
13 is currently the main experimental technique used for understanding and comparing the  
14 effect of different phenomena, such as, alkaline treatment and gamma irradiation of  
15 polymers [15-18]. EPR allows the study of the internal structure of samples in great  
16 detail, since EPR spectra depend on the magnetic moments of the unpaired electrons  
17 which are very sensitive to local magnetic fields within the sample.

18 The aim of this paper is to introduce EPR as a powerful technique for following  
19 membrane ageing and monitoring membrane UV grafting. The possibility of using EPR  
20 in the detection of free radicals formed in polymeric membrane materials will be  
21 demonstrated. The detection of these radicals gives important information on molecular  
22 and structural changes that may occur in polymeric membranes, when they are  
23 exposed to oxidation conditions, such as membrane cleaning, and irradiation  
24 conditions.

25 Parameters that influence membrane ageing such as hypochlorite concentration and  
26 pH, will be evaluated as well as the possibility of detecting radicals in cleaning

1 solutions. Additionally, EPR spectra of membranes irradiated under different irradiation  
2 exposure times and intensities will be also obtained, in order to determine the influence  
3 of different grafting irradiation conditions.

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## 5 **2. Materials and Methods**

### 6 2.1. Preparation of membrane samples for ageing studies with EPR

7 The membrane used for the ageing studies was a commercial supported polyamide  
8 membrane (Dow, Filmtec NF270). A polyamide membrane was chosen because  
9 polyamide membranes present high sensitivity to chlorine degradation. In this paper  
10 two different ageing processes were addressed: ageing due to membrane cleaning  
11 with hypochlorite and due to sunlight exposure, which may occur during deficient  
12 membrane storage conditions.

13 In order to simulate membrane ageing due to cleaning, membrane pieces of 5 x 10 cm  
14 were submerged for 24h in bleach solutions (commercial available bleach contains  
15 proximally 3% of NaOCl). Different concentrations of hypochlorite (NaOCl) were tested  
16 (20, 50 and 80% of commercial bleach), as well as different pHs, in order to study the  
17 influence of cleaning agent concentration and cleaning solution pH, in the formation of  
18 membrane radicals. After 24h of contact, the membrane pieces were dried, using paper  
19 tissue and nitrogen gas, and transferred to the EPR quartz tube for analysis. Three  
20 replicas were performed for each study. The concentration of hypochlorite in the  
21 cleaning solutions was determined by titration with potassium iodine and sodium  
22 thiosulfate.

23 Ageing of membranes due to sunlight exposure was simulated by exposing membrane  
24 pieces of 5 x 5 cm to direct sunlight for 1 hour, with and without the presence of water.

1 After exposure, the membranes were analysed with EPR; sample preparation was the  
2 same as previously described for membrane cleaning.

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#### 4 2.2. Membrane UV grafting protocol

5 An UV illumination system (UV point source LQ-400, Dr. Gröbel UV-Elektronik GmbH,  
6 Germany) equipped with a liquid light guide and a medium-pressure mercury lamp ( $\lambda >$   
7 280 nm) was used. UV intensity measurements were performed using an ILT 393  
8 uniformity view (NIST traceable light measurements systems)

9 Commercial poly(ether sulfone) (PES) membrane (Millipore, Biomax PBTK02510) with  
10 a 30-kDa cut off were used due to its UV-light sensitivity.

11 Membrane pieces of 7 x 10 mm were transferred to an EPR quartz tube filled with 3  
12 ml of grafting solution. The presence of oxygen influences negatively the membrane  
13 grafting efficiency since it competes with the monomer for radical binding along  
14 polymerisation process. In order to minimize the presence of oxygen during membrane  
15 grafting process a degassing protocol was applied to the grafting solution. This  
16 degassing procedure involved bubbling the grafting solution with an argon stream for  
17 10 minutes.. After this procedure, the quartz tube was immediately sealed and  
18 transferred to the EPR cavity. Membrane irradiation under different conditions were  
19 performed inside the EPR cavity and the ESR acquisition was performed online. Each  
20 EPR spectra acquisition takes approximately 20 seconds, consequently the EPR signal  
21 acquired in each 20 sec. period correspond to the average of the radical concentration  
22 present in the membrane in this time frame. Tests under different intensities (60  
23 mW/cm<sup>2</sup> and 30mW/cm<sup>2</sup>), irradiation time (180, 300 and 600 seconds) and grafting  
24 solutions (pure hexane solution or a 1% N-Vinylpyrrolidone (NVP) hexane solution)  
25 were performed.

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### 2.3. EPR experiments for determination of radical species

The identification of free radicals was performed by using a Bruker EMX 6/1, EPR Spectrometer. EPR analyses of membranes were performed in quartz tubes with 8 mm diameter at room temperature and a modular frequency of 100 kHz.

In order to identify radicals in cleaning solutions a spin trap had to be used in order to capture the extremely reactive radicals present in the solutions. The 5,5-dimethylpyrroline N-oxide (DMPO) was used with this purpose. The EPR measurements of cleaning solutions were performed in a WG-812-S-Q, Wilmad LabGlass Quartz cell.

EPR ageing protocol measurements were performed using a microwave power of 6.33 mW and a modulation amplitude of 10 G, while in the EPR study of the UV grafting measurements were performed using a microwave power of 2 mW and a modulation amplitude of 4 G. The time necessary for aged membrane sample preparation, between radical generation and measurement, was equal for all the samples (5 min), to uniform the initial measurement conditions, preventing different initial free radical decays.

1           **3. Results and discussion**

2           3.1. EPR as a technique for characterisation of membranes submitted to ageing  
3 protocols

4 As explained, ageing is caused by the oxidation of membrane polymers due to the  
5 formation and reaction of free radicals during chemical cleaning or during radiation  
6 exposure. The reactions of these radicals result in scissions of the membrane polymer  
7 chains and/or alterations in chain structure, leading to membrane degradation.  
8 Therefore, knowledge on the mechanisms responsible for membrane free radical  
9 formation is crucial for identifying ways to prevent their formation and reducing  
10 membrane ageing and degradation.

