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Core-shell piezoelectric nanofibers for multifunctional composite materials

D. Fabiani[1,3], A. Zucchelli[2,3], T. M. Brugo[2,3], G. Selleri[1], F. Grolli[1], M. Speranza[1],
[1]*DEI-LIMES –University of Bologna, Bologna, Italy*
[2]*DIN-University of Bologna, Bologna, Italy*
[3]*CIRI MAM-University of Bologna, Bologna, Italy*

***Abstract*- This paper deals with the realization of core-shell piezoelectric nanofibers for the production of a multifunctional composite material. The nanofibers are integrated in a hosting material, such as epoxy resin or PDMS (silicon rubber). The aim of this work is to realize a material that is able to recognize a mechanical impact thanks to the specific disposition of the piezoelectric nanofibers.**

I. INTRODUCTION

Piezoelectric effect is used for several applications, such as the realization of energy harvesting or electromechanical sensing devices. In particular, they are considerably interesting for the production of electronic sensors that are able to detect mechanical impacts or structural vibrations [1].
Among all the piezoelectric materials, it is possible to classify them in ceramic and polymeric ones. The ceramic materials, such as PZT (lead zirconate titanate), are characterized by a higher piezoelectric response if compared to the piezoelectric polymers, and they are preferable for energy harvesting applications. On the other hand, the piezoelectric polymers are promising materials for sensing applications, due to their flexibility and thin film shape, even if they present a lower piezoelectric coefficient. In particular, Poly(vinylidene fluoride) (PVdF) and its copolymer PVdF-TrFE are promising materials thanks to its strong dipole moment.
A further aspect of interest regarding the piezoelectric polymer such as PVdF is the possibility to produce a thin nanofibrous layer, having high porosity rate (up to 80%). This nanofibrous mat can be immersed in a hosting material, ensuring an intimate contact that avoids mechanical delaminations.
The electrospinning process is considered to be a functional technique for the production of nanofibrous polymeric layers, e.g. PVdF based polymers [2].
Once the nanoporous layer is realized, it can penetrate the hosting material and by covering the two opposite surfaces of the layer with electrodes, it is possible to extract a piezoelectric signal as a mechanical stress is applied. If the electrodes and the hosting material (e.g. silicon rubber) of this device exhibit flexibility, the whole device would be suitable for rough and not flat surfaces. That flexibility represents an important feature for wearable and biomedical applications.
At the same time there are some specific applications, e.g. in the biomedical field, where a metallic electrode is not desirable since a free insulating surface area is required.

This work focuses on the production of this kind of sensors and their characterization. With the coaxial electrospinning technique it's possible to obtain core shell nanofibers, where the core is a conductive polymer (PEDOT:PSS) and the shell is the piezoelectric polymer (PVdF-TrFE) [3]. The shell is then covered with a metal coating for the realization of the external electrode, thus realizing a coaxial nano-piezoelectric device. As a mechanical impact is applied, a piezoelectric signal is generated and collected by two electrodes that can be placed on the edges of the sensor, leaving in this way a free surface area. By displacing those coaxial nanofibers in an appropriate arrangement and integrating them in a polymeric matrix [4], it's possible to realize a multifunctional material that is able to detect the exact position of a mechanical stress applied on the surface.
In this work, a deep study on the coaxial electrospinning technique, the optimization of the piezoelectric response and the geometrical disposition of the coaxial nanofibers is carried out.

II. MATERIAL AND METHODS

All the steps for the realization of the multifunctional composite material are described in this paper. First, the optimal setup for a high quality coaxial electrospinning is explored; secondly, the conditions for a better piezoelectric response are investigated and, lastly, the process for the geometrical disposition and integration of the nanofibers in the polymeric matrix is described.

Coaxial electrospinning
PVdF-TrFE Solvene (75/25 mol%, M_w=410 kDa) kindly provided by Solvay Specialty Polymers (Bollate, Italy), is used as piezoelectric material for the shell part of the fiber. The shell polymeric solution is prepared by dissolving 24% wt of PVdF-TrFE (available as polymeric powder) in dimethyl-formamide (DMF) (21% wt) and methyl ethyl ketone (MEK) (55% wt).

