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# Electrospun PEO/PEDOT:PSS Nanofibers for Wearable Physiological Flex Sensors †

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**Abstract:** Flexible sensors are fundamental devices for human body monitoring in application areas ranging from health care to soft robotics. During the last decade the possibility to couple sensing of mechanical strain and physiological parameters have attracted ever increasing interest to design novel, robust and low-cost wearable sensing units. Stretchable and pH sensitive piezoresistive strain sensors made by blending intrinsically conductive polymers and polymeric electrolyte can serve this purpose. In this work, we specifically investigate a Crosslinked Nanofibers (NFs) Flex Sensor able to detect mechanical flexion and pH change. The optimized sensitive element of the NFs Flex Sensor is based on crosslinked electrospun NFs mats made of a blend of (polyethylene oxide) PEO as the polymeric electrolyte, and poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) as the intrinsically conductive polymer. The NFs Flex Sensor has been obtained by directly collecting the nanomaterial on a flexible and biocompatible polydimethylsiloxane (PDMS) slab and thermally treating it to promote electrical conductivity of the PEO/PEDOT:PSS NFs. The thermal treatment was optimized to crosslink PEO and PSS while preserving the nanostructuration, to optimize the mechanical coupling with PDMS substrate and to improve water resistance. In this work, we demonstrate excellent mechanical sensing of the NFs Flex Sensor coupled to electrochemical pH detection. Change of pH was detected by Electrochemical Impedance Spectroscopy (EIS), obtaining a linear dependence of the capacitance with the pH value. The piezo-resistive characterization of the Crosslinked NFs Flex Sensors demonstrated the ability of nanomaterials to recover their initial configuration after release of the mechanical strain in both compression and traction mode. The Gauge Factors (GFs) values were 45.84 in traction and 208.55 in compression mode, reflecting the extraordinary piezoresistive behavior of our nanostructured PEO/PEDOT:PSS NFs.

**Keywords:** blend polymeric solution; piezoresistivity; flex mechanical sensor; pH sensor; wearable physiological flex sensors

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## 1. Introduction

Flexible and wearable devices able to sense bending are more and more developed for application like smart clothing, rehabilitation, prosthetic limbs, sport and research.[1–3] Usually, flex sensors are composed of a flexible substrate (PDMS, textile, Kapton) and a sensitive element that can be made of nanomaterials, intrinsically conductive polymers, conductive inks or optical fiber. [4–8] Moreover, devices able to give information not only on the mechanical strain but also on the physiological parameters are attracting interest to extend the application field to health monitoring devices, designing novel, robust and low-cost wearable sensing units [9–12]. The combination of sweat-pH and joint bending information obtained by stretchable and pH-sensitive piezoresistive flex sensors are part of these multisensing devices. Sweat pH is a very important physiological parameter

for these fields of application since it is directly related to the health state of the body (cystic fibrosis, dehydration, diabetes, cancer, etc.) and to the physical activity.[13–15] However, two-sensing units on one single device often requires long and complicated fabrication process-flows, unless if the same sensitive material is used for the two units. ICPs have a tremendous potential for application in flexible wearable sensing [16] and among them, poly(3,4-ethylenedioxythiophene) (PEDOT), doped with poly(styrene sulfonate) (PEDOT:PSS) is the most widely used due to its high stability, high electrical conductivity and excellent processability [17,18]. Further improvement of ICPs is possible by shaping them in nanostructures [19], such as electrospun nanofibers [20]. The inherent high porosity and high surface area to volume ratio of nanofibers can be exploited at their best to enhance the ICPs behavior. Moreover, the piezoresistive behaviour of PEDOT:PSS is already known in literature [4,21,22]and in this work, we show, for the first time in literature, that blended with polyethylene oxide (PEO), as polymer electrolyte and in nanofiber form, the same material can be also sensitive to pH. The presented device is made of two sensitive units integrated on the same substrate in order to couple the detection of mechanical flexion and pH change in sweat at body joint. For the first time, these two sensitive units are composed of the same material, i. e. NF, simplifying a lot the process flow for the whole platform. Electrochemical Impedance Spectroscopy (EIS) is used to monitor pH variation, showing an excellent linear dependence of the capacitance with the pH value, both in acid and basic environments. The Crosslinked NFs pH-Flex Sensors demonstrate optimal mechanical behaviour in both compression and traction mode. The extraordinary elastic behaviour of the PDMS slab ensures optimal transfer of the mechanical deformation from the joint to the sensing nanofibers. This excellent behaviour is directly reflected in the large values of the Gauge Factors (GFs) which are 45.84 and 208.55 in traction and compression mode, respectively.

