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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 influences fiber average size (~400 ± 200 nm), morphology, electroactive β-phase content (~80–85%) or the degree of crystallinity (X_c of 42 ± 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.

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 has 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

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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 O_2 (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), O_2 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

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 and 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 Eq. (1):

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

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 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 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 (Fig. 1a). PVDF membrane porosity was estimated using the pycnometer method and an overall membrane porosity of 79 ± 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 Fig. 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.