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Develompment of flexible sensors based on piezoelectric nanofibers

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***Abstract*- This paper deals with the production of nanofibrous piezoelectric sensors for flexible applications. The nanofibers produced via electrospinning are integrated a soft hosting material (epoxy resin and polyurethane rubber) and the electrodes are manufactured by using conductive carbon powder. The process described in this work leads to the realization of a piezoelectric sensor suitable for flexible applications without any delamination risks or mechanical failures that could occur by using traditional piezoelectric films and metallic electrodes. The piezoelectric response results to be comparable with traditional piezoelectric devices.**

Keywords—Electrospinning, piezoelectric nanofibers, flexible sensors, self-sensing materials, flexible electrodes.

I. Introduction

Piezoelectric materials are used in several applications, in particular in the mechanical sensing or energy harvesting fields, because they are able to convert mechanical energy into an electric voltage. Accordingly with their conversion efficiency, they are thought to be appropriate for different purposes. For example, ceramic piezoelectric materials present high piezoelectric response and they are commonly used for energy harvesting applications. On the other hand, piezoelectric polymers (i.e. PVdF and its copolymers) are often preferable for mechanical sensing applications thanks to their possibility to be produced in thin film shape and their flexibility, even if they present a lower piezoelectric coefficient.

Despite this, when the polymeric film is used in a composite material, a risk of mechanical delamination could be high. In order to prevent it, piezoelectric polymers present the possibility to be produced in a nanofiber shape via electrospinning technique [1]. In this way, the nanofibrous layer can be immerged in a hosting material, such as epoxy resin or rubber, preventing the delamination risk thanks to the intimate contact between the nanofibers and the hosting matrix. Moreover, this aspect leads to the production of a self-sensing material that is able to detect any mechanical stress applied on it [2]. The piezoelectric properties of the polymeric nanofibers can be enhanced through a polarization process, where appropriate electrodes are necessary to extract the electric signal [3]. Typically, metallic layers or conductive thin films are used as electrodes. In these cases, again, the delamination risk could occur for high mechanical impacts, particularly in cases of flexible devices.

In this paper a peculiar kind of signal collection system is explored, by dispersing conductive carbon nanopowder in thin layers that are made of the same material where the nanofibers are hosted in [4], [5]. In this way, it is possible to create thin conductive layers working as electrodes without creating any discontinuity in the composite material which could eventually lead to mechanical failure. This kind of self-sensing materials can be used as flexible sensors for artificial skin or health monitoring system for structural applications.

II. Materials and Methods

The experimental steps to produce flexible piezoelectric nanofibrous sensors are described in the following. A schematic overview of the whole process is depicted in Fig. 1.

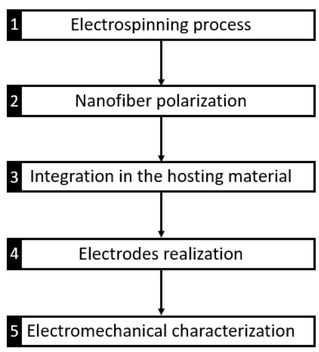

Fig. 1 Experimental steps for the sensor realization

First, the nanofibrous layer is produced via electrospinning process, by optimizing the polymeric solution and the setup parameters [1]. Once a layer of about 100 µm thickness is collected, the polarization process is carried out in order to achieve higher piezoelectric properties [3]. The layer is then ready to be immerged in the hosting material, that can be a tough material, such as epoxy resin, or a soft one, such as silicon or polyurethane [2]. In this work epoxy resin was used with the addition of a polyurethan rubber in order to make the device resistant to high mechanical stress by maintaining, at the same time, its flexibility. Finally, layers of epoxy resin doped with carbon nanopowder are realized to work as electrodes on the two opposite surfaces of the material [4].

A. *Electrospinning process*

Poly(vinylidene fluoride–trifluoroethylene) (PVdF-TrFE) Solvene (80/20 mol%, Mw=600 kDa), kindly provided by Solvay Specialty Polymers (Bollate, Italy), is used as piezoelectric material. The polymeric solution is prepared by dissolving 7% wt of PVdF-TrFE (available as polymeric powder) in dimethyl-formamide (DMF) (23% wt) and acetone (AC) (70% wt).

The electrospinning apparatus used to manufacture the nanofibers is a Spinbow Lab Unit (Spinbow S.r.l., Italy). Its working principle is shown in Fig. 2.

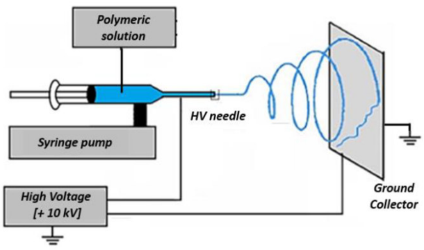

Fig. 2 Electrospinning apparatus

The high voltage (about 12 kV) is applied to the needle, and the plane collector is grounded. The distance between the needle and the ground collector is fixed to 15 cm.

