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The Role of Electrospinning Parameters for Optimizing Poly-Vinylidene-Fluoride Nanofibers Piezoelectricity †

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Abstract: The main aim of this work is the design of a new piezoelectric nanostructured sensors, able to combine response to mechanical deformation with self-powering and collecting current, achieved by potential change induced by the mechanical deformation itself. One of the winning strategies, suitable to provide the enhancement of PVDF's piezoelectric features, was based onto the exploiting of nanoconfinement during the electrospinning nanofiber deposition. In the present work, we investigated piezoelectric properties of PVDF nanofibers can be influenced by electrospinning parameters, with a focus on applied electric field during and onto the final arrangement of nanofibers.

Keywords: electrospinning process; polyvinylidene fluoride nanofibers; piezoelectric properties

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1. Introduction

Several works in the literature in the last years demonstrated the strategic role of piezoelectricity in a wide range of applications, ranging from flexible pressure sensors [1] to energy harvesting [2]. In this scenario, flexible pressure sensors exploit the piezoelectrical principle, i.e., if mechanically deformed they are able to generate a potential difference, and vice versa, i.e., if electrically stimulated they are able to respond with a given mechanical deformation [3–7]. The great advantages of such sensors, therefore, are their inherent ability to combine response to mechanical deformation with self-powering and collecting current, achieved by potential change induced by the mechanical deformation itself [8,9]. For this kind of sensors, the piezoelectricity properties of sensible materials determine the sensitivity and response time of sensor itself. To this purpose, piezoelectricity is an intrinsic property of materials that are able to convert an electrical potential that they are subjected into a mechanical deformation [10]. The most popular piezoelectric materials belonged to the class of inorganic ceramic materials, such as lead zirconium titanate (PZT), barium titanate (BTO), characterizing by excellent piezoelectric properties combined with some impacting constraints, such as high production costs, mechanical fragility, chemical toxicity of some constituents' elements. With the main aim to overcome all these limitations, several works in the literature proposed Poly-vinylidene-fluoride (PVDF) as organic piezoelectric polymer [11,12]. PVDF is not only suitable to be applied as sensitive materials in flexible and wearable sensors, but it can be applied as most promising piezo-electric materials, thanks to its properties, such as flexibility, transparency, lightweight, good chemical and mechanical resistance, biocompatibility, high thermal stability, cheap, and high duration in body. PVDF exhibits five different polymorphs, defined as crystal phases and identified as α, β, γ, δ and ϵ. Several works in the literature attribute a direct correlation between piezoelectricity properties and the presence of polar phases such as β, γ and δ-phases, while α and ϵ-phases, commonly presented inside PVDF, result to be non-polar. Furthermore a PVDF must be arranged in a β-phase to show piezoelectric features, that employs the best piezoelectric property, contrary to the α-phase that is the commonest, the most stable crystal phase but it is not effective for piezoelectric properties. Commonly, several research works in the literature synthetize, starting from a commercial PVDF, a thin film, focusing their attention onto several artificial polarizations, post-process treatments, such as thermal annealing, suitable to affect the conversion of α-phase into β-phase with the main purpose to optimize the piezoelectric properties of PVDF-thin film [13–15]. Although all these methods showed their own advantages, leading thus to achieve ah high performing piezoelectric PVDF film, such processes also have important disadvantages including a complex synthesis of the piezoelectric material by implementing complex processes to ensure its piezoelectric property. One of the winning strategies, to overcome all above limitations and widely investigated in the literature, provided the enhancement of PVDF's piezoelectric features, exploiting the nanoconfinement during the electrospinning nanofiber deposition [16]. Electrospun nanofibers, indeed, received an increasing interest in the sensing field, leading thus to combine their intrinsic properties, such as high surface area to volume ratio, high mechanical properties and lightweight, with a versatile and simple manufacturing methods. All these considerations lead thus to demonstrate that PVDF nanofibers are good candidates for the realization of wearable and flexible pressure sensors exploiting piezoelectric effect. In the present work, we investigated the role of electrospinning parameters to tune the piezoelectric properties of PVDF nanofibers, (PVDF_NFs), with a focus onto applied electric field, defined, during the electrospinning process, as the ratio between the applied voltage and working distance. Applied electric fields were varied from 1.5 kV/cm to 3 kV/cm, obtained by maintaining a constant applied voltage equal to 26 kV and varying the working distance from 17 cm to 8.5 cm. We are able also to demonstrate that the PVDF-NFs distributions do not affect the instauration of β-phase inside the nanofibers. Finally, the ferroelectric hysteresis loop and displacement loop demonstrated that the presence of β-phase peaks was related to piezoelectric properties, leading thus to confirm the capability of electrospinning process to induce the formation of β-phase inside the nanofibers, without further prost-processes.

