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Additional Information

Influence of oxygen plasma treatment parameters on poly(vinylidene fluoride) electrospun fiber mats wettability

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Abstract

Electrospun poly(vinylidene fluoride) (PVDF) fiber mats find applications in an increasing number of areas, such as battery separators, filtration and detection membranes, due to their excellent properties. However, there are limitations due to the hydrophobic nature and low surface energy of PVDF. In this work, oxygen plasma treatment has been applied in order to modify the surface wettability of PVDF fiber mats and superhydrophilic PVDF electrospun membranes have been obtained. Further, plasma treatment does not significantly influence fiber average size ($\sim 400 \pm 200$ nm), morphology, electroactive β -phase content (~ 80 - 85%) or the degree of crystallinity (X_c of $42 \pm 2\%$), allowing to maintain the excellent physical-chemical characteristics of

PVDF. Plasma treatment mainly induces surface chemistry modifications, such as the introduction of oxygen and release of fluorine atoms that significantly changes polymer membrane wettability by a reduction of the contact angle of the polymer fibers and an overall decrease of the surface tension of the membranes.

Keywords: Electrospun membranes, electroactive PVDF, oxygen plasma treatment, surface modification, surface wettability, oxidation mechanism

1. Introduction

PVDF is a semi-crystalline polymer with strong piezoelectric properties, high mechanical strength, thermal stability, high electric and chemical resistance and good processability [1-5]. This polymer has at least four known crystalline phases (α , β , γ and δ), being the β phase the one with the largest piezoelectric response [3, 6].

PVDF has been used in various fields including tissue engineering, filtration, air cleaning, rechargeable batteries and sensors, among others [2, 7, 8]. In particular, electrospun PVDF fiber mats have attracted a large interest due to their high surface area, small fiber diameters and porous structure [2]. However, the high hydrophobicity, poor wettability and low surface energy characteristic of PVDF are major drawbacks for several applications [2, 7]. In order to overcome these limitations, surface modification by introducing specific functional groups on the surface is often used in order to tailor polymer wettability [2, 7, 9].

A wide range of surface modification methodologies have been used to modify the properties of materials, including surface hydrolysis, chemical grafting, self-assembly or plasma treatment [10, 11].

Plasma treatment is one of the most extensively used techniques to modify surface properties of polymers [11, 12]. Gas plasma represents a reactive chemical environment in which different plasma-surface reactions occur [12].

Plasma treatment is typically used for modifying the chemical and physical surface properties of polymers without affecting their bulk characteristics [11]. It is thus commonly used to tailor surface adhesion and wetting properties by changing the surface chemical composition of the polymers [11]. With plasma surface modification and deposition it is possible to introduce functional groups, to control surface roughness and crosslinking, graft polymerization and thin film coating adhesion [11]. Generally, plasma treatment has been used to insert chemically reactive functional groups on polymer surface changing the surface chemical composition and to promote covalent immobilization of different components onto the polymer surface [2, 11]. A careful selection of plasma source types, time and gas are the key issues. In this sense, plasma treatments by oxygen, ammonia or air could generate carboxyl or amine groups on polymer surfaces [11]. The application of oxygen plasma on different polymer substrates has generated promising results on promoting cell growth owing to the incorporation of hydrophilic and oxygen functional groups [13].

Plasma treatment has been used to promote surface modifications on PVDF [7, 13-19]. Duca *et al.* [20] investigated the surface modifications of PVDF under RF Argon (Ar) plasma, and the results showed an improvement of the PVDF surface wettability under plasma exposure. The surface of PVDF can be also modified by Ar, He (helium) and O₂ (oxygen) plasma, however, oxygen plasma was not effective in decreasing the contact angle of PVDF sheet surface [15]. Plasma-induced free radical polymerization was used to modify PVDF membranes prepared by solvent casting [18] to support neural cell culture.

To the best of our knowledge, few studies exist on PVDF electrospun fiber surface modification by plasma in order to improve hydrophilicity. Furthermore, it has been demonstrated that Ar plasma-induced grafting of acrylic acid significantly improved the wetting behavior of electrospun PVDF nanofiber membranes [2].

This work reports the modification of electrospun PVDF fibers wettability by oxygen plasma to improve hydrophilicity of the polymeric membranes. The influence of different parameters such as treatment time (s), O₂ flow rate (mL min⁻¹) and the power (W) were studied. Furthermore, the influence of plasma treatment on fiber morphology, degree of crystallinity and polymer phase were evaluated, as these are also relevant for the different application of this electroactive material.

2. Experimental Section

2.1. Materials

Poly(vinylidene fluoride) (PVDF) with reference Solef 1010 was acquired from Solvay. Analytical grade N,N-Dimethyl Formamide (DMF) was purchased from Merck.

2.2. Electrospinning

PVDF electrospun fibers were processed according to the previously reported method of Ribeiro *et. al.* [21]. Briefly, a 20% (w/w) solution of PVDF in DMF was prepared under magnetic stirring at room temperature until complete dissolution of the polymer. Then, the polymer solution was placed in a plastic syringe (10 mL) fitted with a steel needle with inner diameter of 0.5 mm. The electrospinning procedure was conducted at 20 kV with a high voltage power supply from Glassman (model PS/FC30P04) with a solution feed rate of 1 mL h⁻¹ applied with the help of a syringe pump (from Syringepump). The electrospun fibers were collected in an aluminum plate.

