Surface wettability modification of poly(vinylidene fluoride) and copolymer films and membranes by plasma treatment

Daniela M. Correia[a,b,*,1], João Nunes-Pereira[c,1], Denis Alikin[d], Andrei L. Kholkin[d,e], Sónia A.C. Carabineiro[f], Luís Rebouta[b], Marco S. Rodrigues[b], Filipe Vaz[b], Carlos M. Costa[b,g], Senentxu Lanceros-Méndez[h,i,**]

[a] Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal
[b] Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[c] C-MAST – Centre for Mechanical and Aerospace Science and Technologies, Universidade da Beira Interior, Rua Marques d'Ávila e Bolama, 6200-001, Covilhã, Portugal
[d] CICECO-Aveiro Institute of Materials and Department of Physics, University of Aveiro, 3810-193, Aveiro, Portugal
[e] School of Natural Sciences and Mathematics, Ural Federal University, 620000, Ekaterinburg, Russia
[f] LCM – Laboratório de Catálise e Materiais, Laboratório Associado LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465, Porto, Portugal
[g] Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[h] BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain
[i] IKERBASQUE, Basque Foundation for Science, 48013, Bilbao, Spain

HIGHLIGHTS

- Surface wettability of PVDF and copolymer has been modified by plasma treatment.
- Polymer films and membranes were evaluated after plasma treatments under argon and oxygen atmospheres.
- The morphology and the gas type play an important role in the plasma treatment efficiency.
- Oxygen atmosphere is more efficient to promote a better hydrophilicity of the surface.
- The surface modification mechanism for each (co)polymer is provided.

ARTICLE INFO

ABSTRACT

This manuscript reports on the modification of the surface wettability of poly (vinylidene fluoride) (PVDF) and PVDF copolymer films and membranes by plasma treatments at different conditions, under oxygen and argon atmospheres. It is shown that a more pronounced decrease of the contact angle after O_2 plasma treatments is obtained, with a decrease of ~20-30° for PVDF and its copolymers films, leading also to superhydrophilic membranes. This effect is related to a defluorination process, followed by the incorporation of oxygen atoms onto the surface of membranes that occurs during the surface modification. The influence of plasma treatments on surface morphology and topography was studied by atomic force microscopy, showing a decrease in the mean surface roughness with the plasma treatments, being more noticeable for Ar treatments. Finally, it is also shown that plasma treatments under Ar and O_2 did not induce modifications in the physicochemical and thermal properties of PVDF and PVDF copolymers. The chemical reaction mechanism after plasma treatment is proposed for the different copolymers.

1. Introduction

The modification of fluorinated polymer surfaces, widely used because of their high chemical inertness, thermal stability and electrical insulating properties, has been receiving increasing attention due to their negligible adhesion to other materials and hydrophobicity, mainly

caused by the low surface tension [1,2].

Poly (vinylidene fluoride) (PVDF) is a semi-crystalline polymer composed by the monomer $-CH_2-CF_2-$ with at least five distinct crystalline phases related to different chain conformations, being the β phase the one with the largest piezoelectric response [3,4]. PVDF and its copolymers (produced from the monomers of tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE) and hexafluoropropylene (HFP)) are among the most interesting and promising fluorinated polymers due to their outstanding properties [2]. More specifically, their prominent piezoelectric, pyroelectric and ferroelectric properties, high dielectric constant and electroactive response allows these polymers to be suitable for a large range of applications, such as tissue engineering [5], sensors and actuators [6], batteries [7], and filtration membranes [8,9], among others [2,3].

The low surface energy of PVDF and its copolymers results in a high hydrophobicity and poor wettability of their surfaces, which is a key issue for the development of various applications [5]. Further, it represents a relevant drawback in areas such as water purification [10], bio-separation [3,11], tissue engineering [5] and battery separator membranes [12]. The hydrophobic nature of PVDF is one of the major problems of PVDF membranes applied to aqueous solution, since it leads to a decrease of the permeability and the overall performance of the membrane [11,13].

Different surface modification approaches have been used so far to tailor the polymer surface wettability of PVDF, such as plasma treatments, surface coating/deposition, defluorination-sulfonation, O_3/O_2 reactivation, blending, and electron beam radiation, among others [11,13]. Plasma treatments stand out among the most appropriate approaches due to their high versatility, being applied to both porous and non-porous polymer surfaces retaining their main physicochemical bulk properties [5,14].

Plasma treatments enable the introduction of functional groups into the polymer surface, allowing to control the surface roughness and crosslinking, graft polymerization and thin film coating adhesion [15]. Selecting the type of plasma source, different functional groups can interact with the polymer surface, modifying the roughness and/or the chemical surface composition and tailoring the surface wetting and adhesion properties [16,17]. Furthermore, the exposure of the polymer surface to plasma generates active sites on the surfaces, thus promoting chemical reactions [15].

Different plasma sources have been used to modify the surface wettability of PVDF. Low pressure plasma treatments with O_2, Ar and O_2 + Ar resulted in increased hydrophilicity, the gas mixture of O_2 + Ar being effective to improve surface adhesion properties [18]. O_2 plasma treatment was also successfully used to promote the biocompatibility of PVDF resulting in four-fold increase of cell density [19]. N_2 and O_2 plasmas were used for the defluorination of PVDF, leading to a more hydrophilic polymer surface [20]. Similarly, H_2 plasma was used for the same purpose and it was reported as the most efficient treatment for defluorination as compared to Ar and O_2, the latter being more efficient for the dehydrogenation of the PVDF surface [21]. Ar plasma treatments were also reported to produce notable dehydrofluorination effects on PVDF surface due to $C-H$ and $C-F$ bond ruptures, which promoted the polymer surface roughening and hydrophilicity [22]. Plasma induced free radical polymerization was promoted by Ar plasma treatments to modify PVDF membranes surface and successfully support neuronal cells cultivation [23].

On the other hand, and despite their increasing scientific and technological interest, only a few studies report on the surface modification of PVDF copolymers by plasma treatments. Poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) membranes were modified under Ar and O_2 atmospheres for their application as separators for lithium-oxygen batteries, plasma treatments leading to increased discharge capacity and rate performance [24]. PVDF-HFP electrospun membranes treated with Ar plasma were shown to induce grafting copolymerization, leading to polymeric fibers with high antibacterial

activity [25]. Oxygen plasma treatments on the copolymer poly (vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) were reported to render the polymer surface hydrophilic and thus using it for the development of organic thin-film transistors [26].

In this context, this work reports on the surface properties modification of PVDF and its copolymers PVDF-TrFE, PVDF-HFP and poly (vinylidene fluoride-chlorotrifluoroethylene) (PVDF-CTFE) porous (membranes) and nonporous (films) samples, morphologies, which are used in an increasing number of applications [27]. The surface modifications were achieved by plasma treatments with different gas atmospheres (Ar and O_2), under different plasma treatment times. The effects of plasma treatment on surface wettability, roughness, physicochemical and thermal properties of the samples were evaluated.

2. Experimental

2.1. Materials

PVDF (Solef 1010), PVDF-TrFE (Solvene 250, molecular weight (Mw) = 150–400 kg/mol; 30 wt% TrFE content), PVDF-HFP (Solef 21216; Mw = 600 kg/mol; 12 wt% HFP content) and PVDF-CTFE (Solef 31508; Mw = 270–290 kg/mol; 18.66 wt% CTFE content) were supplied by Solvay. The solvent *N, N*-dimethylformamide (DMF) (99.5%) was purchased from Fluka.

2.2. Sample preparation

The polymer powders were added, separately, to the DMF solvent in a polymer/solvent ratio of 10/90 vol%. Then, the mixture was magnetically stirred until complete polymer dissolution, which happened when a homogenous and transparent solution was obtained. Once dissolved, the polymer solutions were placed on clean glass substrates and spread by doctor blade technique at room temperature. Finally, the solvent was completely evaporated within an air oven (Binder, ED23) at 25 °C to obtain membranes with porous morphology and at 210 °C to melt the polymer and obtain polymer films with a compact morphology, according to Ref. [27]. A thickness of ~50 μm and 100 μm was obtained for films and membranes, respectively.