As the polymeric solution is pumped in the syringe, the drop coming out from the needle is stretched by the electric field and the nanofibers are formed and collected to the ground. An overview of the nanofibrous layer realized is shown in Fig. 3, where the dimensions and the morphology of the nanofibers is observable. The nanofibrous layer presents a random distribution of the fibers and a high porosity grade (up to 80%) that allows a proper integration of the layer in the hosting material.

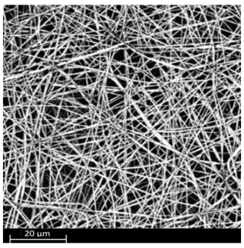

Fig. 3 SEM view of the nanofibrous layer

The electrospinning process takes place until the thickness of the nanofibrous layer reaches a homogeneous value of 100 µm all over its surface.

B. *Nanofibers polarization*

As the nanofibrous layer is realized, a polarization process is needed in order to achieve higher piezoelectric response. The aim of this process is to align all the dipoles of the polymeric chains in the direction of an external electric field that is applied perpendicularly across the layer, as shown in Fig. 4. During this process, the amount of the β phase of the polymeric chains, the one that is responsible of the piezoelectric properties, is expected to increase [3].

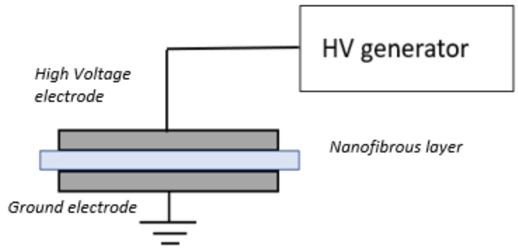

Fig. 4 Polarization setup

A DC generator is connected to the high voltage electrode placed on the layer, while the ground electrode is placed on the other surface. The temperature is increased up to the Curie temperature (130°C), in order to allow the dipoles to move, and the electric field is applied.

If the piezoelectric sample would consist of a thin film of PVDF-TrFE, the electric field would be applied totally on the film itself [3]. The main difference with that traditional polarization is the high porosity grade of the layer. The big amount of air cavities in the sample would lead to electric breakdowns across its thickness. So, an embedding medium able to fill the porosity during the polarization process and with good dielectric properties is needed.

A deep investigation on the appropriate embedding medium has been conducted, by considering its electrical properties, such as electric breakdown, permittivity and electric conductivity. An approximation of the distribution of the electric field in the two different materials can be obtained by modeling the problem as a multilayer system. In the first period, the electric field distribution is governed by the permittivity of the two materials, until a certain period of time which is governed by the time constant τ, calculated as follow:

$$\tau = \tau_{em} * \tau_p * \frac{\frac{1}{\varepsilon_p} + \frac{h}{\varepsilon_{em}}}{\frac{1}{\sigma_p} + \frac{h}{\sigma_{em}}} \quad (1)$$

$$\tau_{em} = \frac{\varepsilon_{em}}{\sigma_{em}} \qquad \tau_p = \frac{\varepsilon_p}{\sigma_p} \quad (2)$$

where ε_p and ε_{em} are the permittivity of the piezoelectric material and the embedding medium's one; σ_{em} and σ_{em} are the electric conductivity of the piezoelectric material and the embedding medium's one and h is the ratio of the thickness of the two materials.

After a period of time of about 5-10τ, the electric field that is applied for the polarization process will be distributed in the composite material according to the conductivity of each layer, i.e. higher on the material with lower electric conductivity.

By considering PVDF-TrFE dielectric properties (ε_p=10 and σ_p= 10^{-12} S/m) and using a vegetal oil as embedding medium (electric breakdown=70 kV/mm, σ_{em} = 9.8 *10^{-10} S/m and ε_{em}=3,2) , the τ is evaluated to be in the order of few seconds, accordig to the (1). The polarization process is then carried out for 5 minutes at 130°C with an applied electric field of 40 kV/mm.

Furthermore, the nanofiber layer has been cleaned from the oil by soaking it in a cyclohexane bath for 1 hour. The polarized nanofibrous layer is then ready to be immerged in the desired hosting material.

C. *Nanofibers integration*

Once the polarization process is completed and the oil is removed from the nanofibers, the original high porosity grade is restored and nanofibers can be integrated in a hosting material, such as epoxy resin or silicon rubber. The mechanical delamination risk, that could easily occur by using a polymeric film in a composite material, is avoided thanks to the intimate contact between every single nanofiber and the hosting matrix [1]. In this work, in order to develop flexible sensors that are also able to resist to high mechanical stress, a mixture of epoxy resin (70% wt) and polyurethane rubber (30% wt) has been used as hosting matrix.