The core of the nanofiber is made of a conductive polymer, so PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) is chosen [3]. It is commercially available in water at a concentration of 5%wt. Since PEDOT:PSS cannot be electrospun directly, a polymeric solution has to be created by adding PVP (polyvinylpyrrolidone) as a carrying polymer. PVP in a concentration of 4% wt is first dissolved in DMF (60% wt), then PEDOT:PSS (36% wt) is added.
Such a composition of the shell and core polymeric solutions is the result of deep investigations on the stability of the electrospinning process and the quality of the coaxial nanofibers produced. In particular, a key parameter in order to maximize the quality of the nanofiber is the viscosity of the two solutions and how they interact together. If the viscosity of the solutions stays in a specific range of values, the nanofibers will present a high quality morphology. The polymeric solutions used in this work are the ones that allow the fibers to have an optimal coaxial shape along all their length.
The electrospinning apparatus used to manufacture the coaxial nanofibers is a Spinbow Lab Unit (Spinbow S.r.l., Italy) equipped with coaxial needle. Its working principle is shown in Figure 1.

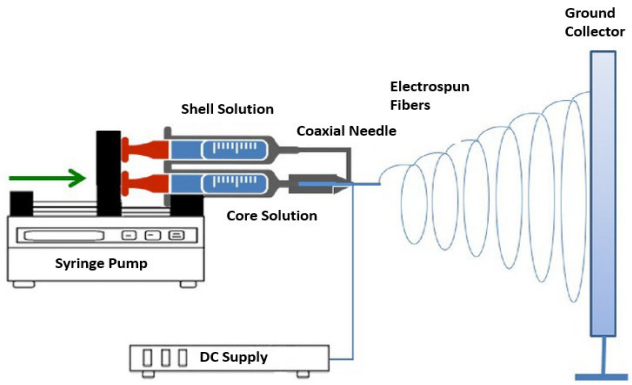

Figure 1 Schematic view of a electrospinning unit

The polymeric nanofibers are produced starting from a solution to be placed in an electric field. The drop coming out from the high voltage needle is stretched until the electrostatic force overcomes the surface tension; then the nanofiber is deposited on the ground collector.
The morphology of the produced core shell nanofibers has been observed by analyzing the images acquired with SEM and TEM microscopes. The SEM images have been acquired by looking at the cross section of the nanofiber layer (Figure 2a). The cross section has been obtained operating a fragile breaking in nitrogen. Then, the core of the nanofibers has been dissolved in water, where PEDOT:PSS is soluble in. By observing the TEM images it's possible to evaluate the morphology of the fiber along its length, as shown in Figure 2b. Figure 2a show a large number of hollow fiber in a cross section at 10000X, and Figure 2b evidences the good core shell structure of the fiber, whose total diameter is around 1μm.

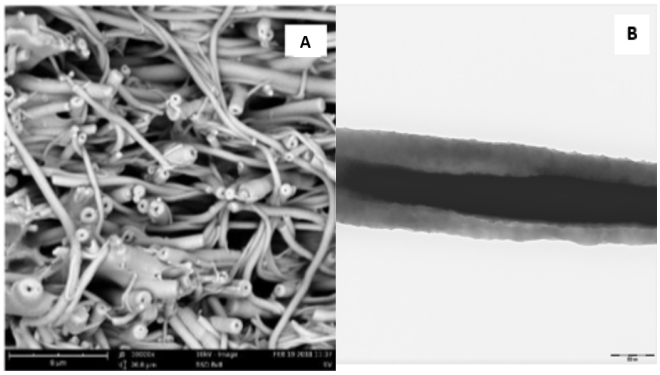

Figure 2 Cross section of the core-shell nanofibers layer in a SEM image (A) and TEM image of a single coaxial nanofiber (B)

Piezoelectric response
For the purpose of this work, the nanofibers have to be collected in the ground collector in an aligned configuration. The ground plane collector is so substituted with two cylindric electrodes connected to the ground and oriented in parallel. In this way, during the electrospinning process the nanofibers will deposit aligned perpendicularly to the electrode direction. Another technique to obtain a high alignment grade is to use a high-speed rotating drum as ground collector (up to 2500 rpm) that mechanically stretches and aligns the fibers as they reach it.
Once collected, the fibers are finally metallized in order to create the outer electrode on the surface of the shell, as described in Figure 3. On the other hand, the electrical signal of the core is gathered by a conductive material to be applied on the cross section of the fibers, e.g. silver paint.