2.3. Surface modification

The plasma treatments were conducted in a Zepto plasma chamber from Diener Electronic (Ø = 105 mm, L = 300 mm, V = 2.6 L) equipped with a 40 kHz radio frequency plasma generator. The base pressure of the system was 20 Pa. Plasma working gases were Ar and O_2, independently, for different times from 200 to 600 s at a plasma power of 100 W, under a total pressure of 80 Pa.

2.4. Sample characterization

The surface wettability of the samples was evaluated by contact angle measurements (sessile drop in dynamic mode) at room temperature in a Data Physics OCA20 device with ultrapure water (3 mL droplets) as test liquid. At least 3 measurements were performed on each sample, in different locations, and the average contact angle was calculated.

The roughness analysis was carried out by atomic force microscopy (AFM) using commercial scanning probe microscope NTEGRA Aura (NT-MDT, Russia) in a tapping mode. NSG01 non-coated silicon probes with 1–5 N/m spring constant were used to evaluate the surface topography. The roughness was calculated as a median value of the topography averaged across the scan from $3 \times 3 \, \mu m^2$ up to $10 \times 10 \, \mu m^2$. The scan size was selected according to the maximal lateral feature size. The error value was calculated as a root-mean-square deviation of the average topography values.

The crystalline phases of PVDF polymer and its copolymers were

determined by Fourier transformed infrared spectroscopy (FTIR). Measurements were performed with a Jasco FT/IR-4100 in attenuated total reflectance (ATR) mode over a range of 600–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

The surface element quantification was evaluated by X-ray photoelectron spectroscopy (XPS). The measurements were 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 Kα 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 a charge neutralization system was used. All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 285 eV. Curve fitting of the high-resolution spectra used 30% Gaussian/70% Lorentzian mixed line shapes for each component.

The thermal characteristics and the degree of crystallinity of the polymers were evaluated by differential scanning calorimetry (DSC) with samples of ∼4 mg weight. Measurements were performed in a Perkin-Elmer Diamond instrument from 25 to 200 °C, at a rate of 10 °C/min under a flowing argon atmosphere.

3. Results and discussion

Plasma treatments allow to induce hydrophilicity of polymeric surfaces [28,29]. Thus, to evaluate the efficiency of surface treatments in different fluorinated matrixes in the form of films and membranes, plasma treatments were performed under Ar and O$_2$ for different times (200–600 s) and a supplied power of 100 W. The effect of the plasma treatments in the physico-chemical and thermal properties is shown and discussed.

3.1. Surface wettability

In general, plasma treatments promote a reduction of the contact angle of the samples and an increase in the surface energy [5,30]. To study the influence of the plasma treatments, in the wettability of the different samples, the variation of the contact angle for films and membranes before and after O$_2$ and Ar plasma treatments, for the maximum treatment time of 600 s, is shown in Fig. 1. It is observed that all untreated samples present a strong hydrophobicity, which is characteristic of PVDF based materials [5,31]. For films, a contact angle between 80 and 100° is observed and for membranes a higher contact angle between 95 and 135° is obtained.

After the plasma treatments, more hydrophilic film and membrane surfaces are obtained. Table 1 presents the water surface contact angles for the PVDF and PVDF copolymers treated under O$_2$ and Ar during 200 and 600 s.

The more pronounced decrease in the contact angle value was observed for membranes treated under O$_2$ (Fig. 1 and Table 1). As indicated in Fig. 1, after O$_2$ plasma treatments, a decrease of approximately 20–30° is obtained for PVDF and its copolymers films and for PVDF-HFP membranes. For the PVDF-CTFE membrane treated during 200 s and for PVDF, PVDF-TrFE and PVDF-CTFE membranes treated during 600 s, the surface contact angle cannot be measured because the water drop was rapidly absorbed by the membrane, indicating a superhydrophilic behavior. The exception of this behavior is detected in PVDF-HFP membranes, where a contact angle of 69° is obtained. This increase in the hydrophilicity of the water surface membranes can be explained by the porous surface of the membranes, which leads to a capillarity effect [5]. Furthermore, variations in the polymer surface roughness and polymer mat morphology result in an associated variation of the surface tension of the membrane, leading thus to a penetration of the water drop into the membrane and a consequent hydrophilic process.

With respect to the films, Fig. 1 and Table 1 show that plasma treatments under O$_2$ and Ar atmosphere enhances the hydrophilicity. However, a decrease of the contact angle for the films treated under Ar is less pronounced as compared to O$_2$ plasma treatments.

The overall wettability results suggest that the effect of the chemical surface modifications, promoted by the O$_2$ treatments, prevails in relation to the effect of roughness modifications by the Ar plasma treatments, in modifying the surface wettability of PVDF and copolymers.

3.2. Chemical characterization and β phase content

The possible chemical modifications in PVDF and its copolymers after plasma treatments were evaluated for films and membranes by FTIR-ATR measurements. Fig. 2 shows the FTIR-ATR spectra of the untreated and treated films. It is observed that PVDF and PVDF copolymer films display characteristic absorption bands of α and β crystalline phases of PVDF. The absorption bands at 408, 532, 614, 766, 795, 855, 976 cm^{-1} are assigned to the α phase characterized by the TGTG′ (trans-gauche–trans-gauche) chain conformation and the absorption bands at 440, 510, 840 and 1279 cm^{-1} are related to all trans (TTT) planar zigzag of the β-phase [3,32]. As presented in Fig. 2a–d, untreated and treated plasma samples of PVDF, PVDF-CTFE and PVDF-HFP preferably display bands corresponding to the α-phase, appearing at 532, 614, 766, 795, 855 and 976 cm^{-1}, while weaker signals could be observed for the electroactive β-phase at 840 and 440 cm^{-1} [3,5]. Similar results are obtained for untreated and treated membranes (results not shown).

The β-phase content (Table 2) of the samples was calculated by measuring the absorbance at 766 cm^{-1} and 840 cm^{-1}, according to the following equation and the procedure described in Ref. [3]:

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

(1)

where A_α and A_β are the absorbance of α-PVDF at 766 cm^{-1} and β-PVDF at 840 cm^{-1} respectively, and K_α and K_β are the absorption coefficients at their respective wavenumbers ($K_\alpha = 6.1 \times 10^4$ cm^2 mol^{-1} and $K_\beta = 7.7 \times 10^4$ cm^2 mol^{-1}) [3].

The resulting β-phase contents of different samples are presented in Table 2. It is observed that the samples of PVDF-TrFE demonstrate high β-phase contents, between 82 and 86% (Table 2), as also indicated by the strong absorption bands at 1280-1288 cm^{-1} and 505 cm^{-1} (Fig. 2b), values that remain unchanged with the plasma treatments. For the rest of the samples, the electroactive phase content remains around 45%, being also unchanged after the surface treatment.

Thus, no significant change of the phase of the samples is observed, indicating, as expected, that the plasma treatments only induced surface modifications of different samples. It is also to notice that all samples present an enough β-phase and therefore a suitable piezoelectric coefficient [33], suggesting their applicability in the field of sensors and actuators, among others.