2. Materials and Methods

2.1. Synthesis of PVDF Nanofibers through Electrospinning Process

To demonstrate and confirm the correlation between the β-phase formation inside PVDF-NFs and the electrospinning parameters, we optimized the initial polymeric solution, containing 19 wt% of PVDF (Mw 534.000, Sigma-Aldrich) dissolved in a solvent-mixture of DMF and acetone (Sigma-Aldrich, volume ratio 1:1). The polymeric solution was properly loaded into a syringe and electrospinning equipment of MECC NANON 01 A was employed. In this works, the electrospinning parameters were selected to enhance solvents' evaporation, nanofibers' stretching and their alignment. A main focus was dedicated to applied-electric field, (i.e., the ratio between applied voltage and working distance), and the collector used during nanofibers depositions, (planar versus drum-rotating collector). For what concerning the applied-electric field, we defined three different PVDF-NFs samples, obtained by defining three different working distances and by applying the same applied voltage value, equal to 26 kV. We obtained 3 different nanofibers mat: (i) PVDF-NFs_1.5 obtained with an applied electric field equal to 1.5 kV cm^{-1}; (ii) PVDF-NF_2 reached when an electric field of 2 kV cm^{-1} was defined; (iii) PVDF-NFs_3 obtained with an electric field of 3 kV/cm^{-1}. With the main goal to verify how the nanofibers 'distribution can affect the formation of β-phased inside the nanofibers, two counter electrodes, planar and drum collectors, were used. We defined a rotation speed of drum collectors close to 900 rpm, to guarantee an aligned distribution of PVDF-NFs. All other electrospinning parameters processes were the same that were defined to obtain PVDF-NFs_2 with the planar counter electrode.

2.2. Morphological Characterization and Physico-Chemcial Characterizations

Field Emission Scanning Electron Microscopy (FESEM ZEISS SUPRA) was employed to verify the morphological properties of PVDF-NFs, leading thus to correlate them with different electric applied fields and with different nanofibers distributions, obtained by provided two collectors. With the main purpose to define the instauration of 5 crystals phases inside the PVDF-NFs, correlating the presence of β-phase with several parameters of electrospinning process, Spectroscopy Fourier-Transformed-Infrared-Spectroscopy (FTIR) was implemented. The FT-IR spectroscopy sample analysis was performed to identify all polar and non-polar phases inside nanostructured materials, defining wavenumbers' range from 400 cm^{-1} to 1500 cm^{-1}, [17]. To confirm the piezoelectric properties of final PVDF_NFs, ferroelectric hysteresis loop, obtained as graph polarization vs. voltage, and the displacement loop, represented in the trend polarization vs. displacement, loop was analyzed and reported. Piezo Evaluation System (PES, TF Analyzer 2000 HS, Aixacct) coupled to a single point laser vibrometer (Polytec OVF-505) were employed to determine ferroelectric polarization hysteresis loos and displacement measurements, using the piezo evaluation system to apply a voltage to the nanofiber mat. To perform this kind of piezoelectric characterization, for all PVDF-NFs, deposited on both planar and drum collectors, a sheet of polyimide-copper was used as substrate. Polyimide-copper was used to ensure a good electrical contact with PVDF-NFs and, at the same time, make it possible to have a system capable of transferring mechanical deformation without inducing nanofibers' rupture.

3. Results and Discussion

3.1. Morphological Properties

FESEM characterizations allowed highlighting the correlation between electric field applied, during the electrospinning process, and the PVDF-NFs features. Figure 1a reported the morphological properties of all nanofibers 'mats, PVDF-NFs_1.5, PVDF-NFs_2 and PVDF-NFs_3. All nanostructured samples were characterized by smooth nanofibers arranged in a random way into the mat, and it was possible to appreciate that diameter distribution of PVDF-NFs resulted to be strictly correlated with the applied electric field. The higher is the electric field applied, the higher is the diameter distribution of nanofibers, as depicted in Figure 1b.