11 The membrane ageing studies aimed at demonstrating the potential of using EPR for  
12 detection of free radicals during two different ageing situations: membrane cleaning  
13 and exposure to irradiation.

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15           3.1.1. Ageing of polymeric membranes due to membrane cleaning

16 Different parameters that influence the cleaning of membranes were studied, such as  
17 hypochlorite concentration and pH. Membrane pieces of 5 x 10 cm were submerged in  
18 bleach solutions with different concentrations of hypochlorite during 24h, in order to  
19 determine the influence of its concentration in the formation of radicals in the  
20 membrane polymer. Figure 1 represents the EPR spectra of the radicals formed in the  
21 membrane, under these conditions, while Figure 2 depicts the influence of the  
22 hypochlorite concentration in the peak-to-peak amplitude of the EPR spectra. The  
23 peak-to-peak amplitude is a measure of EPR signal intensity which depends on the  
24 concentration of free radicals formed in the membrane polymer. The results obtained  
25 show that the EPR radical signal is directly proportional to the bleach (hypochlorite)

1 solution concentration where the membranes were submerged. This behaviour implies  
2 that the concentration of the cleaning agent is directly responsible for the number of  
3 radicals formed in the membrane polymer.

4 As reported by Kang et al., [2], and Causserand et al., [6], the degradation of  
5 membranes during cleaning depends not only on the concentration of hypochlorite but  
6 also on the pH of the cleaning solution. In order to study the influence of pH in the  
7 formation of radicals in the membrane, pieces of membrane with 5 x 10 cm were  
8 submerged in solutions of 20% of bleach at pH of 8 and 9. As shown in Figure 3 and  
9 Table 1, even a small difference in the pH of the cleaning solutions causes an increase  
10 in the concentration of free radicals formed in the membrane. This result is consistent  
11 with the results obtained by Kang et al., [2], and Causserand et al., [6], that reported a  
12 high influence of the cleaning solution pH in the degradation of the membrane polymer  
13 and a larger effect in membranes exposed to cleaning solutions at lower pH values.

14 The identification of the free radicals formed in the membrane polymer during cleaning,  
15 Figures 1 and 3 is unfeasible, due to the absence of hyperfine structures in the  
16 obtained EPR spectra. Hyperfine structures give information on interactions between  
17 magnetic moments of unpaired electrons in free radicals with nearby nuclear spins, this  
18 information allows to determine the position of unpaired electrons and identify the free  
19 radicals.

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#### 21 3.1.1.2. Detection of radicals present in the cleaning solutions

22 As reported by Causserand et al., [6], the degradation of the membranes, due to  
23 ageing, is a result of the action of radicals present in the cleaning solution. These  
24 radicals react with the membrane polymer to form the membrane radicals that were  
25 detected by EPR and shown in Figure 1. The majority of radicals expected to be

1 formed in solution are  $\text{ClO}\cdot$ ,  $\text{OH}\cdot$ , and organic free radicals resulting from the oxidation  
2 of organic matter. Therefore, additionally to the detection of radicals formed in the  
3 membrane polymers, crucial information can be obtained by analysing the nature of the  
4 radicals that are formed in the cleaning solutions. The radicals present in solution are  
5 extremely reactive and can only be detected with the addition of a spin trap. A spin trap  
6 is a molecule that reacts with the short life time radical to form a more persistent radical  
7 that can be detected by EPR. Figure 4 shows an example of a radical detected using  
8 the spin-trap 5,5-dimethyl-pyrroline N-oxide (DMPO) in a solution of 10% of bleach.  
9 The addition of DMPO to the cleaning solution results in the formation of a nitroxide-  
10 based persistent radical, within the solution, that is detected by EPR (Figure 4), the  
11 detected radical spectra is consistent with the 5,5-dimethyl-2-pyrrolidone-N-oxyl radical  
12 (DMPO-X), a radical usually detected in NaOCl solutions were DMPO is used as spin-  
13 trap [19]. The possibility of detecting radicals in the cleaning solution using EPR may  
14 provide information about the reactions occurring during membrane cleaning, between  
15 the radicals in solution and the formed radicals in the membrane.

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### 17 3.1.2. Ageing of membranes due to solar exposition

18 Ageing of membranes can also be caused by deficient storage conditions. Exposure to  
19 humidity and light during long periods of storage may increase the degradation of  
20 polymeric membranes. To simulate an accelerated ageing due to membrane exposition  
21 to light and humidity, membrane pieces of 5 x 5 cm were exposed to direct sunlight, for  
22 about one hour, with and without the presence of deionised water. Radical signals  
23 were detected in all the samples exposed to sunlight:  $1.04 \cdot 10^5$  peak-to-peak  
24 amplitude/g of membrane for the dried membrane and  $2.25 \cdot 10^5$  peak-to-peak  
25 amplitude/g of membrane for the membrane under water. This indicates that the  
26 exposition of a membrane to sunlight creates membrane radicals. These radicals are

1 formed due to oxidation of the polymer caused by UV radiation. These radicals may  
2 propagate through the membrane polymers, causing cleavage of polymer bounds and  
3 eventuality diminishing membrane performance. The EPR spectra, obtained for the  
4 water submerged membrane samples exposed to sunlight is two times stronger than  
5 the signal obtained for the membranes exposed to the sunlight in dry conditions. This  
6 behaviour occurs because water acts as a free radical propagation medium within the  
7 membrane polymer. Additionally, a solution of water under irradiation is also a source of  
8 OH• radicals, which may also react with the membrane polymer, causing further  
9 membrane radicals and bound cleavage. Therefore, the higher amount of radicals  
10 formed in the membrane submerged in water is a combination of two phenomena:  
11 radical propagation and reaction with water radicals.