3.3. Thermal analysis and degree of crystallinity

To investigate the influence of the plasma treatments on the thermal stability of the films and melting behavior, a DSC analysis was performed. Fig. 3 shows the DSC thermograms of the untreated and treated films under Ar and O$_2$. A similar trend can be observed for all samples. Independently of the used gas, characteristic melting is approximately between 120 and 172 °C for the different PVDF and copolymers. The endothermic peak, corresponding to the Curie temperature of the PVDF-TrFE films (Fig. 3b), appears around 96 °C, which is consistent with the literature [3]. Similar results are obtained for untreated and treated PVDF and PVDF copolymers membranes. Plasma treatments do not induce any significant modification of the thermal behavior of the samples.
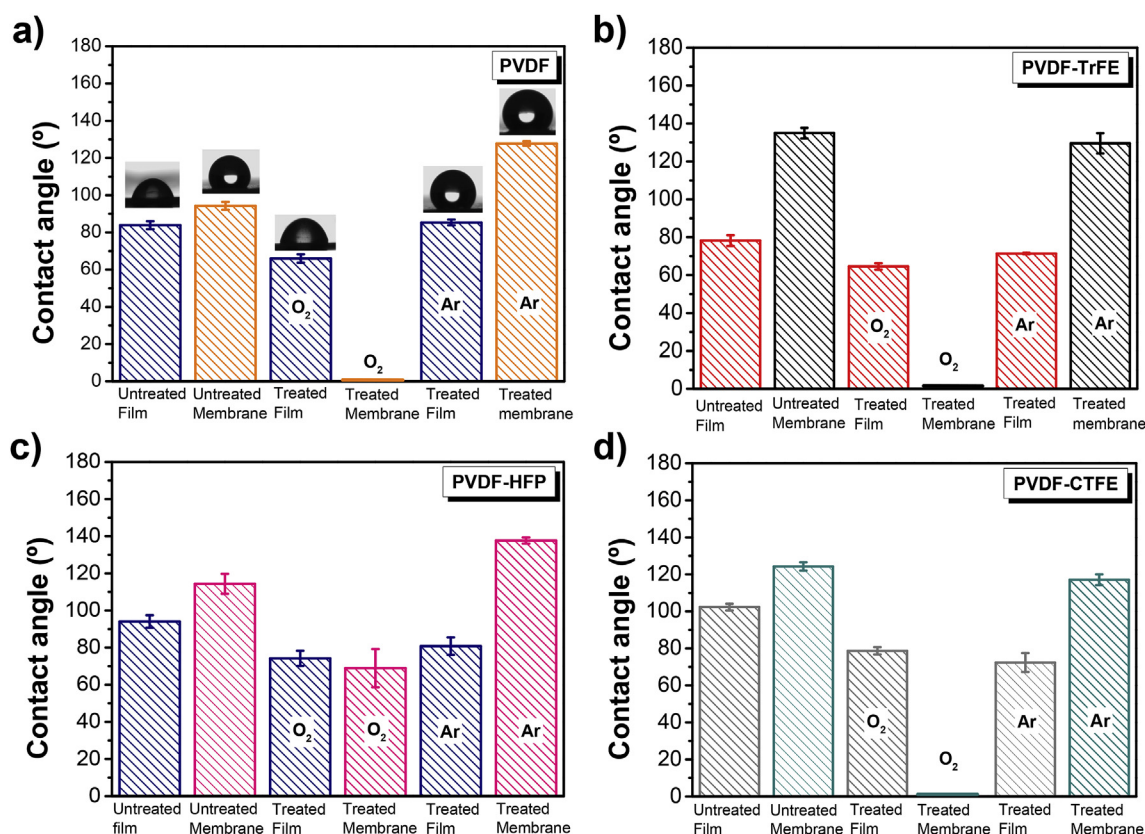
Fig. 1. Influence of the O_2 and Ar plasma treatments during 600 s in the contact angle of PVDF and PVDF copolymer films and membranes. The bars in the graph represent the standard deviation.

The degree of crystallinity (χ_c) was estimated from DSC thermograms by the following equation:

$$\chi_c(\%) = \frac{\Delta H_m}{x\Delta H_\alpha + y\Delta H_\beta} \times 100 \tag{2}$$

where ΔH_m is the melting enthalpy of the endothermic peak appearing at higher temperature, 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-phases present in the sample, respectively [3].

Table 2 shows that plasma treatments under Ar and O_2 does not induce any significant variation of crystallinity in the PVDF and PVDF copolymers samples, being the differences within the experimental errors. The untreated and treated PVDF samples displayed the highest degree of crystallinity around 54% [34]. The remaining samples of the copolymers show very similar values ranging between 18 and 22% [35].

3.4. Surface topography

The ion bombardment and UV radiation generated during plasma treatments can lead to pronounced changes in the surface morphology [36]. Fig. 4 shows the SEM images of PVDF and PVDF copolymers membranes after O_2 plasma treatments. Similar results are observed for the treated membranes under Ar gas, indicating that plasma treatments under both gases do not alter the membranes morphology (see inset of the untreated PVDF membrane in Fig. 4a).

To evaluate the influence of plasma treatments on the surface topography, AFM analysis was performed on the PVDF and PVDF copolymer films both untreated and treated with the largest plasma treatment time (600 s) and power (100 W). Due to its high porosity, the same procedure was not performed in the membranes [27,35,37].

Fig. 5 shows the AFM images for the untreated PVDF (Fig. 5a) and PVDF-HFP (Fig. 5c) films and treated films under O_2 (Fig. 5b and d for

Table 1

Contact angle values of untreated and treated PVDF and PVDF copolymer films and membranes under O_2 and Ar atmospheres.

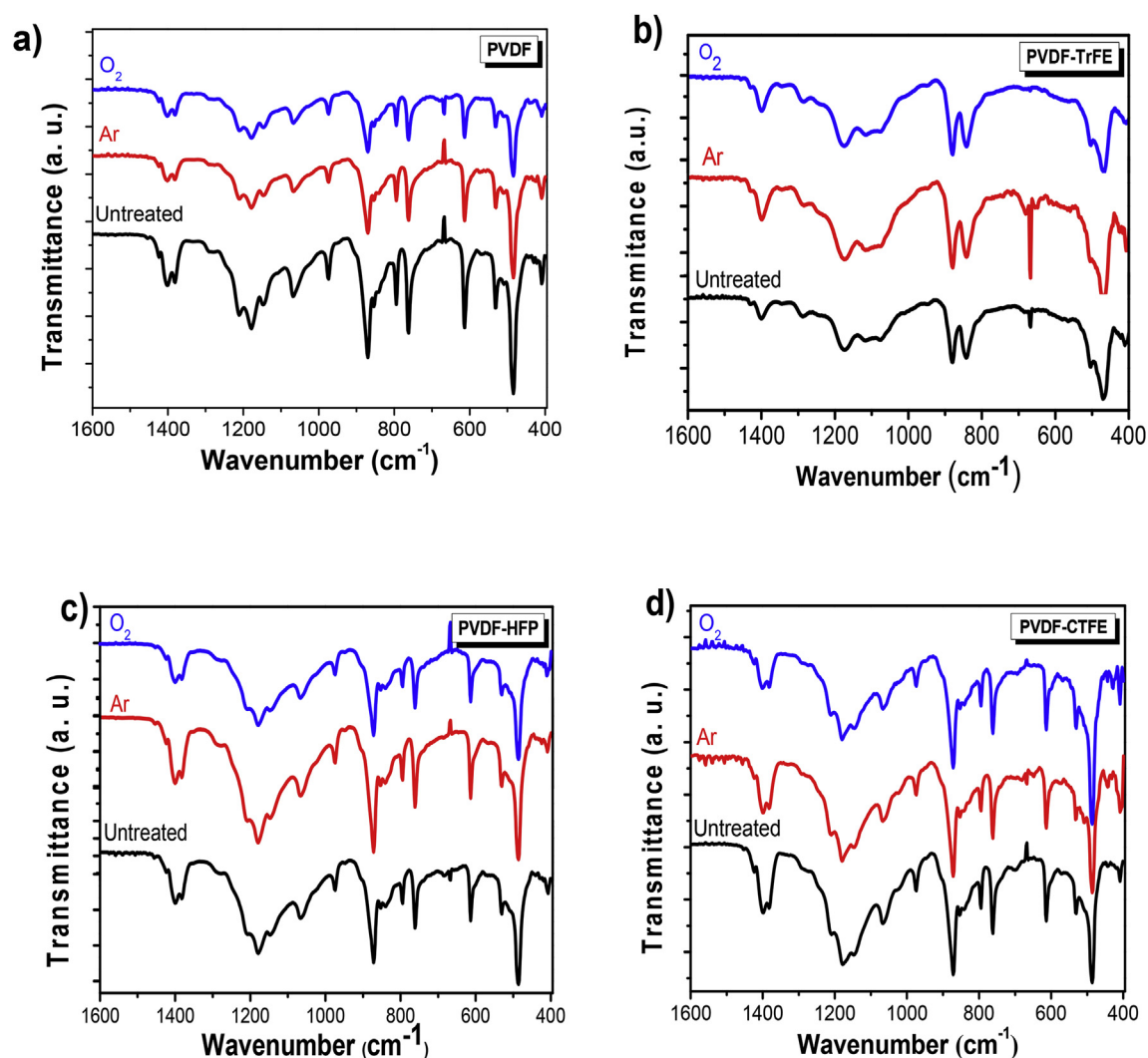|	Samples	O_2			Ar	
		Untreated	200 s	600 s	200 s	600 s
		(°)	(°)	(°)	(°)	(°)
Films	PVDF	84 ± 2	64 ± 2	66 ± 2	86 ± 3	85 ± 2
	PVDF-TrFE	78 ± 5	69 ± 2	65 ± 2	89 ± 2	71 ± 1
	PVDF-HFP	94 ± 4	78 ± 2	74 ± 4	86 ± 4	81 ± 5
	PVDF-CTFE	102 ± 2	72 ± 8	79 ± 2	82 ± 2	72 ± 5
Membranes	PVDF	94 ± 4	132 ± 4	–	85 ± 14	128 ± 1
	PVDF-TrFE	134 ± 5	128 ± 3	–	134 ± 2	129 ± 5
	PVDF-HFP	114 ± 5	94 ± 4	69 ± 4	132 ± 5	138 ± 2
	PVDF-CTFE	124 ± 2	–	–	130 ± 5	117 ± 3