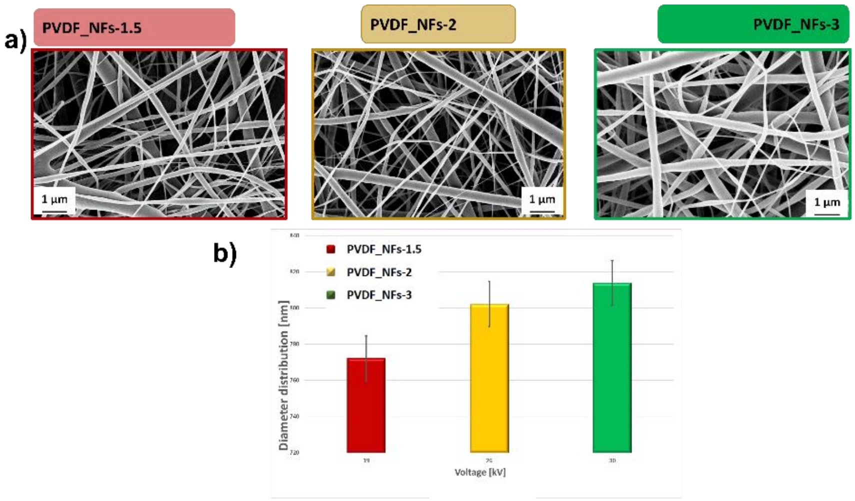

Figure 1. (**a**) morphological properties of all nanostructured materials obtained by increasing electric field applied PVDF-NFs_1.5 (red box); PVDF-NFs_2 (yellow box) and PVDF_NFs_3 (green box);

(**b**) reported the diameters' distribution of all PVDF-NFs strictly dependent with applied electric field, that increase as electric field augments.

As deeply investigated in several research works [18], Figure 2 allowed appreciating the aligned distribution of PVDF-NFs_2 obtained by implementing a drum collector during the electrospinning process. Indeed, it was possible to observe how the PVDF-NFs within the mats tend to distribute parallel to one another, differently from PVDF-NFs_2 obtained with planar counter electrode.

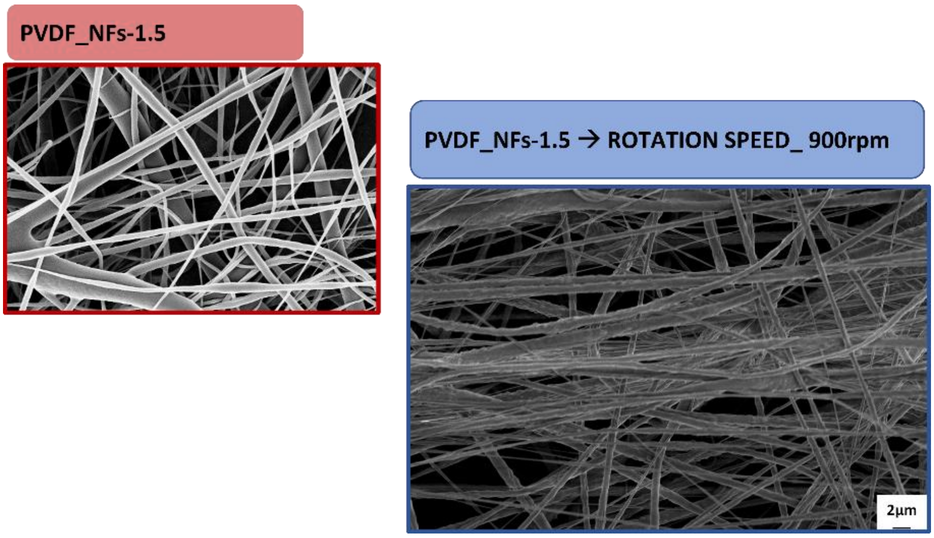

Figure 2. (**a**) morphological properties of aligned PVDF-NFs_1.5 obtained by providing a drum collector and defining its rotation speed equal to 900 rpm.

3.2. Piezoelectric Properties

Fourier Transformed infrared (IR) spectroscopy evidenced the presence of both β-phase and γ-phase fractions, which played a pivotal role to define r piezoelectric behaviour of PVDF-NFs. Figure 3 reports FTIR plots for each different sample and Table 1 summarizes the wavenumber of the peaks belonging polar β-phase and γ-phase. All samples show peaks at 532 cm^{-1} and 761 cm^{-1} belonging to the α-phase and larger peaks belonging to the β-phase at 510 cm^{-1} and 840 cm^{-1}. Peaks belonging to the β-phase at 445 cm^{-1}, 1274 cm^{-1} and 1430 cm^{-1} are present only in PVDF-NFs_1.5, processed at low electric-field, confirming that higher electric-field can negatively affect the instauration of the β-phase. From all the FTIR plots, the presence of peaks related to β and γ phases, was confirmed for each analyzed PVDF-NFs, confirming also the key role of electrospinning process to tune piezoelectric features of final nanostructured PVDF.