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13 3.2. EPR as a technique for monitoring membrane functionalisation using UV  
14 irradiation

15 As discussed in the introduction a possible strategy for the minimisation of membrane  
16 fouling consists in the functionalisation of the membrane surface, enhancing its fouling  
17 resistance. This can be achieved by using UV irradiation grafting methods, where  
18 radical sites, acting as polymerization initiators, are produced in the membrane by UV  
19 irradiation. In order to optimise the membrane functionalisation methodology, deeper  
20 knowledge about the mechanisms influencing radical formation and monomer grafting  
21 is necessary.

22 The work performed regarding membrane grafting, aimed at showing the potentialities  
23 of EPR as a technique to optimise and monitor radical formation under different  
24 conditions, during the grafting phase.

25

### 3.2.1. Influence of UV irradiation intensity in EPR spectra

UV Irradiation intensity can play a very important role in membrane grafting. Higher intensities are generally related with higher membrane grafting degrees [20], but also with higher membrane degradation. As showed by Georges Belfort et al., [20], higher UV light intensities and irradiation times cause a higher degradation of the membrane structure, creating a membrane with lower selectivity and higher permeability. This happens because in UV grafting radicals are formed due to polymer chains cleavage. For this reason, the cleavage of polymer chains and thus the formation of membrane radicals increase with the increase of the intensity and energy of the irradiation light. Therefore, lower UV light intensities and shorter irradiation times are normally preferred when using UV grafting techniques. This strategy benefits the maintenance of membrane bulk characteristics while guaranteeing that only the membrane surface is modified, but limits the achievement of higher grafting degrees.

To evaluate the influence of UV irradiation intensity in the formation of membrane radicals, two PES membranes were irradiated for 300 seconds in pure hexane under different intensities (30 mW/cm<sup>2</sup> and 60 mW/cm<sup>2</sup>). Both EPR spectra are shown in Figure 5.

As expected, radical concentration increases with increasing light intensity. The highest radical concentration was achieved when an intensity of 60 mW/cm<sup>2</sup> was used.

By using the EPR as a monitoring technique, a direct relationship between radical concentration, irradiation intensity and membrane degradation can be found, which allows for determination of the optimum irradiation intensity.

As reported for the membrane cleaning studies the absence of hyperfine structures in the obtained EPR spectra Figure 5 prevents the identification of the free radicals formed in the membrane polymer.

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### 2 3.2.2. Influence of different irradiation times in the EPR spectra

3 Another important parameter of the membrane UV grafting technique is the irradiation  
4 time. Longer irradiation times are normally associated with higher grafting degrees [20].

5 To study the change of radical concentration during irradiation time, a PES membrane  
6 was irradiated with an intensity of 30 mW/cm<sup>2</sup> in pure hexane. EPR measurements  
7 were performed online while the membrane was irradiated. EPR spectra are shown in  
8 Figure 6, while the spectra peak-to-peak amplitude variation over time is shown in  
9 Figure 7.

10 As can be seen in Figure 6 and 7, radical concentrations increase with irradiation time.  
11 However, at longer irradiation times the radical concentration variation tends to a  
12 plateau. This may reflect the presence of a steady state stage, due to the  
13 establishment of an equilibrium between radicals formation and decay. The existence  
14 of a plateau at longer irradiation times, may indicate that although longer times are  
15 always associated to higher grafting degrees, an optimal grafting irradiation time should  
16 exist and its value is lower than the steady state phase exposure time.

17 The use of EPR to monitor the changes of radical concentration during irradiation,  
18 contributes to a better understanding of the effects of irradiation time on the grafting  
19 procedure, ultimately leading to an optimum irradiation time.

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### 21 3.2.3. EPR signal variation in the presence of monomer

22 The previous experiences were performed in the absence of monomer to demonstrate  
23 that EPR could give solid information regarding the variation of radical concentration  
24 during grafting. However, the presence of monomers is expected to interfere in the  
25 mechanisms of radical formation and fading during grafting. For this reason, a

1 comparison between membranes in the absence and presence of monomer was  
2 performed.

3 Two PES membranes, one immersed in a 1% v/v N-Vinylpyrrolidone NVP hexane  
4 solution and the other in a pure hexane were irradiated, separately, during 300 seconds  
5 using a light intensity of 30 mW/cm<sup>2</sup>. NVP was chosen since it presents high grafting  
6 degrees [10]. Both EPR spectra are shown in Figure 8.

7 As can be seen in Figure 8, the membrane irradiated in the presence of NVP presents  
8 a significantly lower radical concentration than the one irradiated in pure hexane.  
9 Several phenomena may explain this observation, such as the reaction of the formed  
10 membrane radicals with the monomer present in solution or the absorption of part of  
11 UV light by the monomer. According to Georges Belfort et al., [10] both phenomena  
12 may occur when NVP is used as monomer. However, since NVP presents a strong  
13 absorption in wavelengths below 290 nm, and in this work a medium pressure mercury  
14 lamp irradiating with wavelengths superior to 280 nm was used, the reduction of radical  
15 concentration due to absorption of light by the monomer solution should be minimum.

16 This may indicate that, when the membrane is irradiated in the presence of NVP, the  
17 EPR spectra intensity diminishes essentially due to grafting reactions between the  
18 formed radicals and the NVP present in solution. The higher variation of EPR signals,  
19 in the presence and absence of NVP, may indicate that a significant amount of the  
20 radicals formed during irradiation reacted with the monomer and a higher monomer  
21 grafting degree was obtained.

22 These preliminary results suggest that the EPR technique may allow to obtain a  
23 correlation between the radical concentration profiles in the absence and presence of  
24 monomers, with the degree of membrane grafting achieved. It is also expected that  
25 these studies may conduce to further optimisation of NVP grafting procedures.

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#### 2 3.2.4. Study of the decay of the EPR signal

3 It is commonly considered that grafting processes occur essentially during the  
4 irradiation stage, being less important during the radical decay stage, i.e., after  
5 irradiation. However, the study of the membrane radical decay after irradiation may not  
6 only provide insights on radicals dynamics and life time, but also gives relevant  
7 information regarding the importance of this phase.