Fig. 2. FTIR-ATR spectra of PVDF (a), PVDF-TrFE (b), PVDF-HFP (c) and PVDF-CTFE (d) samples before and after plasma modification with Ar and O_2.

Table 2
β-phase content and degree of crystallinity (χ_c) for untreated and treated PVDF and copolymers films.

Sample	β-phase ± 3 (%)	χ_c ± 3 (%)
PVDF	43	54
PVDF + Ar	42	53
PVDF + O_2	43	54
PVDF-TrFE	86	20
PVDF-TrFE + Ar	82	21
PVDF-TrFE + O_2	85	22
PVDF-HFP	47	19
PVDF-HFP + Ar	47	19
PVDF-HFP + O_2	46	19
PVDF-CTFE	47	18
PVDF-CTFE + Ar	46	18
PVDF-CTFE + O_2	48	19

PVDF and PVDF-HFP, respectively). Similar results are obtained for the other treated and untreated samples (results not shown).

Fig. 5b and d demonstrate that the O_2 plasma treatments promote changes in the surface topography of the films, being different for different polymers. The effect of plasma treatments on the surface roughness of the films was also investigated. Fig. 6 shows the

evaluation of the surface mean roughness (Ra) for untreated and treated samples under O_2 and Ar. From Fig. 6 it is observed that the surface roughness of all samples decreases with the plasma treatments under the both gases atmospheres (except for PVDF-HFP). However, the Ra for the films treated under O_2 is higher, as compared to the samples treated under Ar.

In addition, after O_2 plasma treatments, the surface of the samples presents large hills and valleys (Fig. 5c and d) as a result from the interaction between the plasma and the samples surface, namely due to the interactions between oxygen atoms and oxygen metastable molecules and polymer molecules on the surface [16]. This change in the films topography after Ar and O_2 plasma treatment, which is similar for both types of plasma treatments, together with the chemical variations in the polymer surface (see later), can explain the apparent decrease observed in the contact angle of the films.

The decrease in Ra is more pronounced for the PVDF and PVDF-TrFE film treated under Ar, decreasing approximately from 298 to 59 nm and 473 to 210 nm, respectively. The highest value of Ra is observed for untreated (1191 nm) and treated under Ar PVDF-CTFE films (964 nm) and O_2 (937 nm). The evaluation of Ra of the PVDF-HFP films treated under Ar, was not performed once the size of the features on the surface is higher than the scanner range of the microscope. After the O_2 plasma treatment, the Ra slightly increases from 57 to 115 nm.

The observed decrease in the surface roughness is likely due to the smoothening effect of the surface cleaning resulting from the etching
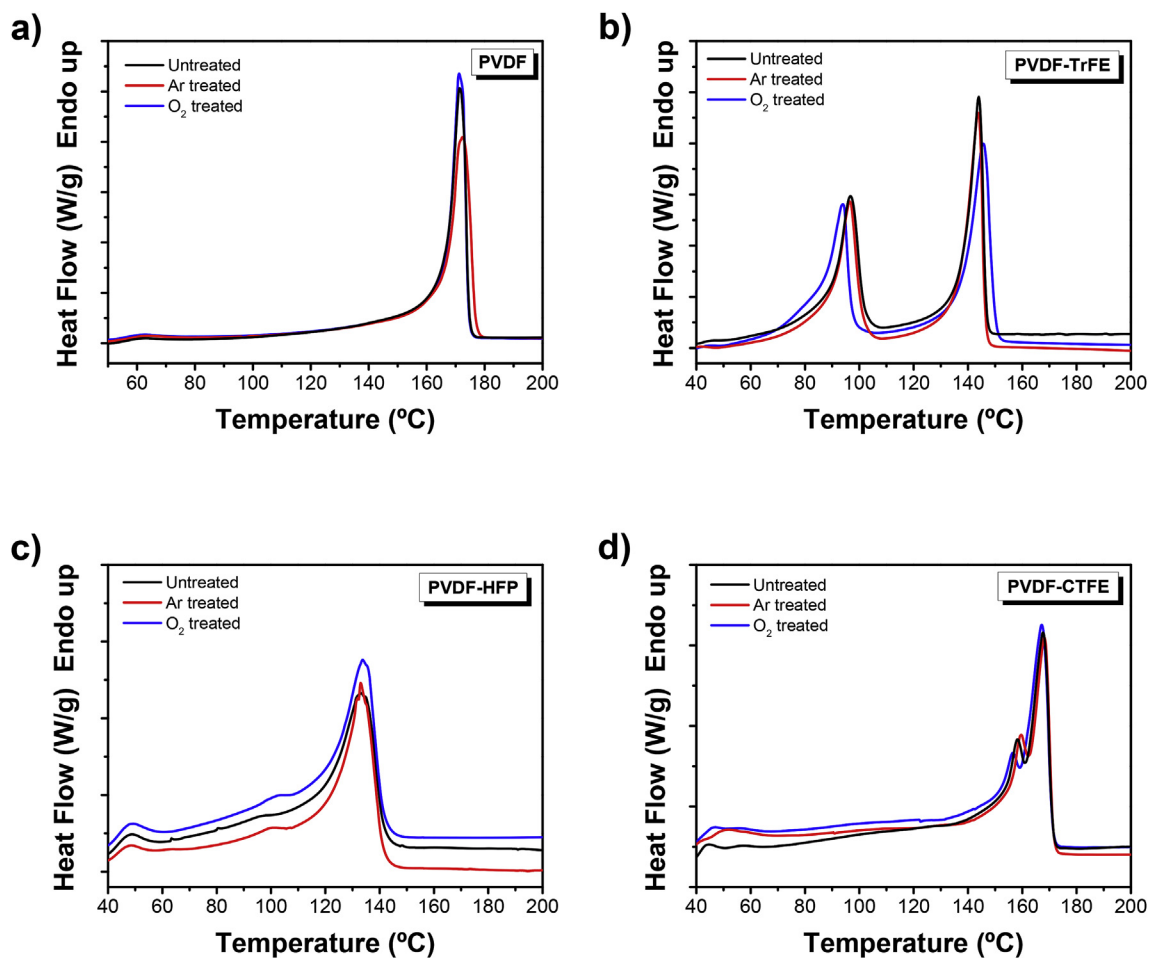
Fig. 3. DSC thermograms of PVDF (a), PVDF-TrFE (b), PVDF-HFP (c) and PVDF-CTFE (d) unmodified and plasma modified samples, during 600 s, at a power of 100 W.
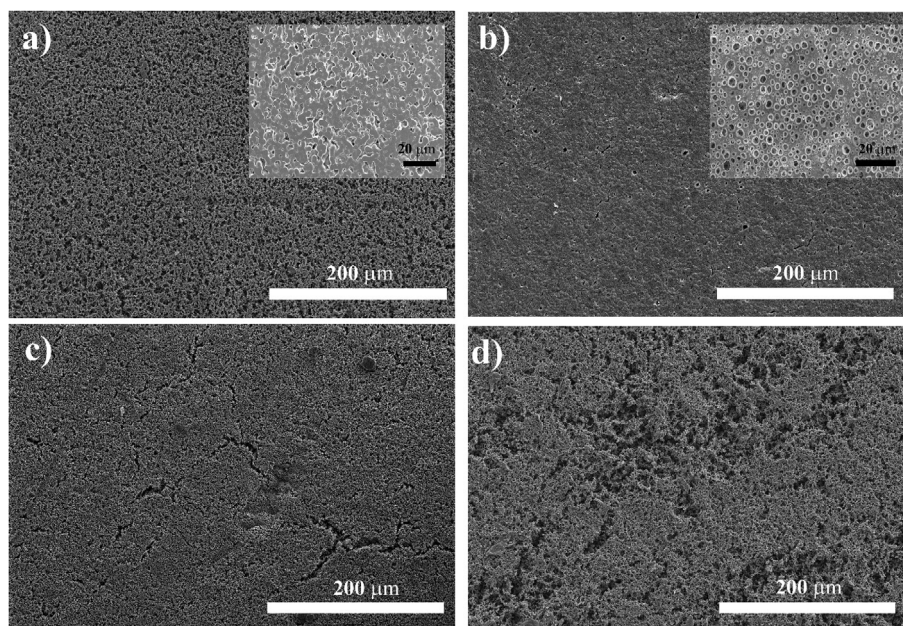