2.3. Surface modification

Surface treatment was conducted in a plasma chamber (Plasma-Electronic PICCOLO) equipped with 13.56 MHz radio frequency plasma generator. Plasma treatments were performed under different conditions with the plasma power varying between 120 to 600 W, the flow rate varying from 20 to 100 mL min⁻¹ and from 60 to 900 s under a total pressure of 20 Pa.

2.4. Characterization

Fiber morphology was analyzed using a scanning electron microscopy (SEM, Quanta 650, from FEI) with an accelerating voltage of 5 kV. The samples were previously coated with a thin gold layer using a sputter coating (Polaron, model SC502).

Infrared measurements (FTIR) were performed at room temperature in a Bruker alpha apparatus in ATR mode from 4000 to 400 cm⁻¹. FTIR spectra were collected after 24 scans with a resolution of 4 cm⁻¹. Differential scanning calorimetry measurements (DSC) were performed in a Mettler Toledo 823e apparatus using a heating rate of 10 °C min⁻¹ under nitrogen purge. Wettability of the samples was determined by measuring the contact angle of distilled water at room temperature, using an OCA15 Dataphysics contact angle analyzer. Six measurements were carried out for each sample at different places. The porosity of the PVDF fiber mats was measured by liquid displacement method using a pycnometer. The weight of the pycnometer filled with ethanol, was measured and labeled as W_1 ; the PVDF fibers, whose weight was W_s , were immersed in ethanol. After the sample was saturated by ethanol, additional ethanol was added to complete the volume of the pycnometer. Then, the pycnometer was weighted and labeled as W_2 ; the sample filled with ethanol was then taken out of the pycnometer

[22]. The residual weight of the ethanol and the pycnometer was labeled W_3 . The porosity of the membrane was calculated according to equation 1:

$$\varepsilon = \frac{W_2 - W_3 - W_5}{W_1 - W_3} \quad (1)$$

The mean porosity of each membrane was obtained as the average of the values determined in three samples. Absolute ethanol (Merck), as a non-solvent of PVDF, was used as a displacement liquid since it can penetrate among the fibers not inducing shrinking or swelling in the fiber mat [23].

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition and CASAXPS software for data analysis in order to evaluate the surface elemental composition and atomic concentration of the samples. The analysis was carried out with a monochromatic Al K α X-ray source (1486.7 eV), operating at 15 kV (90 W), in FAT mode (Fixed Analyser Transmission), with a pass energy of 40 eV for regions ROI and 80 eV for survey. Data acquisition was performed with a pressure lower than 1×10^{-6} Pa, and it was used a charge neutralization system. The effect of the electric charge was corrected by the reference of the carbon peak (284.6 eV). All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 286.4 eV. Spectra were analyzed using the XPSPEAK software (version 4.1). Curve fitting of the high resolution spectra used 30% Gaussian/70% Lorentzian mixed line shapes for each component.

3. Results and Discussion

3.1. Effect of plasma treatment on PVDF fiber morphology

Pristine PVDF electrospun fibers were electrospun into a highly porous non-woven mesh with interconnected pores and smooth fiber surface: no beads were observed in

the fiber mats (Figure 1a). PVDF membrane porosity was estimated using the pycnometer method and an overall membrane porosity of $79 \pm 4 \%$ was obtained.

The effect of the different plasma treatments on PVDF fiber morphology was assessed by SEM. The influence of plasma power was investigated by keeping constant a rich oxygen atmosphere of 120 mL min^{-1} during 120 s. The SEM pictures of Figure 1 show the effect of the applied plasma power on the size of the electrospun fibrils, as well as a histogram of the fiber diameter.

The fiber roughness increased with increasing plasma power (Figure 1). Small “*bumps*” appeared on the fibrils surface leading to some eventual fiber joining, especially for the highest plasma power (Figure 1) which probably is related to surface polymer melting due to the high energy supplied by the plasma source. In spite of the mentioned, fiber surface effects the overall appearance of fiber meshes are similar to that of the pristine ones. Furthermore, no complete fiber melting was detected after plasma treatments, the membranes showing still open spaces between fibers.

The effect of plasma exposure time and oxygen flow rate for a fixed plasma power was also characterized and the variations in fiber morphology are similar to the ones observed after plasma power variation. The influence of different plasma parameters on fiber mean diameter was determined (Figure 2). Pristine polymer mats present a mean fiber diameter of $\sim 400 \pm 200 \text{ nm}$ both before and after plasma treatment (Figure 2), indicating that the plasma treatment induce physical-chemical variations on the fiber surface, without variations of the bulk properties.

3.2. Surface chemical characterization and phase content

In order to evaluate the influence of plasma treatment in the chemical surface of PVDF and on the electroactive β phase content, FTIR-ATR of non-treated and plasma treated polymer fiber mats were measured (Figure 3).