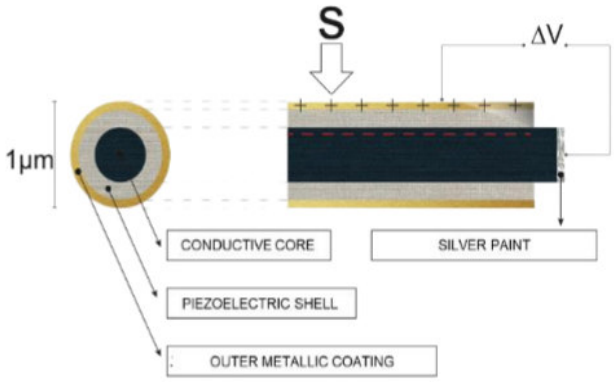

Figure 3 Schematic view of the core-shell nanofiber

Integration in a polymeric matrix
The aim of this work is to realize a multifunctional composite material, where the way the nanofibers are arranged is a key aspect for its functionality. In particular, the nanofibers are aligned in order to create a matrix shape, as represented in Figure 5. The two continuous electrodes are required to extract

the shell electric signal, as in the opposite edges each small electrode is connected to the core of distinct bundle of nanofibers.

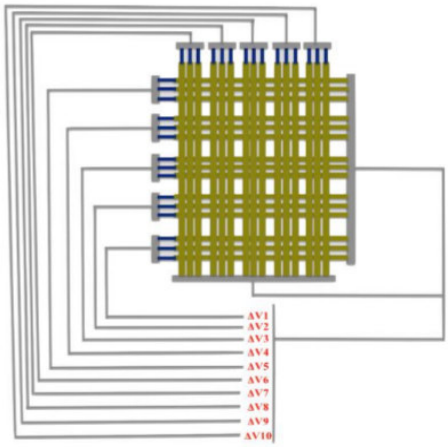

Figure 5 Sketch of the matrix disposition of the nanofibers

As a mechanical force is applied on a specific part of the nanofibers grid, the higher electric output will be gathered by the electrodes, on the edge of the fibers, corresponding to the point where the stress is applied. Therefore, by comparing the electric outputs of the electrodes, this sensor is able to provide the exact position of the force.

An important aspect to be underlined is that this nanofibers grid can be immerged in a hosting material without any delamination risk. It can be hosted in a hard matrix, e.g. epoxy resin, or in a soft and flexible one, e.g. silicon rubber, taking advantage of the nanofiber flexibility.
The material used in this work is PDMS (Polydimethylsiloxane) and the fibers results perfectly integrated as they penetrate it [5].
A further study has been conducted in order to determine a suitable material for the electrodes. A fine Carbon Black powder has been dissolved in PDMS, in order to make it conductive. A concentration of 10%wt of CB nanoparticles is first dissolved in isopropyl alcohol, then PDMS is added (90%wt) (Figure 6). As isopropyl alcohol evaporates, the fillers are integrated in the sensor. The material presents a good conductivity and a perfect adhesion with the PDMS substrate [5,6].

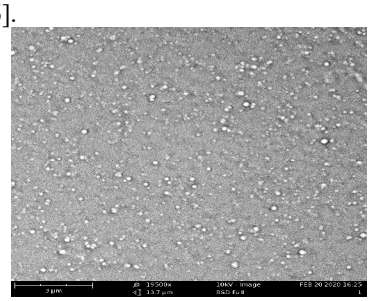

Figure 6 Carbon Black nanoparticles in a PDMS matrix

III. Experimental Results

The electrical response of composite material has been evaluated by testing it with mechanical impacts.
First, a close correlation between the piezoelectric response and the alignment grade has been found out, as described next. Different nanofibers layers were produced, changing the alignment grade of the fibers. By increasing the speed of the ground rotating drum, the alignment grade of the fibers increases and so also the electrical response to a mechanical impact (Figure 4).