## 2. Materials and Methods

### 2.1. Materials and Process of Fabrication

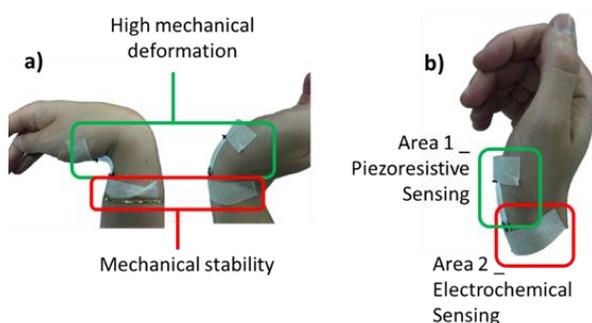
A volume of 5 mL of PEDOT:PSS aqueous dispersion (PH1000, Heraeus Clevios™) was added to a deionized water-based solution with 5 wt% of PEO (600 kDa, Sigma-Aldrich) and the resulting polymeric solution was aged overnight under stirring at room temperature. Nanofibers were obtained by electrospinning (NANON 01A, MECC Ltd.), applying a voltage of 15 kV with a working distance of 15 cm for 15 min, at a flow rate of 0.1 mL h<sup>-1</sup>. As electrospun nanofibers were thermally treated up to 120 °C (VST furnace, Carbolite) in N<sub>2</sub> atmosphere to obtain Crosslinked NFs. Nanofiber mats were directly deposited on a flexible substrate made of PDMS (10:1 ratio, Silgard 184). Flexible conductive electrodes for electric and piezoelectric characterization were fabricated using a paste made of PDMS and MWCNTs (2 wt%). A commercial electrochemical 3-electrodes component (DropSens, Metrohm) was integrated into the PDMS slab. Its counter and reference electrodes were uncovered of NFs thanks to laser ablation (Laser Marking System Slider, 10.6 μm, 30W).

### 2.2. Characterization

Morphology of NFs was analysed by Field Emission Scanning Electron Microscopies (FESEM, Zeiss MERLIN). A Keysight B2912A source measure unit was used to perform I-V measurements. PalmSens4 was used to perform electrochemical characterizations.

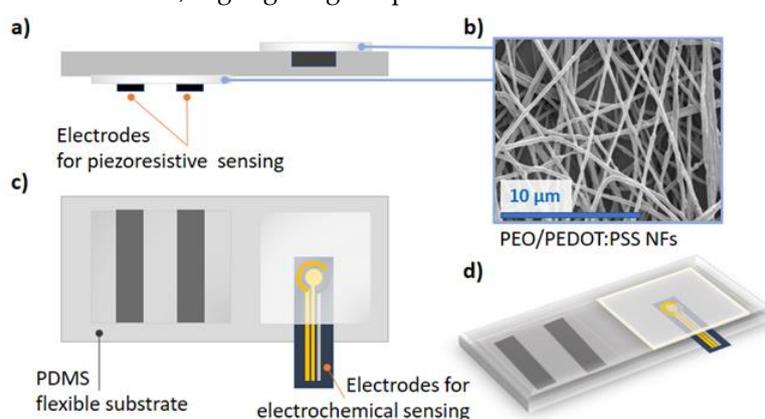
## 3. Results and Discussion

In this work, the application of PEO/PEDOT:PSS Crosslinked Nanofibers (NFs) as common sensitive element for flex sensing coupled with pH sensing in human body joint monitoring was investigated. The great novelty of this device is based on the use of the same sensitive material for both the sensing units, allowing to significantly simplify the whole process flow to fabricate the final platform. This result is possible since PEO/PEDOT:PSS Crosslinked NFs are able to transduce both the two signals by exploiting their different properties. The working conditions of the piezoresistive and the pH sensors being very different, it was essential to determine the zones of the joint in which each should be placed.