PVDF chemical structure is composed by the repetition unit $-\text{CH}_2\text{-CF}_2-$ along the polymer chain and the characteristic vibrational modes can be used to identify the presence of different polymorphs [6]. Figure 3 shows the infrared spectra of the pristine sample and the plasma treated ones after different applied powers. The results are representative of the FTIR spectra obtained for the samples prepared with different O_2 flow rates and different exposure time to plasma treatment. Neither modes are totally suppressed nor do new ones appear due to the change of the plasma processing parameters, compared to the pristine fiber mats. The characteristic absorption modes for the α -phase ($855, 795$ and 766 cm^{-1}) and the β -phase (840 cm^{-1}) are detected (Figure 3) and no traces of the γ -phase ($776, 812, 833 - 838$ and 1234 cm^{-1} modes) appears [6, 21]. The electrospinning method favors the formation of PVDF fibers crystallized in the electroactive β -phase [6, 21], due to the fact of being a low temperature solvent casting process. Moreover, the use of higher electric fields during processing contribute to dipole alignment and consequently to electrical poling of the PVDF fibers [24], leading to high responsive piezoelectric fibers. The quantification of the β -phase content of the electrospun samples can be performed from the FTIR spectra applying (equation 2) and following the procedure explained in [6, 21]:

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right) A_\alpha + A_\beta} \quad (2)$$

where $F(\beta)$ represents the β -phase content, K_α and K_β the absorption coefficient for each phase and A_α and A_β the absorbance at 766 and 840 cm^{-1} , respectively. The absorption

coefficient value is $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ for K_β and K_α , respectively [25].

It was observed that increasing the applied plasma power leads to a decrease of the electroactive β -phase (Figure 3b) while the O_2 flow rate and plasma treatment time have no significant effect on the β -phase content present in the samples (Figure 3c and 3d). The decrease of the β -phase content with the increase of the applied plasma power can be related to local sample temperature increase during surface plasma treatment, leading to β to α -phase transformation [26]. This phase transformation has been reported to take place at temperatures above $70 \text{ }^\circ\text{C}$ in PVDF and has been related to the increase of cooperative segmental motions within the crystalline fraction [27]. It is to notice, nevertheless, that this decrease of $\sim 20\%$ of the β -phase content does not represent a significant reduction of the electroactive performance of the material. Gomes *et al.* [28] reported that the piezoelectric coefficient is proportional to the amount of oriented dipoles, and therefore the number of β -phase present in PVDF films influence the piezoelectric response of the material. Typically, the decrease of the β -phase content promoted by plasma treatment is equivalent to a reduction of $\sim 20\%$ in the piezoelectric coefficient, from 34 down to 28 pC N^{-1} .

3.3. Thermal characterization

Differential scanning calorimetry (DSC) measurements were performed in order to detect possible modifications in thermal stability and melting behavior. DSC data reveal that all plasma treated fiber mats showed a similar trend, regardless the plasma treatment condition, with a broader melting transition (Figure 4) than in the non-treated samples.

FTIR results probe the coexistence of both α and β -crystalline phases among the sample, which suggests that the broad melting peak corresponds to the melting of both phases, which is clearly observed for the sample with higher amount of α -phase (sample treated at 480 W plasma power, Figure 3b). Nevertheless, these kind of results have to be considered with care since DSC heating curves recorded at low heating rates can present more than one endotherm due to the recrystallization taking place during the scan itself after first melting and also a distribution of crystal sizes could produce the same effect [29]. The degree of crystallinity (X_c) of the samples was determined from the DSC thermograms using equation 3 [21]:

$$X_c = \frac{\Delta H}{x\Delta H_\alpha + y\Delta H_\beta} \quad (3)$$

where ΔH is the melting enthalpy of the sample; ΔH_α and ΔH_β are the melting enthalpies of a 100 % crystalline sample in the α and β phase and the x and y the amount of the α and β phase present in the sample, respectively. In this study, the value of 93.07 J g^{-1} and 103.4 J g^{-1} were used for ΔH_α and ΔH_β , respectively [21].

Comparing pristine electrospun samples with plasma modified ones, no significant changes were detected in the degree of crystallinity, independently of the plasma treatment conditions and a crystalline fraction of $42 \pm 2\%$ was obtained for all samples, in accordance to other studies with electrospun mats [21, 30].

3.4. Surface wettability

Figure 5 shows the variation of the contact angle of the plasma modified PVDF fibers as a function of different applied plasma power. The surface water contact angle of the non-modified fibers is $134 \pm 6^\circ$ being in agreement with the strong hydrophobicity of

PVDF materials [2]. Changes in water contact angle were observed when the applied plasma power is applied. In particular, for plasma powers above 360 W, the surface contact angle cannot be measured as the water drop is rapidly absorbed by the membrane, indicating a superhydrophilic behavior (Figure 5a).

The influence of oxygen plasma treatment and oxygen flow rate on the surface wettability of PVDF fibers are also studied (results not shown). Treatment times between 60 and 900 s and flow rates between 40 and 200 mL min⁻¹ at a plasma power ≥ 360 W led to PVDF membranes with superhydrophilic behavior, and the water drop when in contact with PVDF surface almost immediately absorbed by the membrane.