8 To study the membrane radical decay phase, a PES membrane was irradiated for 600  
9 seconds, in pure hexane applying a light intensity of 30 mW/cm<sup>2</sup>. EPR measurements  
10 were performed at different times during radical decay. EPR spectra are shown in  
11 Figure 9, while the variation of the spectra peak-to-peak amplitude over radical decay  
12 time is shown in Figure 10.

13 As depicted in Figure 10, a decrease of the radical concentration over time, after  
14 irradiation, was observed. These results suggest that when irradiation of the membrane  
15 is ceased, annealing reactions between radicals are dominant, causing a decrease in  
16 radical concentration.

17 In Figure 10 it can be seen, that most of the EPR signal variation occurs in the first 50  
18 seconds, while in the following 250 seconds the radical concentration variation is less  
19 abrupt. This may be explained by the higher initial radical concentration which causes  
20 frequent annealing reactions and faster initial signal decay. The radical concentration  
21 diminishes over time, causing a decrease of the annealing reactions and consequently  
22 a decrease in the velocity of radical concentration decay.

23 It is expected that by studying decay profiles of different grafting systems, crucial  
24 information regarding grafting mechanisms and reactions is obtained. By acquiring this  
25 information, further knowledge may be obtained regarding the parameters that  
26 influence grafting, such as grafting environment.

#### 1 **4. Conclusions**

2 The results presented herein demonstrate the potential of EPR as a technique for  
3 monitoring membrane ageing and grafting procedures.

4 This study demonstrates that radicals formed in membrane polymers, due to  
5 membrane exposure to oxidation conditions (membrane ageing) and UV irradiation (UV  
6 grafting), can be identified and their dynamic formation, fading and reaction monitored.  
7 Also, the EPR technique showed to be sensitive to several parameters that influence  
8 membrane structural and molecular alterations.

9 Regarding membrane ageing, this work demonstrates the potential of using the EPR  
10 technique to detect radicals in both membrane and cleaning solutions, under different  
11 conditions. The knowledge that can be acquired with EPR may be very valuable since  
12 it can be applied for the development of new cleaning strategies which minimise their  
13 impact in membrane ageing.

14 Considering membrane grafting, this study demonstrates that EPR can evaluate radical  
15 formation under different UV grafting conditions (UV light intensity, irradiation time and  
16 presence or absence of monomer), allowing for a better understanding of the impact of  
17 different grafting parameters on the final membrane characteristics. The information  
18 provided by EPR may contribute significantly to the implementation of new and more  
19 efficient grafting procedures, allowing enhanced membrane grafting degrees and  
20 simultaneously avoiding membrane damaging caused by UV irradiation.

21 The combination of the EPR information, regarding radical concentration with  
22 membrane characterisation techniques such as, Fourier transform infrared (FTIR)  
23 spectroscopy, x-ray photoelectron spectroscopy (XPS), dielectric relaxation  
24 spectroscopy, scanning electron microscope (SEM) and atomic force microscopy  
25 (AFM), may allow for a molecular interpretation of the structural and morphological

1 changes occurred in membranes during ageing or after functionalisation, caused by the  
2 action of free radicals.

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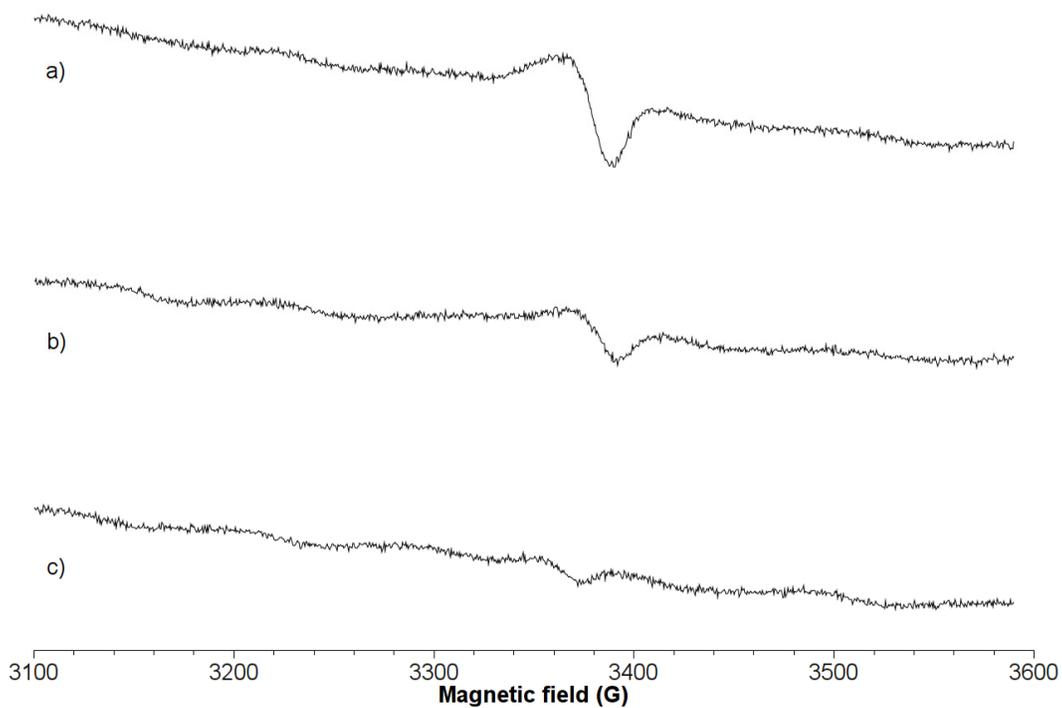
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1 **Figure 1**



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3 Figure 1. EPR spectra of membrane radicals formed after submerging pieces of  
4 membrane in water solutions of 80 % (v/v) a), 50 % (v/v) b) and 20 % (v/v) c) of bleach,  
5 at pH = 9. Blank tests were performed with deionised water and showed no radical  
6 signal (same yy scale).