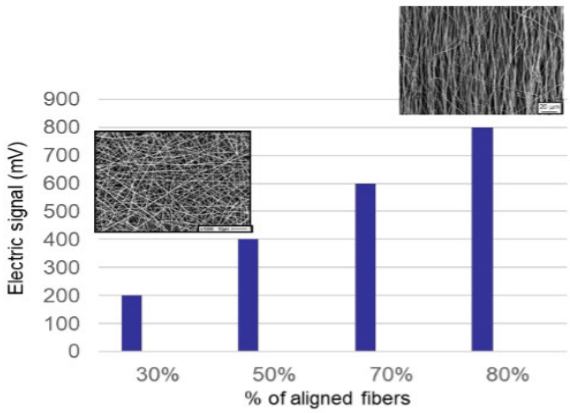

Figure 4 Electric response as a function of the alignment grade of the fibers

As the alignment grade is improved, after the fragile fracture in nitrogen, in the cross section of the nanofibrous layer there would be a larger amount of cores facing the collecting electrode (e.g. silver paint or CB in PDMS); hence the electrical response is enhanced [4].

Secondly, the response of every single electrode of the composite material has been analyzed.
An example of electric signal obtained from a group of mechanically stressed fibers is reported in Figure 7.

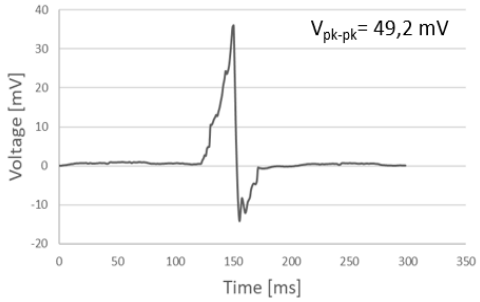

Figure 7a Electric response to mechanical impact of 20 N

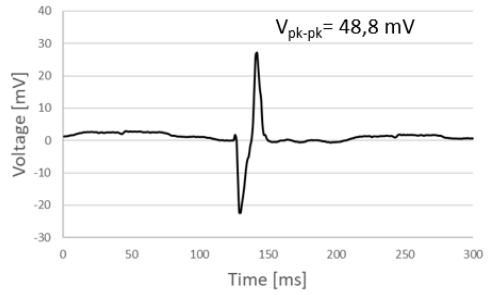

Figure 7b Electric response to mechanical impact of 20 N with reversed polarity

The obtained waveforms shows the typical response of a piezoelectric material. In Figure 7a, the first peak corresponds to the material compression and the second one, with opposite polarity, is associated to the material relaxation. By reversing the electrodes of the acquisition electrical circuit (Figure 7b), the signal polarity is reversed as well, confirming the piezoelectric nature of the electrical output. The peak-to-peak value of the output voltage is comparable for every electrode of the composite material, certifying the homogenous distribution of the fiber.
Moreover, the electric response of the sensor has been analyzed by connecting at the same time all the electrodes. In Figure 8 the electric signals extracted from two different regions of the composite material are graphed: the blue line is the output voltage in the area of the mechanical stress, while the red one is the signal measured in a region far from that area.

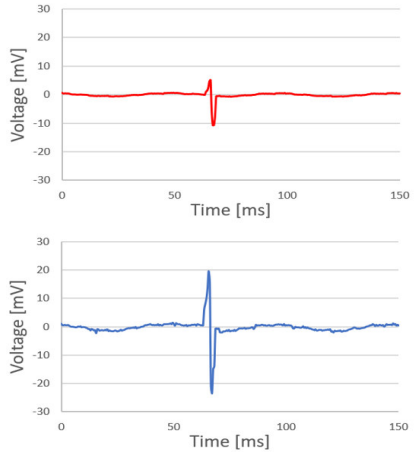

Figure 8 Electric signal from two different electrodes

The amplitude of the blue signal is much higher than the red one, confirming that the higher electric signal is the one collected where the mechanical stress happens.

IV. Conclusions

Coaxial nanofibers have been produced via electrospinning technique in order to integrate them in a hosting matrix, e.g. PDMS or epoxy resin, realizing a multifunctional composite material. Thanks to an appropriate electrospinning process is possible to align those fibers in the desired disposition so to create a smart material able to detect the exact position of a mechanical stress that is applied on its surface.
The nanofibers, once they are immersed in the material, prevent also any risk of delamination under mechanical stress.
If compared with the stiff nanofiber-based sensors, the coaxial nanofibers present the possibility to constrain the electrodes just on the edges of the sensor, leaving a free surface area. This feature makes this device feasible for specific applications in the biomedical/wearable field.

V. Aknowledgments

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VI. References

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