In order to obtain the optimal values for improving the hydrophilicity of the PVDF membranes at an applied power of 360 W (minimum power applied that improves hydrophilicity of electrospun PVDF membranes), the treatment time and oxygen flow rate parameters were studied. The results allowed to conclude that for treatment times and oxygen flow rate below 120 s (Figure 5b) and 60 mL min⁻¹, respectively, the plasma did not induce the hydrophilicity of the PVDF membranes. The optimal values to obtain hydrophilic membranes are summarized in Table 1.

The literature data show that oxygen plasma treatment reduces contact angle up to 20°, depending on the plasma conditions [7, 13, 15]. In the present case, the fact of obtaining hydrophilic membranes is associated to the variation of the contact angle of the polymer and the capillarity of the membranes. Reduction of the polymer fiber contact angles, as observed in the polymer films [7, 13, 15] lead to an associated variation of the surface tension of the membrane, leading thus to a penetration of the water drop in the membrane and the consequent hydrophilic behavior.

3.5. Chemical composition of electrospun PVDF fibers surface

Plasma treatment typically leads to degradation of the polymer surface. The degradation process is accompanied by cleavage of molecular chains and by the formation of free radicals that activate the surface and double bonds that will react forming new oxygen structures [31].

In order to obtain quantitative information about the elemental composition of the non-modified and modified PVDF membranes, XPS analysis was performed. Figure 6 shows the XPS results of PVDF surface elemental compositions at different applied plasma powers. Carbon, fluorine and oxygen were detected in the samples (Figure 6).

The atomic surface composition for the PVDF surfaces was evaluated from C1s, F1s and O1s scanning spectra. Figure 6b shows typical C1s spectra for the non-modified and modified PVDF fibers with oxygen plasma. Deconvolution of Figure 6b was performed to show the individual components of the C1s peak (Supplementary information, Figure A1). It is observed that the PVDF fibers showed two main C1s peaks at 291.4 eV assigned (Supplementary information, Table A1) to CF₂ groups and at 286.4 eV due to CH₂ component. Plasma treated fibers also show a peak with binding energy of about 285.0 eV attributed to C-C group (Figure 6b). The F1s peak at 688 eV is assigned to C-F bond. Plasma treated fibers shows an O1s peak at 533 eV assigned to C-O bond (Figure 6c). These changes indicate that oxygen plasma exposure promotes defluorination and oxidation reactions by the incorporation of oxygen onto the polymer fiber surface. Table 2 summarizes the XPS analysis for the F/C and O/C atom ratios for non-modified and treated PVDF fiber membranes. Though, surface of non-modified PVDF fibers is composed of carbon (51.3 %), and fluorine atoms (48.3%).

The presence of a quite small oxygen amount (0.35 %) may arise from the exposure of the PVDF fibers to the air or due to solvent contaminants [19]. Nevertheless, modified polymer fibers reflected clear alterations in its surface elemental compositions. The signal corresponding to F being higher on the non-modified fibers than in plasma modified fibers plasma treatment leads to a substantial decrease on fluorine content and an increases in oxygen content as a result of the presence of carboxyl groups in the surface of the fibers generated by the O₂ plasma treatment [32]. The oxygen to carbon ratio (O/C) increases from 0.007 to approximately 0.1 while fluorine to carbon ratio (F/C) decreases from 0.54 to approximately 0.21. Results indicate the success of the plasma activation in the surface of PVDF fibers.

It is reported that oxygen plasma surface modification enriches the surface with oxygen species [33]. The surface modifications of PVDF fibers after the plasma treatment, leading to an overall increase of membrane hydrophilicity, are explained by the cleavage of C-F and C-H hydrophobic groups followed by the formation of C=O, OH and COOH hydrophilic groups on PVDF fibers surface during the interaction between the plasma and the samples. Plasma environments have neutral species, energetic ions, photons and electrons that interact with the polymer causing chemical and physical modifications in the polymer surface and not on the polymer bulk properties. Particularly, the electrons present in plasma have sufficiently high kinetic energy to break the covalent bonds, inducing chemical reactions that will change the polarity of the surface [34]. Fluorinated polymers like PVDF are known to be resistant to oxygen species attack that difficult the abstraction of fluorine atoms. However, the results

showed that oxygen atoms are detected in PVDF fibers, indicating that some oxidation reactions occurs in the PVDF fibers after oxygen plasma treatment [15, 35]. This can be explained by the possible recombination of fluorine with carbon radicals. It is known that the stability of the gas product is an important factor in the modification process than bond energy [15]. Figure 7 demonstrates the possible modifications that occur on PVDF surface by oxygen plasma treatment. During the plasma treatment radicals are formed primarily by the scission of carbon-hydrogen bond (C-H), due to the strength of the C-H (410 kJ mol^{-1}) bond when compared to the C-F bond (460 kJ mol^{-1}), into the polymer surface which can react with the atmospheric oxygen after plasma treatment forming hydroperoxides. These compounds can thermally decompose producing secondary radicals that subsequently are able to react with the air exposure. As it is possible to observe in Figure 6 and Table 3, the fluorine content decreases when the plasma modification occurs. In this sense, the step 1 present in Figure 7 occurs predominantly originating newly formed C-O and C=O groups. The later was not observed in the XPS results indicating that, if formed, it would be a residual product [35].