Fig. 4. Surface SEM images of the treated membranes under O_2 during 600s: a) PVDF (untreated PVDF in the insert), b) PVDF-TrFE (untreated PVDF-TrFE in the insert), c) PVDF-HFP and d) PVDF-CTFE.
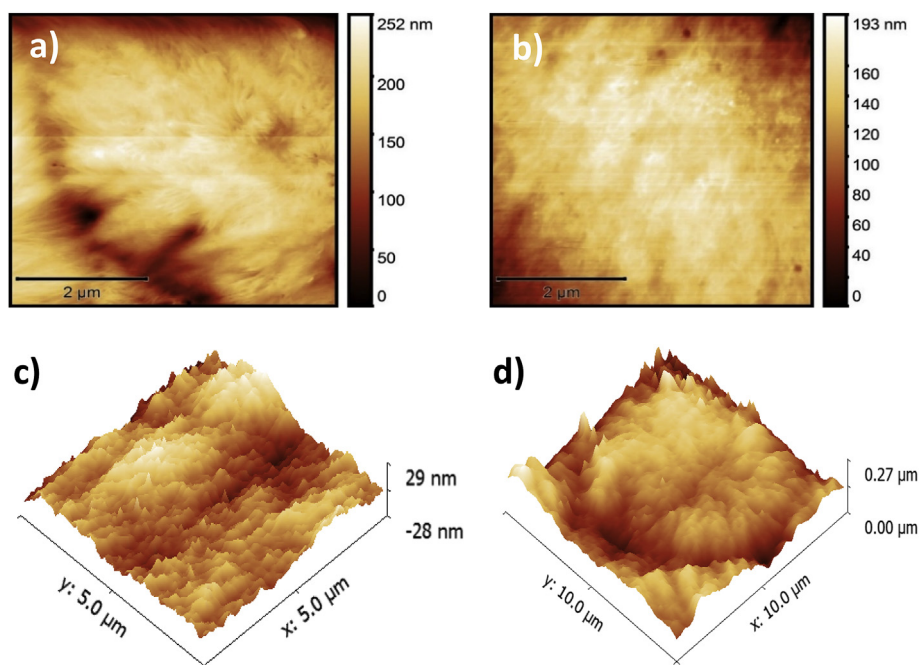
Fig. 5. 2D and 3D AFM images of PVDF (a) and PVDF-HFP (c) samples before and after plasma modification with O_2 (b and d) (600 s and 100 W), respectively.
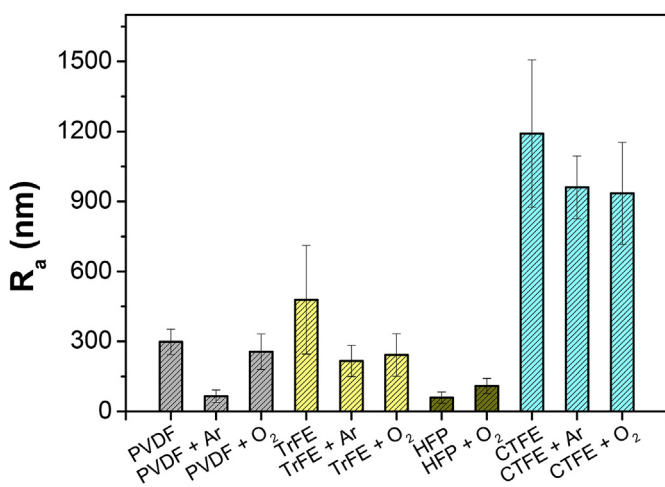
Fig. 6. Roughness value for the different samples before and after plasma treatments under O_2 and Ar (600 s and 100 W).

process. Moreover, the lowest values of Ra obtained after plasma treatments under Ar are an indicative that during the plasma treatments, the etching process was active rather than the introduction of chemical functional groups into the polymer surface [21]. These results are in agreement with the contact angle values presented in Fig. 1, where the films treated under Ar atmospheres displayed the lowest hydrophilicity. This fact is an indication that the surface roughness of the samples does not create an air gap, when the water droplet penetrates into a rough surface, as described by the equation:

$$\cos \theta_{rough} = r \cos \theta_{flat} \qquad (3)$$

Where θ_{rough} is the apparent contact angle, r the roughness and θ_{flat} the smooth and flat surface [38].

However, the untreated films have higher Ra and higher contact angle, which means we cannot disconnect this behavior from chemical effects introduced by plasma treatment.

3.5. Chemical surface variations

To study the largest wettability obtained in the PVDF and PVDF copolymer membranes shown in Fig. 1, XPS analyses were performed for untreated and O_2 plasma treated membranes after the maximum plasma exposure time (600 s). The atomic elements carbon (C), fluorine (F) and oxygen (O) were detected in all membranes, as shown in the XPS spectra of Fig. 7. Table 3 summarizes the quantitative elemental chemical composition for the C, F and O elements of the surface of the membranes before and after O_2 treatment.

