materials proceedings

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Proceeding Paper

Electrospun Nanofibers for an Optimized Fiber-Shape Wearable Sensors †

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† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net.

Abstract: This work discusses the design of highly stretchable piezoresistive flexible sensors obtained by electrospun-nanofibers collected on rotating flexible wires. The resulting nanostructured sensors have a fiber-shape due to the inner plastic core in intimate contact with the nanofibers forming the outer shell. The final fiber-shape, thus facilitating integration of the sensor in soft electronic platforms. Composite nanofibers, made of polyethylene oxide and multiwall carbon nanotubes were selected as the sensitive material, able to combine effective response to mechanical deformation to compatibility in contact with human body. Two flexible wire collectors were selected: a plastic wire and a plastic hollow wire. We demonstrate that the collectors induce a partially ordered distribution of NFs with a good percolation behavior. Piezoresistive characterization confirmed the increase of the nanofibers' electrical resistance with increasing of applied pressure. The dimensionless sensitivity $|\Delta R/R0|$ was calculated and plotted as a function of applied pressure demonstrating a good behavior of the new fiber-shape pressure sensors.

Keywords: Electrospinning; Nanofibers; Composite nanofibers; Piezoresitive sensors; flexible sensors

Citation: Massaglia, G.; Quaglio, M. Electrospun Nanofibers for an Optimized Fiber-Shape Wearable Sensors. *Mater. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx
Published: 5 May 2023

1. Introduction

The development and design of wearable electronic systems required to satisfy several requirements, such as real-time detection and capability to recognize different movements of human body. To this purpose, flexible and stretchable strain-pressure sensors attracted significant interest [1,2]. Performance of sensors is strictly correlated with materials selection, that must satisfy a complex set of requirements, as stretchability, biocompatibility, adaptability, and cheapness. Several works in the literature proposed sensors, characterized by good sensitivity and, at the same time, many limitations mainly addicted to low flexibility and mechanical properties, leading thus to the need to develop sensitive nanostructured materials, capable of overcoming all described limitations [3]. To satisfy all features, we propose electrospun-nanofibers as sensitive elements, since they, thanks to their intrinsic properties, allowed designing flexible sensors with increased electrical and mechanical performance [4–6]. We proposed composite polyethylene oxide/multiwall carbon nanotubes (PEO/MWCNTs) nanofibers as sensitive materials [2]. We investigated two different rotating-collectors to obtain fiber-shape nanomaterials, which were suitable to integrate as wearable sensors [7,8]. The first collector is a non-conductive-wire and the second one is an insulator hollow-wire, both made of highly deformable plastic materials. We demonstrate that both the collectors induce an ordered distribution of NFs with respect to randomly distributed nanofiber mats in planar configuration. At the same time, we found that fiber-shape sensor exhibits a percolation behavior in line with that of their planar counterparts [9]. For what concerned piezoresistive-performance, we demonstrated good electrical behaviour of nanofibers before and after applied-deformations, confirming their complete reliability and reuse as sensitive nanomaterials. Piezoresistive-responses confirmed an increase of nanofibers' resistance with the increasing of applied pressure. A dimensionless parameter $|\Delta R/R0|$ was calculated and plotted as a function of applied pressure to define sensitivity and resolution of sensors. All results highlighted good sensors' resolution and sensitivity achieved when ordered nanofibers were collected onto both wire substrate, thus being able to extend the deformation range to which the sensitive nanomaterial can be subjected. New flexible-pressure sensor is proposed as device direct integrable into textile.

2. Materials and Methods

2.1. Synthesis of PVDF Nanofibers through Electrospinning Process

A polymeric solution, suitable for electrospinning process, was prepared dissolving 5 wt% of PEO (Mw = 600 kDa, purchased from Sigma Aldrich) in a water-based solution containing polystyrene sulfonate (PSS, purchased from Sigma Aldrich). PSS served as the dispersing agent of MWCNTs, improving their wettability in water. PSS was added with a weight ratio of 1:1 with respect to MWCNTs (from Nanocyl). The dispersion was then processed towards probe-type sonication. In order to analyze the percolation behavior, we analyzed and compared nanostructured fiber-shaped sensors made of nanofibers with different compositions, i.e., different MWCNTs concentration. The following values were selected: 1.5, 2.2, 2.5, 3.5 and 5 wt% with respect to PEO. As largely implemented in our works [5,6,9], all prepared polymeric solutions were loaded into a syringe and electrospinning process were provided (NANON 01A by MECC). In this work two rotating collectors were used, both made of PE: one was an insulating wire and the second one a hollow wire. Both of two insulating substrates were fixed to the rotating mandrel and an aluminum blade was used to help NFs accumulation on the insulating substrate [7]. A rotation speed of 100 rpm was selected.

2.2. Morphological Characterization and Physico-Chemcial Characterizations

Field Emission Scanning Electron Microscopy (FESEM ZEISS SUPRA) was used to analyse the morphology of PEO/MWCNTs NFs based fiber-sensors. To perform the electrical characterizations, a multimeter of KEITHLEY 6430 was provided, able to polarize all samples by defining a voltage value of 1 V and to measure current as function of time.