4. Conclusions

Oxygen plasma treatment has been applied in order to modify the wettability of PVDF membranes. It was observed that plasma treatment does not produce significant variation in average diameter, being $\sim 400 \pm 200 \text{ nm}$ thus being independent of plasma processing parameters. However, an increase in plasma power increases fiber roughness and small bumps appear on fiber surface leading to some eventual fiber joining without change membrane overall porosity. Increase plasma power leads to a decrease of the electroactive β -phase from ~ 85 to 70% , O_2 flow rate and plasma treatment time having

no influence on β -phase content of the polymer fiber mats. Also no significant changes were detected on degree of crystallinity, independently of the plasma treatment conditions, being $\sim 42 \pm 2\%$.

The plasma treatment showed to be effective to change polymer membrane wettability turning the neat hydrophobic membranes into superhydrophilic ones. This effect is attributed to the introduction of oxygen compounds and a decrease of fluorine content onto the polymer fibers surface and a mechanism is proposed. This fact leads to a reduction of the contact angle of the polymer fibers and an overall decrease of the surface tension of the membranes, which in turn improves capillarity and water absorption of the membrane. PVDF superhydrophilic surfaces can be achieved applying a plasma power below 360 W for a treatment time of 120 s and a flow rate of 120 mL min^{-1} .

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Figures and Figure Captions

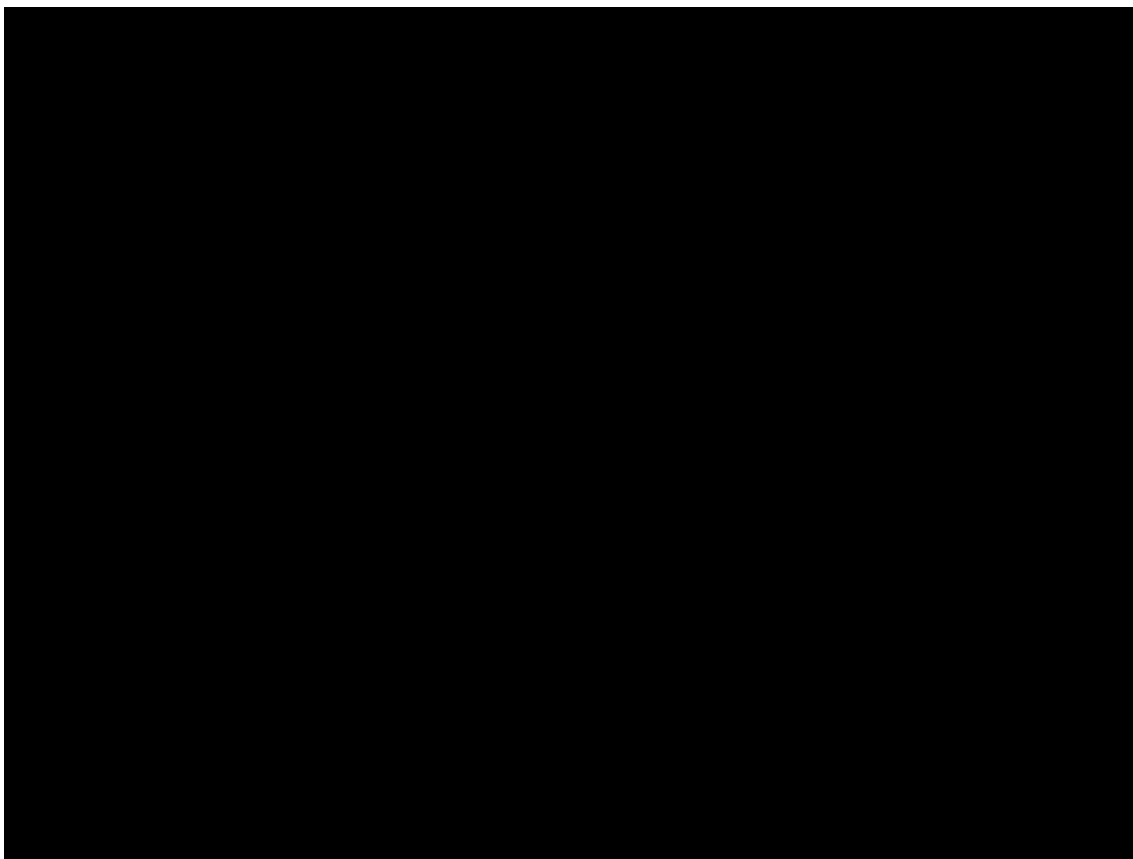


Figure 1. SEM images of electrospun PVDF fibers: a) without treatment and treated with O₂ plasma as a function of the applied power: b) 240 W, c) 360 W and d) 480 W for 120 s using a constant O₂ flow rate of 120 mL min⁻¹.