The analysis of the XPS photoelectron lines of all membranes was performed to obtain the C1s, F1s and O1s components of the spectra. As can be observed in Fig. 7 carbon, fluorine and oxygen elements were detected in the PVDF and PVDF copolymers membranes as shown in the overall XPS spectra. In the C1s core level spectra of untreated PVDF and treated PVDF (top of Fig. 7a), it is possible to observe two major peaks at 291.2 eV and 286.7 eV, typical for PVDF [1], assigned to CF_2 groups and C—CF component, respectively, and a minor at 285 eV attributed do C—C and C—H bonds [1]. A slight decrease in the intensity of the peaks at 291.2 and 286.7 eV can be observed in treated PVDF membranes, as well as a shift to lower energies. For PVDF copolymers, the peaks corresponding to C—F, C—CF and C—C bonds [5,31] are also observed.

The F1s lines are shown in Fig. 7b and the peak located between 688 eV (PVDF) [39] and 689 eV (PVDF-HFP) is assigned to C—F bonds (in —CF_2CH_2, $CHFCH_2$ and CHFCHF species). O1s lines are shown in Fig. 7c and the peak at 533 eV is attributed to C—O bonds [5].

The untreated PVDF-CTFE and TrFE membranes show higher hydrocarbon content (285 eV). This content decreased with O_2 plasma treatment due to C etching and/or oxidation. In the case of PVDF-TrFE membranes (with 18.1% of carbon at that chemical state), with the O_2 plasma treatment a peak located at 289.2 eV appeared, which is usually addressed to C—O bonds, suggesting an oxidation of superficial carbon. The F1s line remains unchanged with the plasma treatment. In case of PVDF-CTFE membranes (with 11.6% of carbon at that chemical state) a broadening of main peaks C1s lines located at 286.8 and 291.3 eV was found, together with a small shift of the F1s line, suggesting that hydrocarbon is etched, and C—F bounds are affected by the plasma treatment. Untreated PVDF and PVDF-HFP membranes have much less hydrocarbon and the shift of F1s with plasma treatment is also seen.
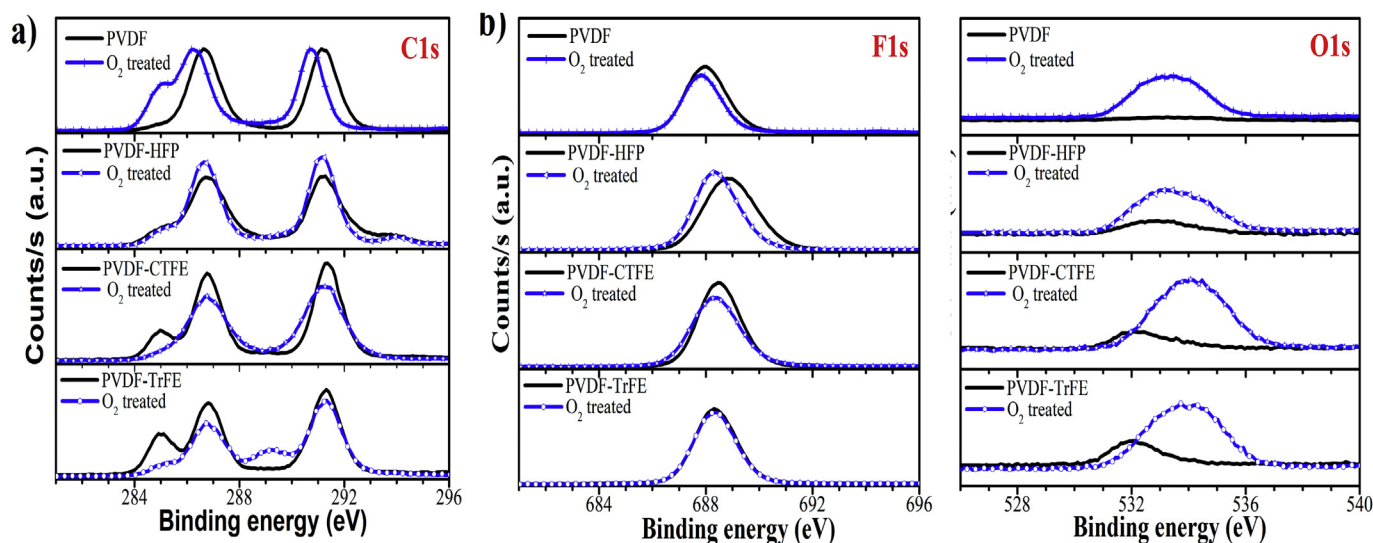
Fig. 7. XPS spectra of untreated and O_2 plasma treated PVDF and PVDF membranes for the maximum treatment time of 600 s of: a) C1s, b) F1s and c) O1s photoelectron lines.

Table 3
Surface chemical composition of PVDF and copolymers membranes after plasma treatment under oxygen during 600 s.

Surface	Elemental composition (%)				
	C	O	F	O/C	F/C
PVDF	51.3	0.35	48.3	0.007	0.94
PVDF + O_2	56.7	5.2	38.1	0.09	0.67
PVDF-TrFE	48.5	2.1	47.6	0.04	0.98
PVDF-TrFE + O_2	45.1	7.4	46.9	0.16	1.04
PVDF-HFP	46.5	1.3	52.3	0.03	1.12
PVDF-HFP + O_2	46.7	4.5	48.7	0.09	1.04
PVDF-CTFE	48.1	1.4	49.1	0.03	1.02
PVDF-CTFE + O_2	45.8	7.3	46.0	0.16	1.00

The shift of F1s line to lower energies can be due to the formation of O−C−F species.

The elemental quantitative analysis results of carbon (C), fluorine (F), and oxygen (O) are summarized in Table 3. The PVDF-TrFE membrane shows a decrease of carbon content and an oxygen increase, supporting the conclusions obtained from the analysis of C1s and F1s line shapes. In case of PVDF-CTFE, membranes show a smaller decrease of carbon content, when compared with TrFE, with already a decrease in F content, which agrees with some F etching followed by oxidation, justifying the shift in F1s line. The carbon content in HFP copolymer remains constant, which means that the F content decrease was similar to the oxygen content increase. The shift of F1s line is higher than those observed in the other two copolymers. The PVDF membrane reveals an increase of carbon content after the O_2 plasma treatment, which can be due to some contamination because an increase of the hydrocarbon peak was also observed after the plasma treatment. A strong decrease on F content is also observed, although the absolute value is influenced by the carbon increase. This results suggest that O_2 plasma treatment induces a defluorination reaction at the surface followed by the incorporation of oxygen (C−O groups) onto the surface, which originates a subsequently decrease in the surface fluorine atomic content [5]. The F/C ratio in PVDF-TrFE and PVDF-CTFE does not decrease due to the reason already above mentioned, mainly because together with some F etching also occurs the etching of hydrocarbon. Due to a similar reason, the decrease of F/C is amplified due to hydrocarbon increase in treated sample, which was not present in the untreated sample. These changes clearly show that O_2 plasma treatment induces clear surface alterations in the membranes.

A small amount of oxygen can be observed in untreated membranes, probably due to the exposure of the membranes to the air or due to the solvent contaminants. The oxygen/carbon (O/C) ratio increases due to the introduction of oxygen groups generated by the O_2 plasma treatment of the surface of membranes [5]. This increase is more noticeable for PVDF, PVDF-TrFE and PVDF-CTFE. This fact can be explained based on the chemical composition of all the polymers. The lowest ratio O/C is observed for the PVDF-HFP membrane. Together with this smaller oxygen addition, when compared with other membranes, the PVDF-HFP membrane does not show any change of C1s line at 285 eV (identified as belonging to the hydrocarbon contamination) and is the membrane with a contact angle around 70° (showing a decrease of about 45°) after the plasma treatment, while the others reveal a superhydrophilic behavior, where it is not possible to measure the contact angle, because the water drop was rapidly absorbed by the membrane.

In this sense, the change in the surface topography after Ar and O_2 plasma treatment, together with the reported chemical modifications, explain the variations in the contact angle of the films.