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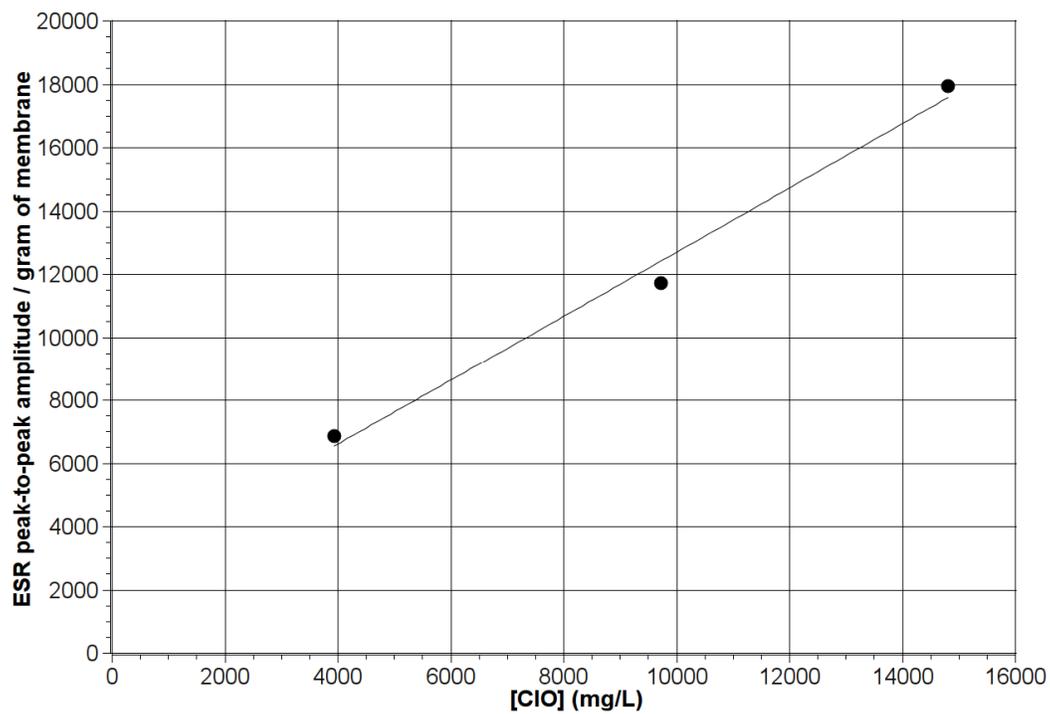
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1 **Figure 2**



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3 Figure 2. Influence of the hypochlorite solution concentration in the radical EPR signal  
4 in the membrane, determined by EPR.

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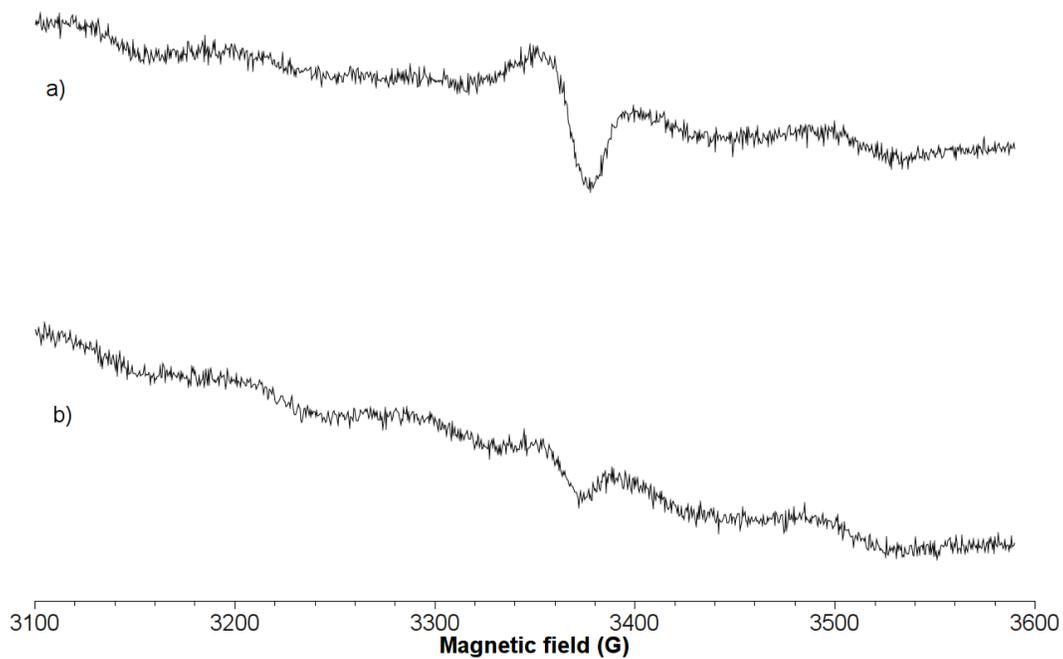
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1 **Figure 3**



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3 Figure 3. EPR spectra of membrane radicals formed after submerging pieces of  
4 membrane in bleach solutions of 20% and pHs of 8 a) and 9 b) (same yy scale).