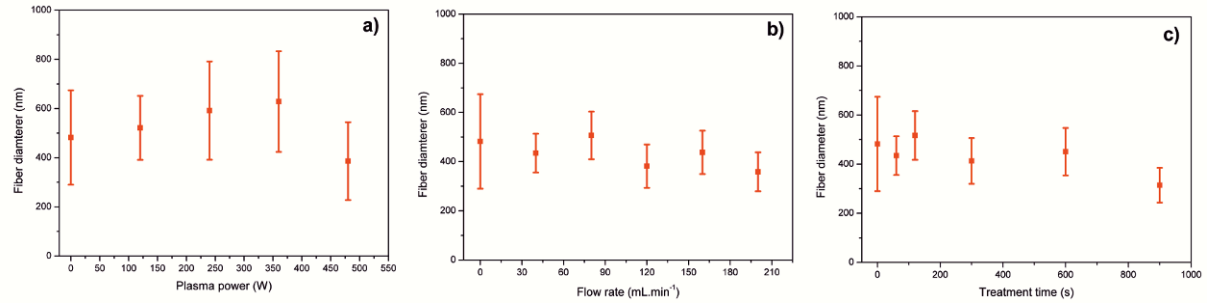


Figure 2. Influence of different plasma treatment parameters in PVDF average fiber diameter: a) plasma power ($t=120$ s; O₂ flow rate of 120 mL min⁻¹); b) O₂ flow rate ($t=120$ s and power of 480 W) and c) time (power of 480 W; O₂ flow rate of 120 mL min⁻¹).

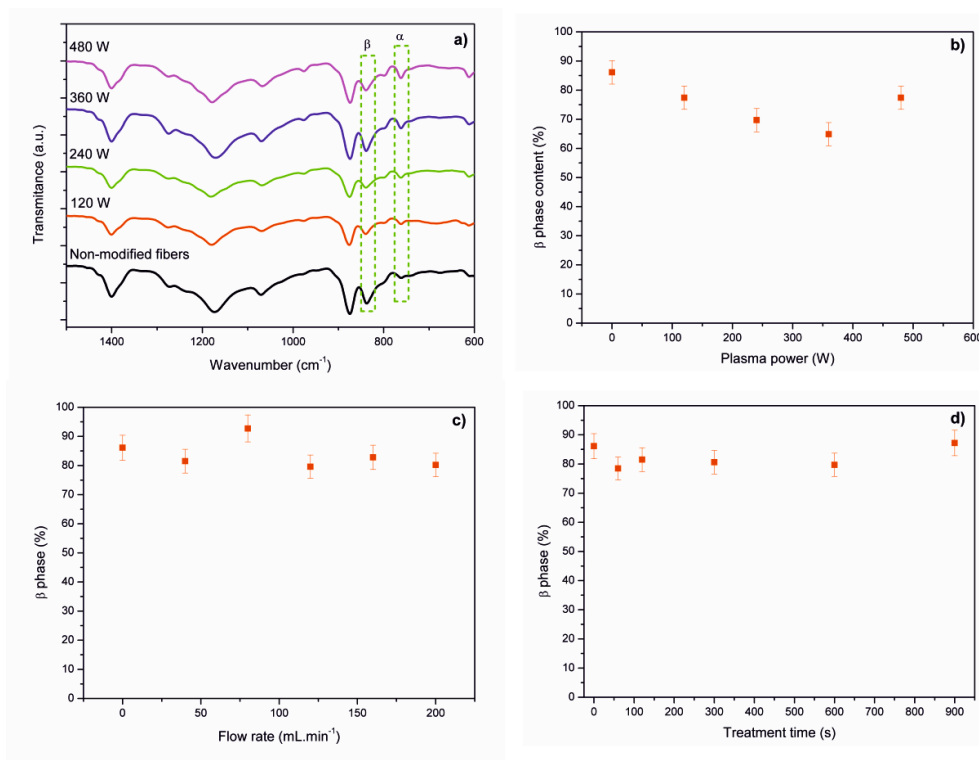


Figure 3. a) FTIR-ATR spectra of non-modified and plasma modified fiber at different plasma power applied for 120 s at a O_2 flow rate of 120 mL min^{-1} ; b) and d) variation of β -phase content with the applied plasma power, c) O_2 flow rate and d) treatment time.

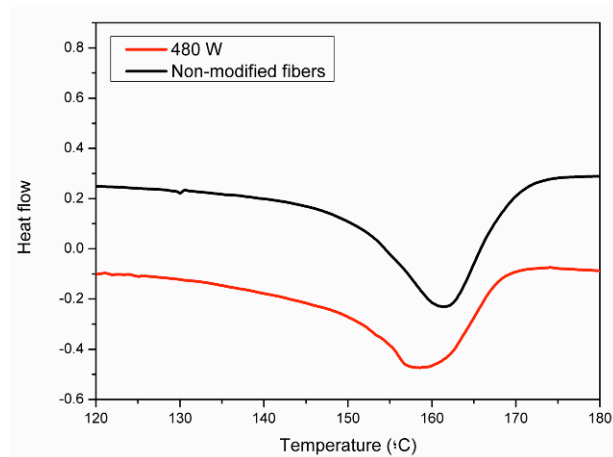


Figure 4. DSC curves for the electrospun PVDF non-modified and oxygen plasma modified fibers at a plasma power applied of 480 W for 120 s and a O₂ flow rate of 120 mL min⁻¹.