**Figure 1.** Application scheme of the the Crosslinked NFs pH-Flex Sensors, with highlight of (a) the two mechanical deformation zones and (b) the disposition of the sensors based on these zones.

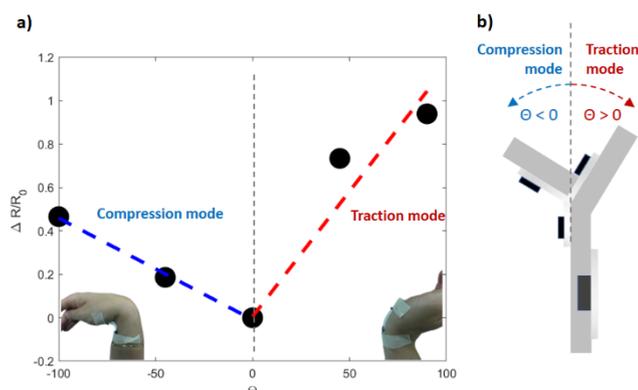
The flex sensor, designed to sense the deformation of the joint, should be applied where this deformation is the biggest and isolated from the skin. On the contrary, the pH sensor, monitoring the acidity/basicity of the sweat, should be disposed in direct contact with the skin, in a zone where the mechanical deformation is the lowest to not disturb the electrochemical signal. Figure 1 depicts the determination of these mechanical deformation zones in the wrist (a)) and the choices made for the disposition of the piezoresistive and electrochemical sensors (b)). Based on this considerations, Figure 2 shows the design of the Crosslinked NFs pH-Flex and in particular, Figure 2a) evidences the NFs disposition for direct contact with the skin (top) in opposition to the willing to isolate them from it (down). The device is composed of a PDMS flexible substrate in which a commercial electrochemical 3-electrode component is inserted. The PEO/PEDOT:PSS nanofibers are directly deposited on the substrate through electrospinning and thanks to laser ablation, the counter and reference electrode are free of nanofiber coerture. Through optimized thermal treatment, the crosslinking of PEO and PSS was performed, leading to higher electrical conductivity, greater mechanical coupling with PDMS substrate and improved water resistance.[4,23,24] Figure 2b) shows the morphology of the NFs mat after thermal treatment, highlighting the preservation of the nanostructuration.



**Figure 2.** Design of the bisensing device. (a) cross view, (b) FESEM of the PEO/PEDOT:PSS Crosslinked Nanofibers, (c) top view of the device and (d) 3D view.

The piezoresistive behavior of the flex sensor was investigated through current-voltage characterization submitting the samples to bending deformations. Figure 3 reports the variation in resistance ( $\Delta R/R_0$ ) with the bending angle (a)) and how this angle was determined (b)).  $R_0$  represents the situation in which the sensor is not deformed. Two linear behaviors were observed, in compression mode as well as in traction mode, demonstrating a good response of the PEO/PEDOT:PSS NFs and an optimal adhesion to the substrate. The Gauge Factors (GFs) obtained thanks to the model of Saggio [25] amounted at 45.84 in traction mode and 208.55 in compression mode. The two very high values highlight how, for the piezoresistive behavior, the nanostructuration

of the material improves the sensitivity of the sensor in comparison with the works published in literature, as shown in Table 1. [21,22,26–28]