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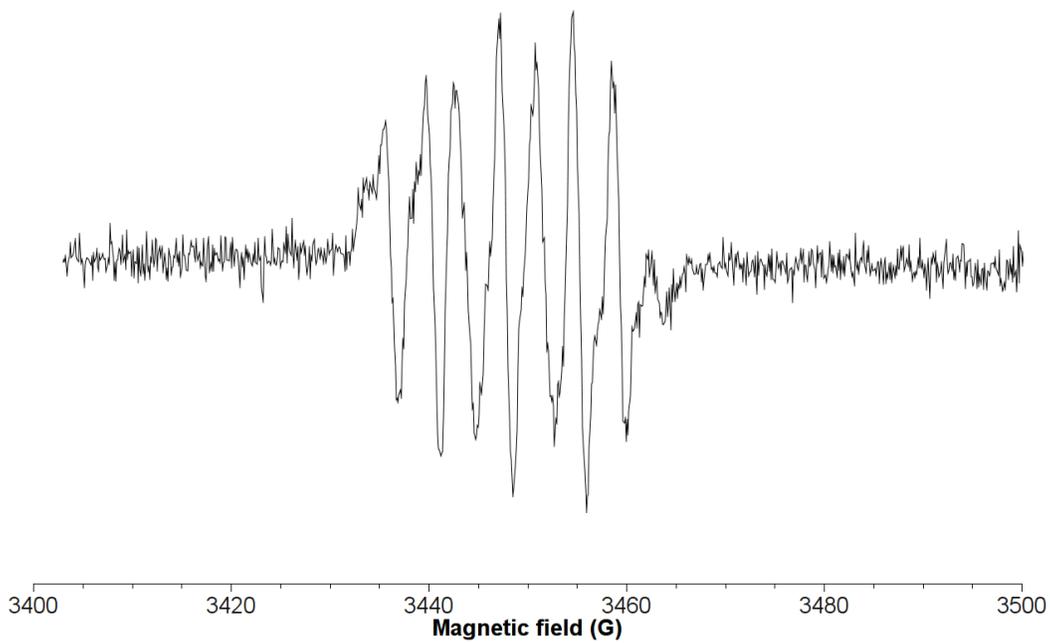
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1 **Figure 4**



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3 **Figure 4. EPR spectra of DMPO in a cleaning solution of 10 % (v/v) of bleach.**

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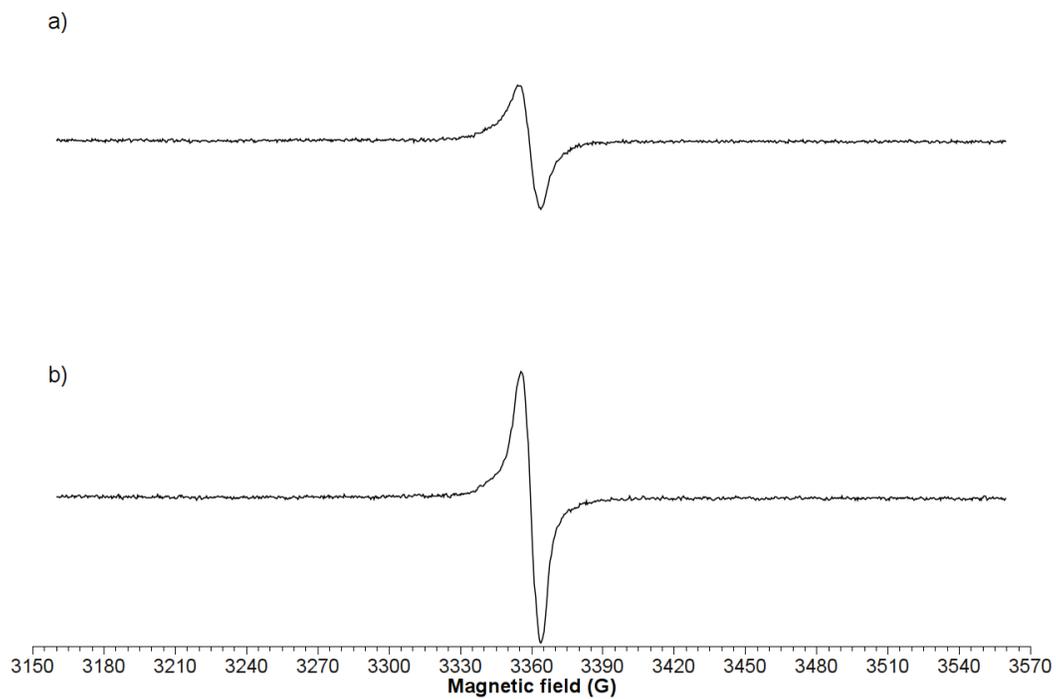
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1 **Figure 5**



2 Figure 5. EPR spectra of PES membranes irradiated in pure hexane solutions using  
3 different light intensities (same yy scale): a) Membrane irradiated with a light intensity  
4 of 30 mW/cm<sup>2</sup>, b) membrane irradiated with a light intensity of 60 mW/cm<sup>2</sup>.

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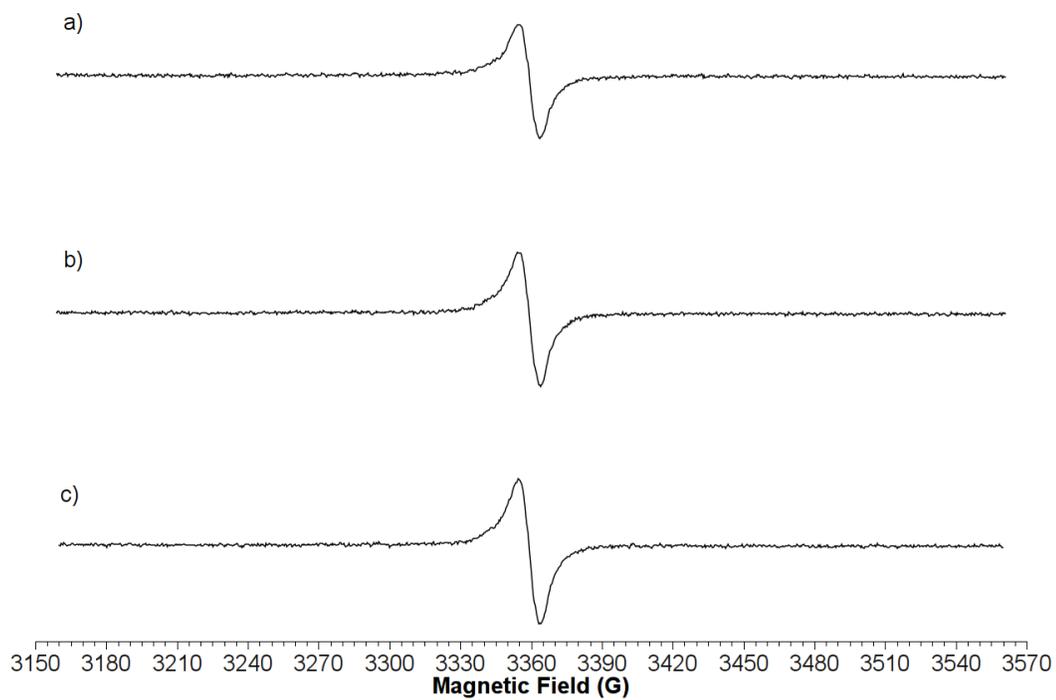
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1 **Figure 6**



2 Figure 6. EPR spectra of PES membranes in pure hexane, obtained after different  
3 times of irradiation (same yy scale): a) After 180 sec of irradiation, b) After 300 sec of  
4 irradiation, c) After 600 sec of irradiation.