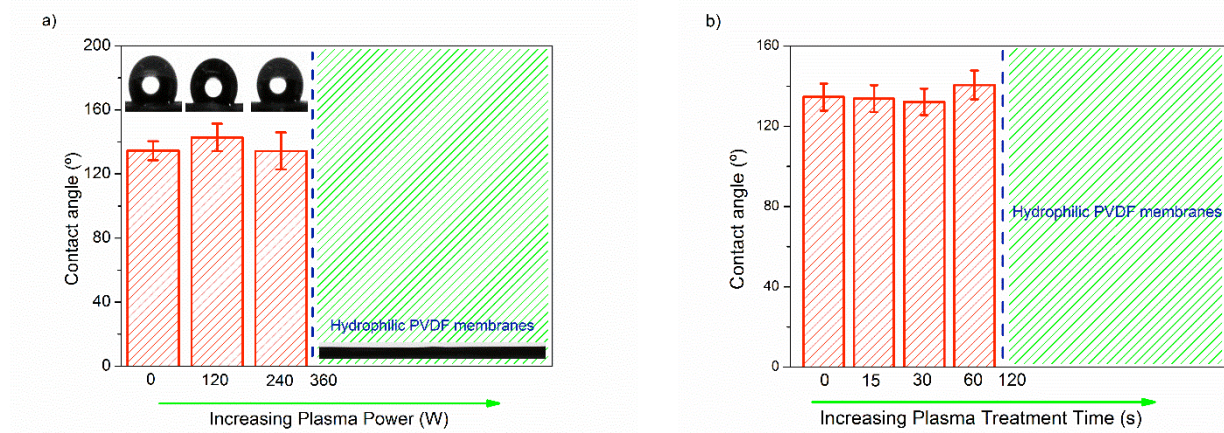


Figure 5. Influence of the (a) oxygen plasma power in the contact angle of PVDF fiber membranes with a treatment time of 120 s and an O₂ flow rate of 120 mL min⁻¹ and b) influence of the treatment time at an applied plasma power of 360 W and O₂ flow rate of 120 mL min⁻¹. The bars in the graph are the standard deviation of the contact angle distribution.

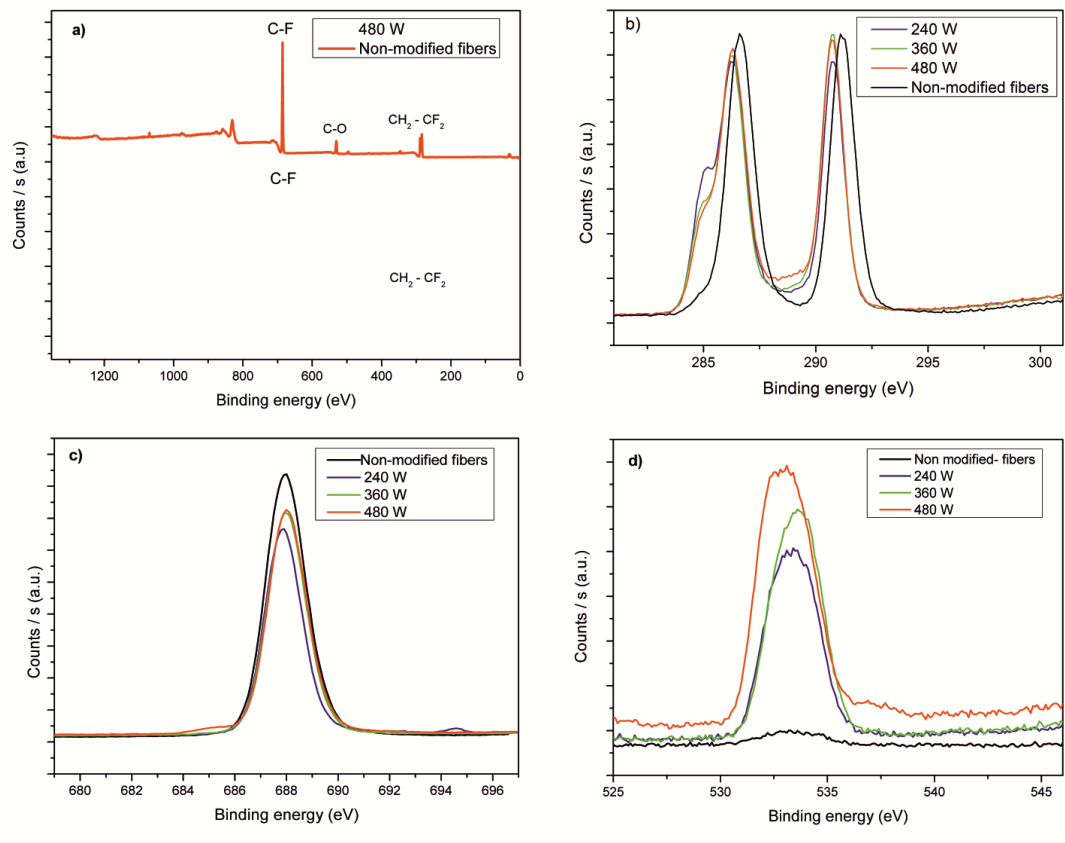


Figure 6. XPS results of non-modified PVDF fibers and oxygen plasma treated fibers for 120 s with an O₂ flow rate of 120 mL min⁻¹: a) XPS scans b) C1s scan spectra, c) F1s spectra and d) O1s spectra.