Piezoresistive analysis were performed applying controlled stress with a laboratory dynamometer by Instron. Fiber-shape sensors were placed on a PDMS (by Sylgard) slab and deformed while recording I(V) curves at each applied load. The resistance was then indirectly calculated by the Ohm's law to obtain $|\Delta R/R0|$. Plotting $|\Delta R/R0|$ versus the applied load allows to evaluate the sensitivity of the sensors.

3. Results and Discussion

3.1. Morphology

Fiber-shape sensors collected on flexible wires had an average diameter of about 450 μm and a thickness of the NFs outer layer of about 3 μm. Figure 1a shows the optical image of a fiber-shape sensor. Details on the NFs morphology have been gained by FESEM, that allowed appreciating the preferential orientation induced to the composite PEO/MWCNTs composite NFS, as depicted in Figure 1b.

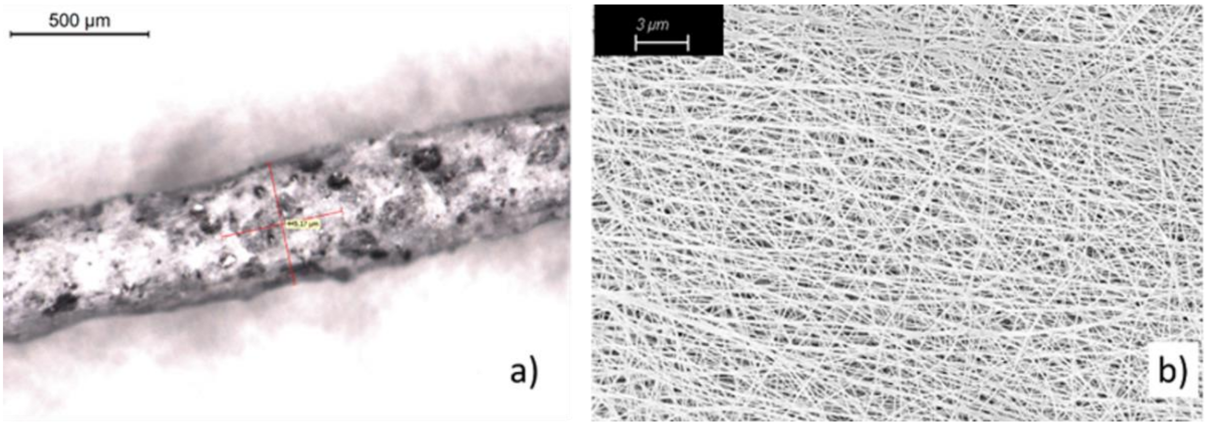

Figure 1. (**a**) analysis of fiber-shape sensor collected on the insulating wire; (**b**) FESEM analysis shows the ordered distribution induced in nanofibers.

3.2. Electrical Characterization

To obtain the percolation curve, we defined electrical conductivity values, reached for each MWCNT amount as summarized in Table 1.

Table 1. Electrical conductivity values corresponding to different MWCNTs' content.

wt%	σ_{final} **[S/cm]**
0	5.62×10^{-7}
1.5	5.45×10^{-7}
2.2	1.65×10^{-6}
2.5	5.62×10^{-4}
3.5	1.59×10^{-2}
5	5.96×10^{-2}

Starting from the definition of experimental values of the electrical conductivity (Table 1), we determined the percolation curve of composite nanomaterials, defining also the trend of electrical conductivity as a function of the MWCNT weight percentages (Figure 2). As deeply described by Massaglia et al. [10], we implemented the percolation model to fit all data, leading thus to describe the electrical conductivity above and below the percolation threshold, defined as amount of conductive filler in correspondence to which the electrical conductivity increases exponentially.

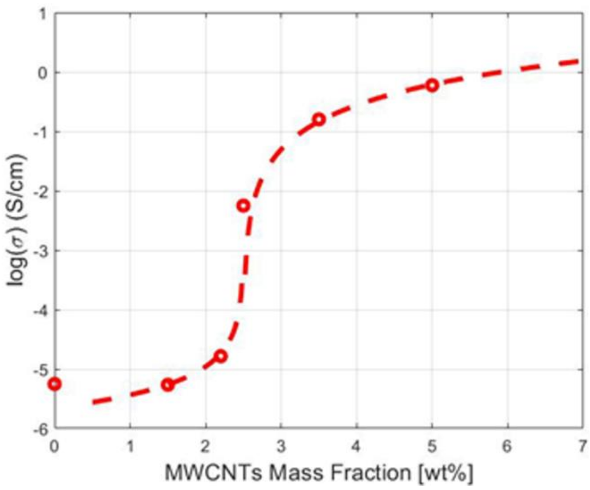

Figure 2. Percolation curve of electrical conductivity expressed as a function of MWCNTs content.