4. Surface chemical reactions of the materials under O_2 plasma treatment

The presence of oxygen atoms in the membranes indicates the occurrence of oxidation reactions after the plasma treatments. Fig. 8 schematizes the possible chemical reactions that occur in PVDF and PVDF copolymers treated under O_2 plasma treatments. During the PVDF plasma treatment under O_2, the energy involved in the process can be sufficiently high to promote the C−F bond scission [1]. The formed radicals can react with the air, forming hydroperoxides that are supposed to decompose producing secondary radicals that are able to react with the ambient air, leading to the formation of oxygen compounds (C=O and OH groups) on PVDF and PVD-copolymers surface (Fig. 8) [1].

The lowest wettability observed for PVDF-HFP membrane (Fig. 1) after O_2 plasma treatment indicates that the extension of the C−F scissions, followed by the oxygenation process in PVDF-HFP co-polymer membrane, is lower comparatively to the other copolymers.

5. Conclusions

Plasma treatments under O_2 and Ar gases were performed on PVDF and PVDF copolymers films and membranes. The surface wettability studies reveal that an O_2 atmosphere is more efficient to promote a
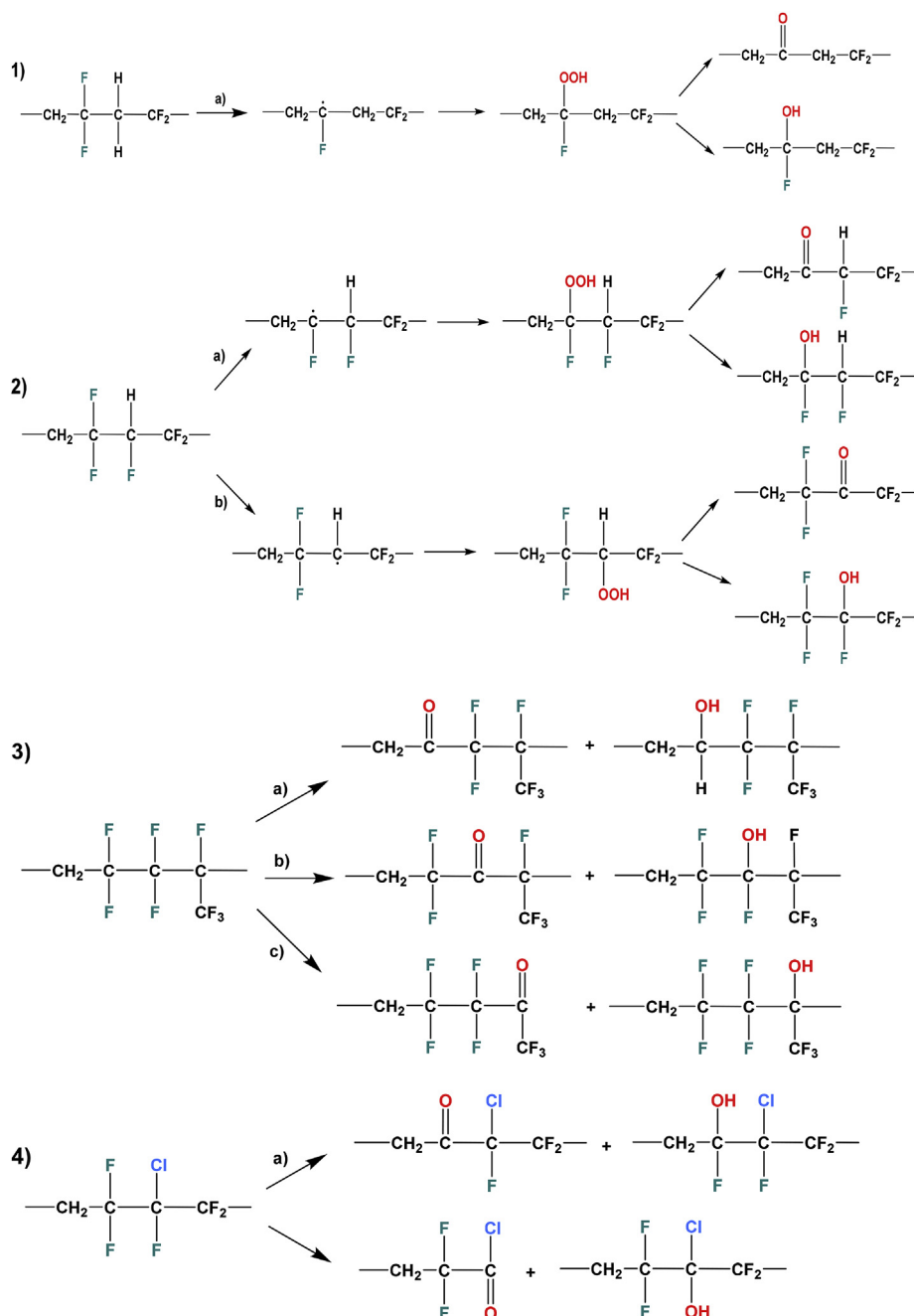
Fig. 8. Schematic representation of O_2 plasma treatment on PVDF and PVDF copolymers membranes: 1) PVDF; 2) PVDF-TrFE; 3) PVDF-HFP; 4) PVDF-CTFE.

better hydrophilicity of the surface. Superhydrophilic porous surfaces can be obtained under O_2 at a treatment time of 600 s, due to the de-fluorination process, followed by the incorporation of oxygen atoms onto the surface of membranes that occurs during the surface modification. It was observed that both gases lead to a decrease in the surface roughness of the films. No variations in polymer chain conformation (phase content) or thermal characteristic and degree of crystallinity occur after the plasma treatments. The highest content of the electroactive β-phase was observed for the PVDF-TrFE samples (~84%) and the highest degree of crystallinity for PVDF (~53%).

The increase in the hydrophilicity of the films and membranes, without changes in its physico-chemical and thermal properties, allow these materials to become suitable for applications such as tissue engineering, drug delivery systems, water remediation membranes and battery separators.

References

[1] D.M. Correia, C. Ribeiro, V. Sencadas, G. Botelho, S.A.C. Carabineiro, J.L.G. Ribelles, S. Lanceros-Méndez, Influence of oxygen plasma treatment parameters on poly(vinylidene fluoride) electrospun fiber mats wettability, Prog. Org. Coating 85 (2015) 151–158.

[2] V.F. Cardoso, D.M. Correia, C. Ribeiro, M.M. Fernandes, S. Lanceros-Méndez, Fluorinated polymers as smart materials for advanced biomedical applications, Polymers (2018) 10.

[3] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683–706.

[4] J.Y. Liu, Y. Yuan, X.M. Ban, Q. Zhang, L. Li, Controlled generation of poly(vinylidene fluoride)-metal nanocomposite thin films with high dielectric constant by Co-evaporation, Nanosci. Nanotechnol. Lett. 6 (2014) 537–540.

[5] C. Ribeiro, V. Sencadas, D.M. Correia, S. Lanceros-Méndez, Piezoelectric polymers as biomaterials for tissue engineering applications, Colloids Surfaces B Biointerfaces 136 (2015) 46–55.

[6] J.C. Dias, M.S. Martins, S. Ribeiro, M.M. Silva, J.M.S.S. Esperança, C. Ribeiro, G. Botelho, C.M. Costa, S. Lanceros-Mendez, Electromechanical actuators based on poly(vinylidene fluoride) with [N1 1 1 2(OH)][NTf2] and [C2mim] [C2SO4], J. Mater. Sci. 51 (2016) 9490–9503.

[7] C.M. Costa, H.M. Rodrigues, A. Gören, A.V. Machado, M.M. Silva, S. Lanceros-Méndez, Preparation of poly(vinylidene fluoride) lithium-ion battery separators and their compatibilization with ionic liquid – a green solvent approach, ChemistrySelect 2 (2017) 5394–5402.