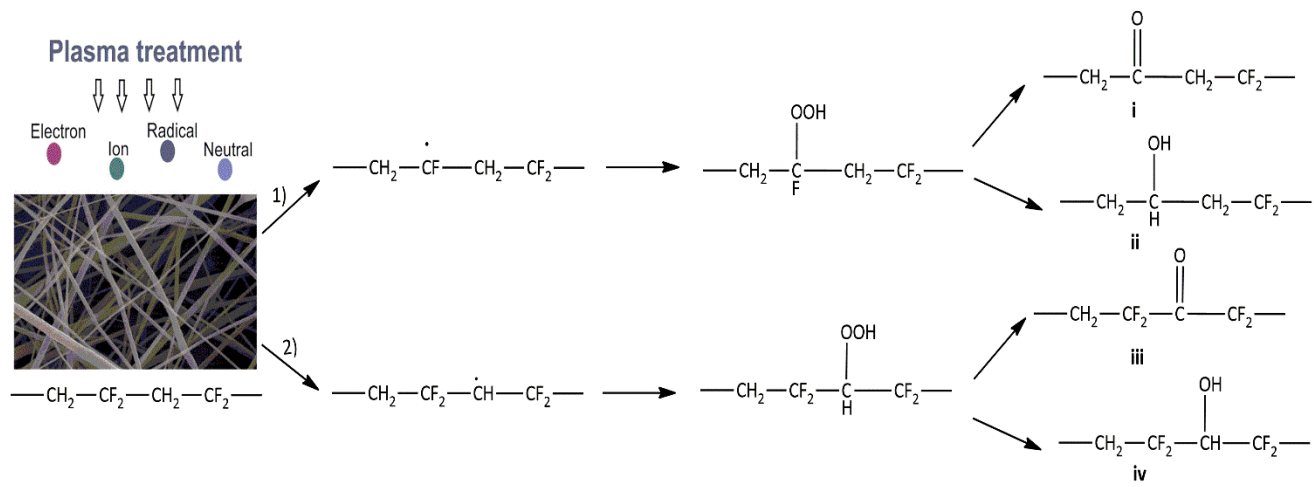


Figure 7. Schematic representation of O₂ plasma treatment on electrospun PVDF fibers.

Plasma introduces free radicals which can react with oxygen.

Tables and table caption

Table 1. Optimal values of plasma parameters in order to obtain hydrophilic membranes.

Plasma parameter	Optimal value
Treatment time (s)	120
Flow rate (mL min ⁻¹)	120
Power (W)	360

Table 2. Surface chemical composition of pristine PVDF fibers and O₂ plasma treated fibers at different applied plasma powers.

Elemental composition (%)					
Surface	C	O	F	O/C	F/C
Pristine fibers	51.30	0.35	48.30	0.01	0.94
Plasma treated fibers					
240 W	56.70	5.20	38.10	0.09	0.67
360 W	53.60	5.80	40.60	0.11	0.76
480 W	52.80	6.80	40.40	0.13	0.77

Influence of plasma treatment parameters on PVDF electrospun fiber mats wettability

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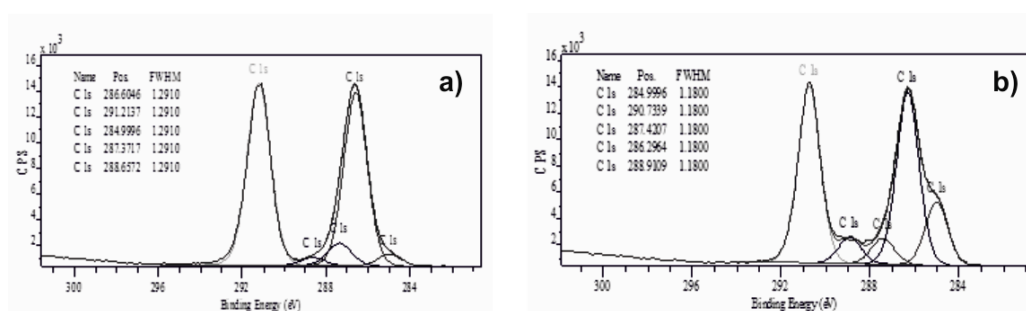


Figure A1. C 1s scan spectra of (a) untreated fibers and (b) O₂ flow of 120 mL min⁻¹, treatment time of 120 s and a power of 480 W.

Table A1. C 1s, F 1s and O 1s components of non-modified electrospun PVDF fibers and oxygen plasma modified fibers [7].

Peak	Binding energy (eV)	Chemical function
C 1s	285	C-C
C 1s	286	C-H
C 1s	291	C-F
O 1s	533	C-O
F 1s	688	C-F