It was possible to define percolation threshold value of 2.5 wt% MWCNTs. Higher is the MWCNTs amount into nanofibers, higher is the electrical properties of composite nanofibers' mats. This behavior was addicted to the formation of a conductive network inside the nanostructured polymer matrix, leading thus to obtain an exponential increment of electrical conductivity for all weight percentage of MWCNTs above the percolation one. After the percolation threshold, the curve tends to a stable value of electrical conductivity when the amount of MWNCTs was around 6 wt%. This obtained value of the percolation threshold results to be higher than that reported in the literature for planar shape nanofibers sensors [10]. These latter results can be explained by considering that, in this work, we implemented two collectors, wire and tubular configurations, that induced a more aligned nanofibers assembly (Figure 1b) in comparison with the random distribution obtained when planar counter electrode was used.

3.3. Piezoresistive Characterization

The sensitivity of a piezoresistive pressure sensor can be defined as:

$$S = \frac{\Delta R / R_0}{P}$$

where $\Delta R/R_0$ is the variation of electrical resistance induced by an applied pressure P. with the main purpose to define the sensitivity of fiber-shaped nanostructured sensors, we selected composite nanofibers, contained 3 wt% of MWCNTs, and compared two different shapes of collectors, wire and tubular counter electrode. I/V curves were obtained by polarizing all samples toward the application of range voltage between −10 V and +10 V and to evaluate electrical resistance variations, we different applied pressure values depending on whether the collector was employed: in the interval from 0 kPa to 60 kPa for tubular collector and between 0 and 0.9 MPa, for the wire substrate. We can indirectly define the electrical resistance for each pressure values and subsequently calculated the variation of resistance induced by pressure respect to that to that inherent resistance of non-deformed material $\Delta R/R_0$. Figure 3 reported the two plots of $\Delta R/R_0$ values for each applied pressure sensors, leading thus to appreciate how the trends are comparable with what is reported in the literature [11,12]

It is possible to observe that the trend is similar for the two fiber-shape types of sensors, with a first region of the curve showing a constant value of the sensitivity followed by a second region with an increase in the electrical resistance variation for high applied pressure. This trend achieved at high pressure can be explained as a result of the destruction of existing percolation channels, which consequently leads to a change in the electron path and thus to an increase in electrical resistance [12]. It is interesting to observe that the fiber shape sensor collected on wires have a significantly higher sensitivity that those collected on hollow wires. This can be explained considering that the effect of pressure in changing the resistivity is enhanced for fiber-shape sensors having a wire core.

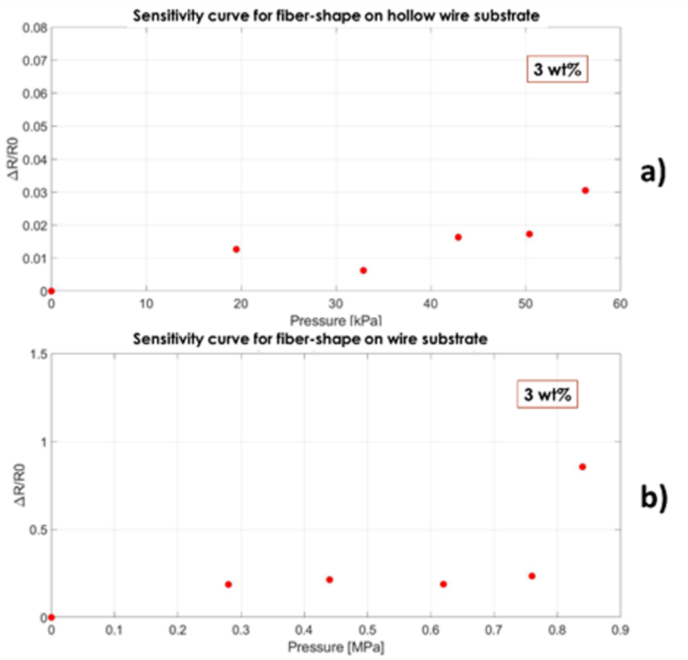

Figure 3. Piezoelectric characterization of fiber-shape sensors with a 3 wt% of MWCNTS collected on the flexible insulating hollow wire in (**a**) and on the flexible insulating wire in (**b**).

4. Conclusions

The main result obtained from the analysis of the electrospun CNT/polymer composite nanofibers demonstrated and confirmed their percolative behavior, even though the aligned arrangements of nanofibers, induced by wire and tubular shaped substrates, resulted to be largely different from the random distribution, achieved with planar collector. In addition, by conducting a preliminary analysis of two series of samples with conductive fill weight percentages close to the percolation threshold, a piezoresistive response was observed, in accordance with the literature, which allowed the best wire collectors to be identified to improve sensitivity.

Author Contributions: All Authors contribute to conceptualization and organization of the work. G.M.: Main focus on experiments and data analysis. M.Q.: Scientific responsible for the project; C.F.P.: Fund raising. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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