[8] J. Nunes-Pereira, R. Lima, G. Choudhary, P.R. Sharma, S. Ferdov, G. Botelho, R.K. Sharma, S. Lanceros-Méndez, Highly efficient removal of fluoride from aqueous media through polymer composite membranes, Separ. Purif. Technol. 205 (2018) 1–10.

[9] Z. Liu, H. Wang, E. Wang, X. Zhang, R. Yuan, Y. Zhu, Superhydrophobic poly(vinylidene fluoride) membranes with controllable structure and tunable wettability prepared by one-step electrospinning, Polymer 82 (2016) 105–113.

[10] Y.L. Yu, H. Chen, Y. Liu, V.S.J. Craig, L.H. Li, Y. Chen, A. Tricoli, Porous carbon nanotube/polyvinylidene fluoride composite material: superhydrophobicity/superoleophilicity and tunability of electrical conductivity, Polymer 55 (2014) 5616–5622.

[11] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, J. Membr. Sci. 375 (2011) 1–27.

[12] C.M. Costa, M.M. Silva, S. Lanceros-Méndez, Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications, RSC Adv. 3 (2013) 11404–11417.

[13] G.D. Kang, Y.M. Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes - a review, J. Membr. Sci. 463 (2014) 145–165.

[14] M.G. Buonomenna, L.C. Lopez, P. Favia, R. d'Agostino, A. Gordano, E. Drioli, New PVDF membranes: the effect of plasma surface modification on retention in nanofiltration of aqueous solution containing organic compounds, Water Res. 41 (2007) 4309–4316.

[15] D. Hegemann, H. Brunner, C. Oehr, Plasma treatment of polymers for surface and adhesion improvement, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 208 (2003) 281–286.

[16] S. Yoshida, K. Hagiwara, T. Hasebe, A. Hotta, Surface modification of polymers by plasma treatments for the enhancement of biocompatibility and controlled drug release, Surf. Coating. Technol. 233 (2013) 99–107.

[17] C.M. Chan, T.M. Ko, H. Hiraoka, Polymer surface modification by plasmas and photons, Surf. Sci. Rep. 24 (1996) 1–54.

[18] A. Kaynak, T. Mehmood, X.J. Dai, K. Magniez, A. Kouzani, Study of radio frequency

[19] plasma treatment of PVDF film using Ar, O₂ and (Ar + O₂) gases for improved polypyrrole adhesion, Materials 6 (2013) 3482–3493.

[19] D. Mangindaan, I. Yared, H. Kurniawan, J.R. Sheu, M.J. Wang, Modulation of biocompatibility on poly(vinylidene fluoride) and polysulfone by oxygen plasma treatment and dopamine coating, J. Biomed. Mater. Res. 100 A (2012) 3177–3188.

[20] N. Vandencasteele, D. Merche, F. Reniers, XPS and contact angle study of N₂ and O₂ plasma-modified PTFE, PVDF and PVF surfaces, Surf. Interface Anal. 38 (2006) 526–530.

[21] Y.W. Park, N. Inagaki, Surface modification of poly(vinylidene fluoride) film by remote Ar, H₂, and O₂ plasmas, Polymer 44 (2003) 1569–1575.

[22] M.D. Duca, C.L. Plosceanu, T. Pop, Surface modifications of polyvinylidene fluoride (PVDF) under rf Ar plasma, Polym. Degrad. Stabil. 61 (1998) 65–72.

[23] T.H. Young, H.H. Chang, D.J. Lin, L.P. Cheng, Surface modification of microporous PVDF membranes for neuron culture, J. Membr. Sci. 350 (2010) 32–41.

[24] Y. Li, Y. Yin, K. Guo, X. Xue, Z. Zou, X. Li, T. He, H. Yang, Tuning pore structure of the poly(vinylidene difluoride hexafluoropropylene) membrane for improvement in rate performance of Li-oxygen battery, J. Power Sources 241 (2013) 288–294.

[25] C. Yao, X. Li, K.G. Neoh, Z. Shi, E.T. Kang, Antibacterial activities of surface modified electrospun poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) fibrous membranes, Appl. Surf. Sci. 255 (2009) 3854–3858.

[26] S.J. Kang, I. Bae, Y.J. Park, T.H. Park, J. Sung, S.C. Yoon, K.H. Kim, D.H. Choi, C. Park, Non-volatile ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) memory based on a single-crystalline tri-isopropylsilylethynyl pentacene field-effect transistor, Adv. Funct. Mater. 19 (2009) 1609–1616.

[27] C. Ribeiro, C.M. Costa, D.M. Correia, J. Nunes-Pereira, J. Oliveira, P. Martins, R. Gonçalves, V.F. Cardoso, S. Lanceros-Méndez, Electroactive poly(vinylidene fluoride)-based structures for advanced applications, Nat. Protoc. 13 (2018) 681.

[28] S.M. Pawde, K. Deshmukh, Surface characterization of air plasma treated poly vinylidene fluoride and poly methyl methacrylate films, Polym. Eng. Sci. 49 (2009) 808–818.

[29] L. Wu, J. Sun, F. Tong, Surface modification of a PVDF membrane by cross-linked collagen, RSC Adv. 4 (2014) 63989–63996.

[30] M.N. Sarip, R. Mohd Dahan, Y. Seong Ling, M. Wahid, M. Hafiz, A.N. Arshad, D. Kamarun, XPS study of plasma modified PVDF-TrFE films surface, Advanced Materials Research, Trans Tech Publ, 2016, pp. 12–15.

[31] A. Kaynak, T. Mehmood, X.J. Dai, K. Magniez, A. Kouzani, Study of radio frequency plasma treatment of PVDF film using Ar, O(2) and (Ar + O(2)) gases for improved polypyrrole adhesion, Materials 6 (2013) 3482–3493.

[32] D.M. Correia, C. Ribeiro, V. Sencadas, L. Vikingsson, M. Oliver Gasch, J.L. Gómez Ribelles, G. Botelho, S. Lanceros-Méndez, Strategies for the development of three dimensional scaffolds from piezoelectric poly(vinylidene fluoride), Mater. Des. 92 (2016) 674–681.

[33] J. Gomes, J.S. Nunes, V. Sencadas, S. Lanceros-Mendez, Influence of the β-phase content and degree of crystallinity on the piezo- and ferroelectric properties of poly (vinylidene fluoride), Smart Mater. Struct. 19 (2010) 065010.

[34] V. Sencadas, R. Gregorio, S. Lanceros-Méndez, α to β phase transformation and microstructural changes of PVDF films induced by uniaxial stretch, J. Macromol. Sci., Part B 48 (2009) 514–525.

[35] J. Nunes-Pereira, S. Ribeiro, C. Ribeiro, C.J. Gombek, F.M. Gama, A.C. Gomes, D.A. Patterson, S. Lanceros-Méndez, Poly(vinylidene fluoride) and copolymers as porous membranes for tissue engineering applications, Polym. Test. 44 (2015) 234–241.

[36] D.M. Correia, C. Ribeiro, G. Botelho, J. Borges, C. Lopes, F. Vaz, S.A.C. Carabineiro, A.V. Machado, S. Lanceros-Méndez, Superhydrophilic poly(l-lactic acid) electrospun membranes for biomedical applications obtained by argon and oxygen plasma treatment, Appl. Surf. Sci. 371 (2016) 74–82.

[37] C.M. Costa, A. California, V.F. Cardoso, V. Sencadas, L.C. Rodrigues, M.M. Silva, S. Lanceros-Méndez, Electroactive poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) microporous membranes for lithium-ion battery applications, Ferroelectrics 430 (2012) 103–107.

[38] A. Bayat, M. Ebrahimi, A.Z. Moshfegh, Correlation between surface roughness and hydrophobicity of GLAD RF sputtered PTFE/W/Glass nanorod thin films, Vacuum 101 (2014) 279–282.

[39] High resolution XPS of organic polymers: the scienta ESCA300 database (Beamson, G.; Briggs, D.), J. Chem. Educ. 70 (1993) A25.