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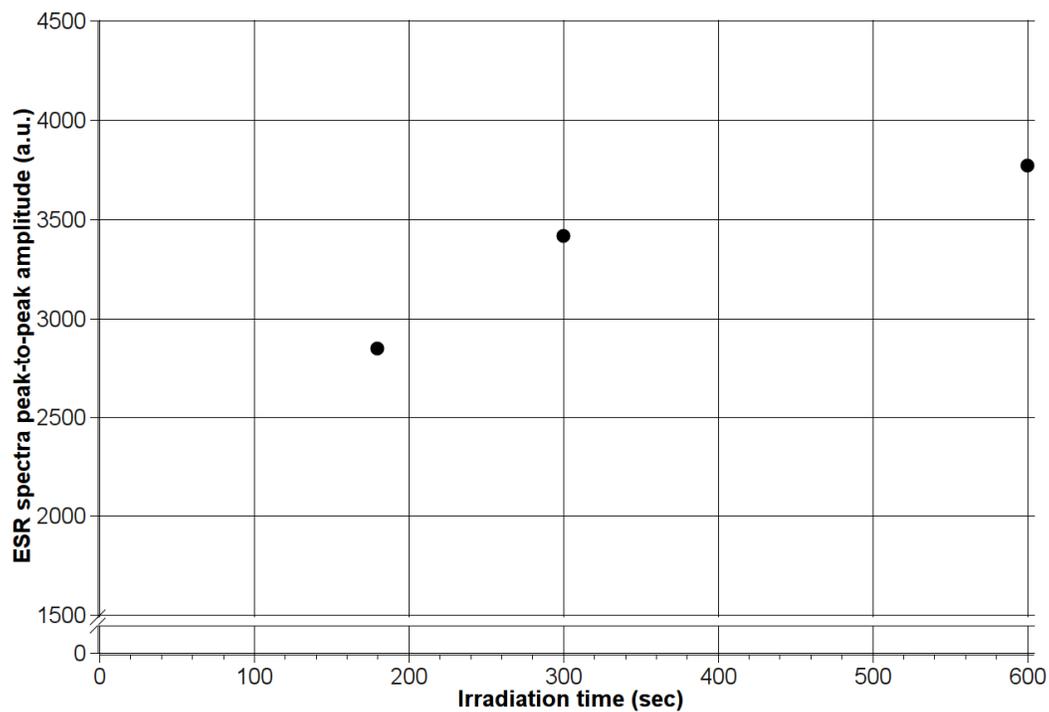
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1 **Figure 7**



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Figure 7. Variation of EPR spectra maximum peak-to-peak amplitudes obtained for

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PES membranes at different irradiation time.

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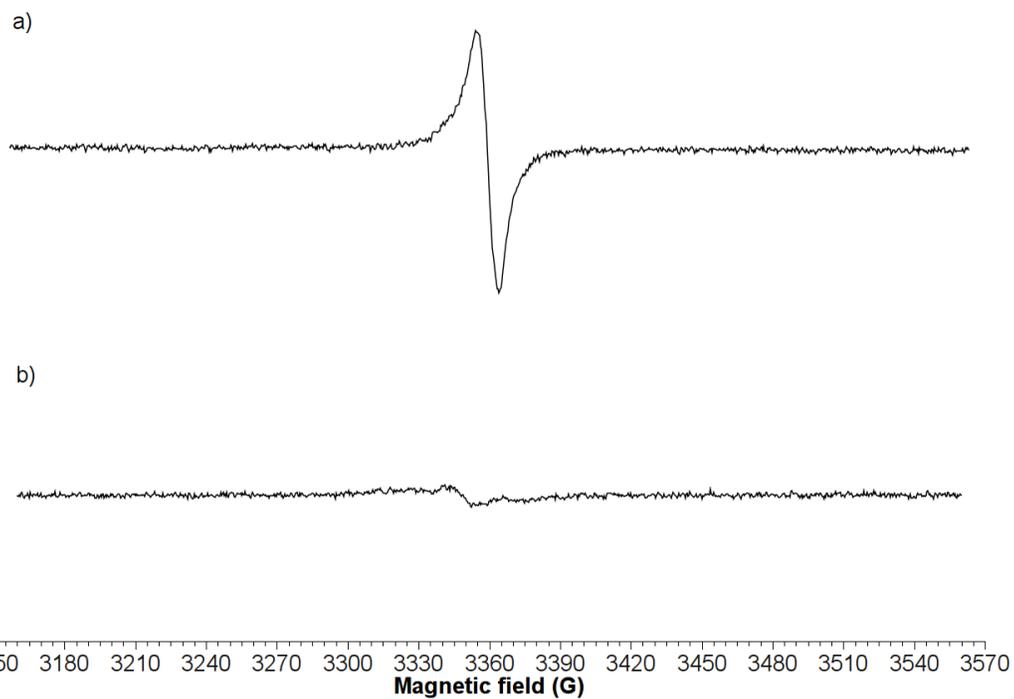
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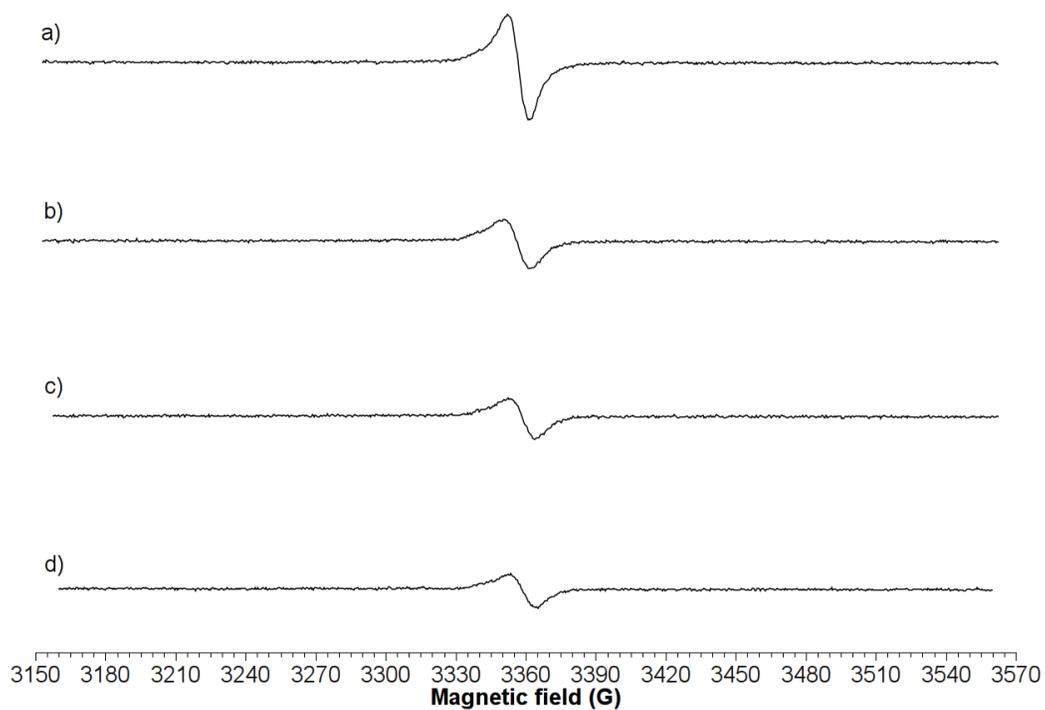
1 **Figure 8**