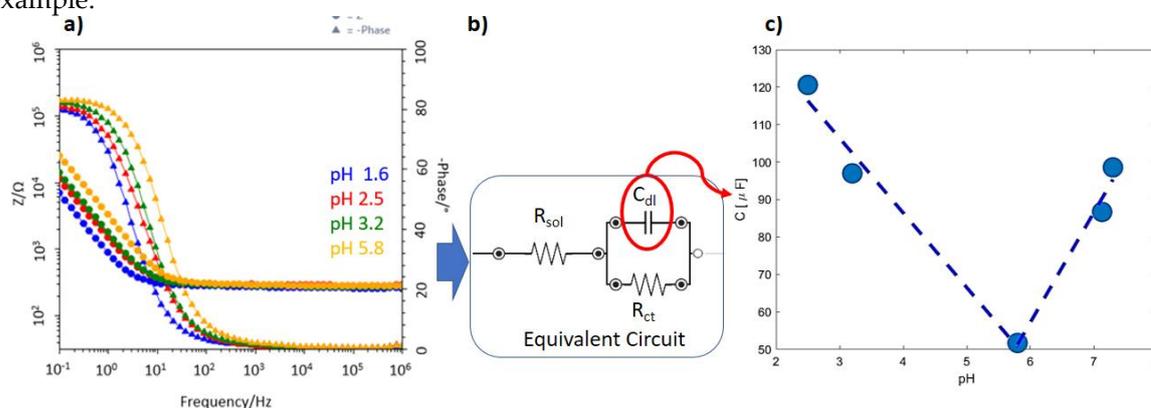


**Figure 3.** (a) Resistance variation when bending the sample; (b) model describing the bending and the determination of the compression/traction mode.

**Table 1.** Material, bending range and Gauge Factor of works already published about the use of PEDOT:PSS as main piezoresistive component for strain and flex sensors.

Material	Bending range	GF	Ref.
PEDOT:PSS/PI	0-60°	17.8 ± 4	21
PEDOT:PSS/PI	-	0.83	22
PEDOT:PSS/PET	0-20 mm bending radius	5.2	26
CNTs–PEDOT:PSS/PU	-	8.7–62.3	27
AgNWs–PEDOT:PSS/PU	-	1.07–12.4	28

The pH unit is an electrochemical one, and it is conceived to be placed in direct contact with the skin, while the piezoresistive mechanical unit is placed on the opposite side and in a position that maximizes flexion of the sensitive material. pH sensing was analyzed through Electrochemical Impedance Spectroscopy (examples for the acid pH showed on Figure 4a)) and thanks to the Equivalent Circuit (Figure 4b)), the capacitance value of the interface could be plotted in function of the pH value (Figure 4c)). Never before, a device made of the same sensing material was proposed in literature for bending deformation and pH sensing. Moreover, the two sensing units showed high sensitivity and of relevant information in the context of multisensing for physical activity monitoring, for example.



**Figure 4.** (a) EIS curves obtained with the sensor at 4 pH values as example; (b) Equivalent Circuit used to obtain electrochemical parameters (c) Capacitance variation of the sensor with pH values.

#### 4. Conclusions

We developed a Crosslinked NFs pH-Flex Sensors platform able to monitor the deformation of a human body joint as well as the pH of the skin. The common sensitive element of the sensors leads

to a simplified process flow reduced at two steps: the electrospinning of the sensitive material on the PDMS slab support and the optimized thermal treatment offering a higher electrical conductivity, a greater mechanical coupling with PDMS substrate and an improved water resistance. The piezoresistive part of the platform showed very good sensing performance, with Gauge Factors amounting to 45.84 in traction and 208.55 in compression mode. pH sensor exhibited two linear behaviors and two zones could be determined: the one in which all is good and the one in which the alert signal is given and more analysis are required. Thanks to the design of the device, the two signals can be monitored contemporaneously, offering an innovative, simple and convenient bi-sensing platform for, as example, physical activity monitoring.

**Author Contributions:** E.V., G.M. and M.Q. conceived the work and analyzed the results. E.V. worked on the material and sensor developing and characterization. C.F.P. and M.Q. organized the activity. E.V. and M.Q. contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript.

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