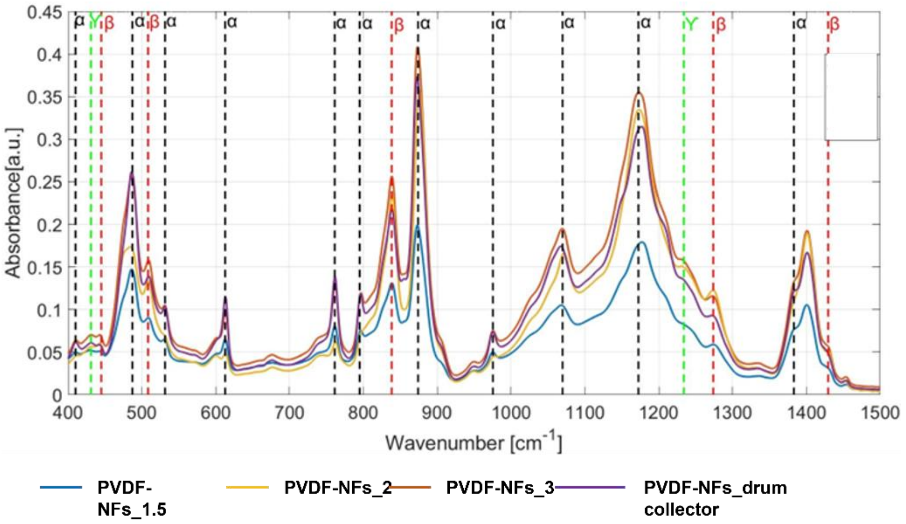

Figure 3. IR spectra of samples in planar (PVDF-NFs_1.5; PVDF-NFs_2; PVDF-NFs_3) and drum (PVDF-NFs_Drum collector) deposition configurations. The β-phase, γ-phase and non-polar α-phase are underlined in red, green and black, respectively.

Table 1. β and γ phases peaks position (wavenumber).

β-Peaks [cm^{-1}]	γ-Peaks [cm^{-1}]
445	431
510	1234
840	
1274	
1430	

Another important result is that the sample made of nanofibers collected in planar configuration (PVDF-NFs_1.5, blue line) showed no differences with respect to the spectrum obtained from for NFs deposited on drum (PVDF-NFs_Drum collector, pink line), confirming then that the stretching of nanofibers, induced by aligned deposition, do not affect the polarization phases distribution.

PVDF-NFs_1.5 was selected among the sample fabricated in planar configuration to analyze its piezoelectric response. Figure 4 represents a hysteretic behavior with a remanent polarization of about 0.02/cm^2 and a coercive voltage of about 100 V, giving evidence of the piezoelectric activity of the nanofibers. Together with the coercive voltage, the remanent polarization is an important parameter since it defines the residual amount of polarization into the material also when the electric field was removes. The black line represents hysteresis curves, which tends to the rectangular shape of ideal ferroelectric materials, but with a slight distortion of that trend, probably correlated to some defects inside the sample, which increase its electrical conductivity, inducing a worsening of its the ferroelectric properties.

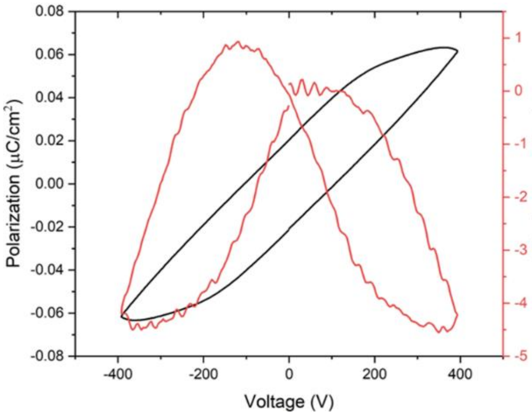

Figure 4. Displacement loop and ferroelectric hysteresis loop of sample PVDF-NFs_1.5.

To define the mechanical deformations induced by electric field applied onto PVDF-NFs, the displacement curve (red line) showed the common butterfly shape, leading thus to reach a larger displacement for lower values of the applied volatge for PVDF-NFs respect to the ones referred to piezoelectric PVDF film, deeply investigated in the literature [20,21]. This improvement can be addicted to the low diameter distribution characterizing PVDF-NFs_1.5. All obtained results demonstrated the direct correlation between the presence of β-phase peaks and the good and improved piezoelectric properties, characterizing final PVDF-NFs.

4. Conclusions

We confirmed the capability to tune the presence of polar β-phase, responsible for piezoelectric properties of PVDF-NFs, by varying the electrospinning process. In particular, we demonstrated the key role of applied field to modulate the formation of β-phase, leading thus to define that the lower applied electric field resulted to be effective for the improvement of β-phase, as confirmed by FTIR characterizations. In line with these results, moreover, we alcos confirmed the good piezoelectric properties for PVDF-NFs obtained by implementing an electric field of 1.5 kV/cm, defined as PVDF-NFs_1.5. FTIR-results confirmed no correlation among the piezoelectricity and nanofibers ‘distribution.

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