2 Figure 8. EPR spectra obtained for PES membranes irradiated in different solutions  
3 (same yy scale): a) pure hexane, b) 1% v/v NVP.

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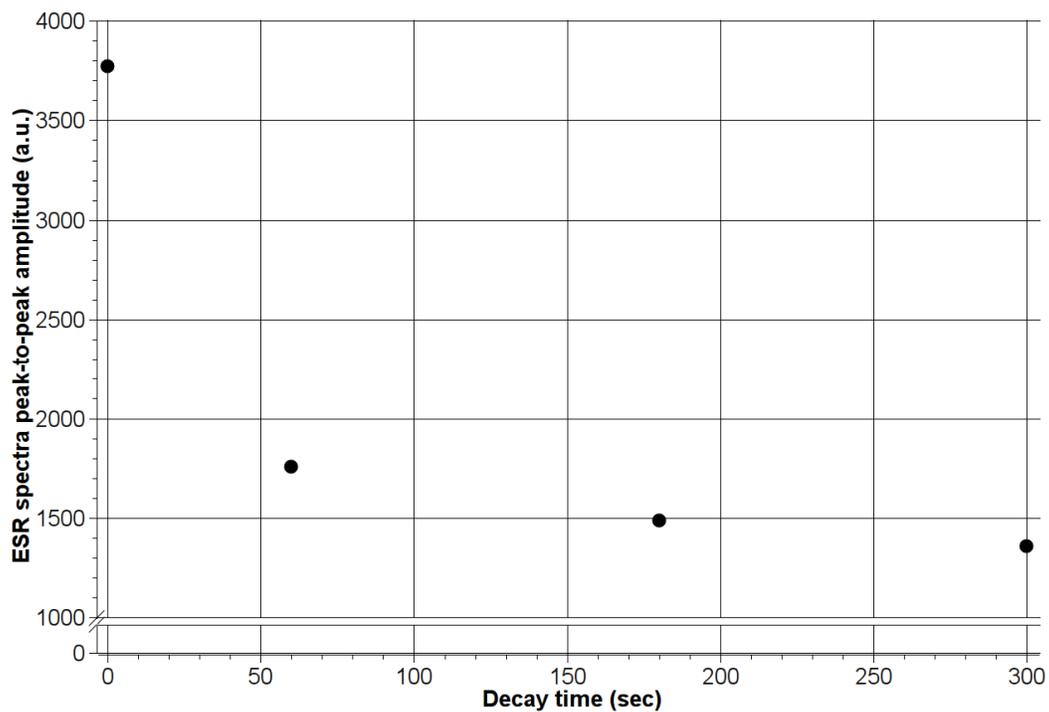
1 **Figure 9**



2 Figure 9. EPR spectra of irradiated PES membranes obtained after different times upon  
3 ceasing the irradiation: a) at the moment irradiation is stopped, i.e. 0s, b) 60 seconds  
4 after irradiation, c) 180 seconds after irradiation and d) 300 seconds after irradiation.

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1 **Figure 10**



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3 Figure 10. Variation of EPR spectra maximum peak-to-peak amplitudes obtained for  
4 irradiated PES membranes at different times after ceasing irradiation.

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- 1 **Table 1.** EPR spectra signals achieved in different conditions of chemical cleaning:
- 2 influence of pH and concentration of cleaning agent

| <b>Percentage of bleach in cleaning solution</b> | <b>pH of the cleaning solution</b> | <b>EPR Spectra peak-to-peak amplitude /g of membrane <math>\cdot 10^4</math></b> |
|--|------------------------------------|--|
| 20%  | 8                                  | $1.19 \pm 0.13$  |
| 20%  | 9                                  | $0.69 \pm 0.03$  |
| 50%  | 9                                  | $1.17 \pm 0.16$  |
| 80%  | 9                                  | $1.79 \pm 0.20$  |

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