The embedding process of the nanofiber into the epoxy resin and polyurethane rubber has been carried out by means of a slurry process, whose working principle is described in Fig. 5. As the nanofibers are totally embedded in the hosting matrix, the excess material is removed by a blade.

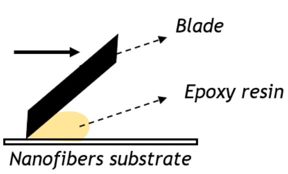

Fig. 5 Slurry integration process

In the end, the curing process of the substrate is carried out at 50°C for 2 hours.

In Fig. 6 a SEM view of the cross section of the nanofibrous layer shows the good integration of the nanofibers in the resin and the high efficiency of the slurry process in removing the resin in excess on the two surfaces layer.

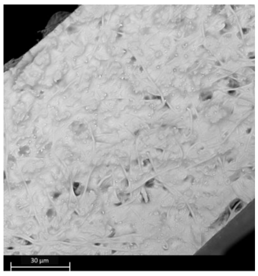

Fig. 6 SEM view of nanofibers integrated in epoxy resin and polyurethane rubber

D. *Electrode realization*

In order to develop the entire structure of the sensor, the electrodes are required to be placed on the two opposite surfaces of the layer.

Traditionally, a metallic film or a metallized layer are used for this purpose, but in the case of flexible devices or high mechanical loads some mechanical damages could occur.

A different kind of electrode has been developed in this work, by adding carbon conductive nanoparticles to the same material where the nanofibers were integrated in [4].

By mixing 10% wt to the epoxy resin and polyurethane rubber (70-30% wt), and by curing it at 50°C for 2 hours, a semiconductive and flexible material can be obtained to be deposited on the two opposite surfaces of the nanofibrous layer, working as electrodes for the signal collection [5]. The total thickness of the device results to be around 300 μm, as shown in the SEM cross section view in Fig. 7.

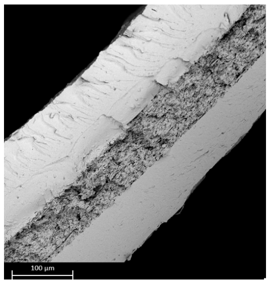

Fig. 7 SEM cross section view of the sensor

III. Experimental Results

The electromechanical response of the realized composite material is evaluated by testing it at different mechanical loads. The equivalent electrical circuit to be considered for such a piezoelectric sensor is sketched in Fig. 8.

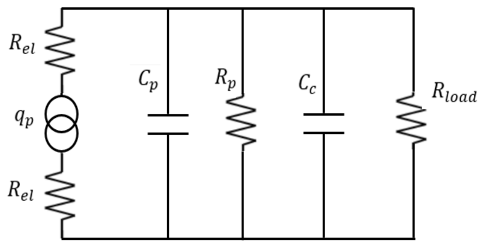

Fig. 8 Equivalent circuit of the realized piezoelectric sensor

The piezoelectric device is represented as a charge generator q_p, with an associated resistance R_p and capacity C_p. The capacitance C_c is associated to the cables of the systems and R_{el} represents the electric resistances referred to the semiconductive layers with carbon nanopowder working as electrodes. The measured R_{el} value is about 2 kΩ.

As a mechanical force is applied, an electric signal is measured across the load resistance R_{load}, that in this work is set at 1 GΩ. Typically, the piezoelectric materials are used to work for mechanical sensing under dynamic stresses, i.e. detection of mechanical impacts, vibration or shock measurements. By connecting in parallel to the piezoelectric generator a high impedance (R_{load}), the output voltage of the sensor is able to detect properly also quasi static loads, as shown in Fig. 9, where a sinusoidal force of 65 N is applied on its surface. The sinusoidal force is applied perpendicularly to the surface of the piezoelectric layer by a linear motor that stresses completely the area of the sensor (2 cm^2). A preload of 30 N is applied to avoid movements or triboelectric noises.

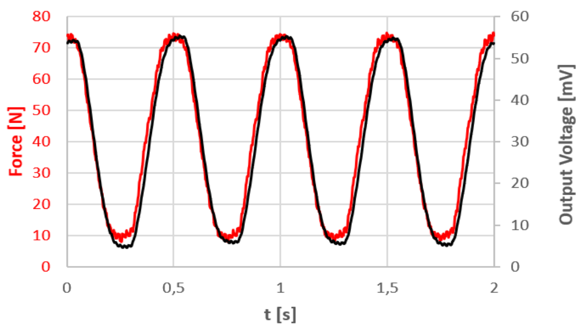

Fig. 9 Piezoelectric response in the time to a sinusoidal stress, f= 2Hz (V_{pk-pk}=48 mV, F_{pk-pk}= 65 N)

The piezoelectric response of the sensor is measurable without any amplification system in the circuit and the output voltage measured on R_{load} is directly acquired on the electrometer. The transducing coefficient, calculated as the ratio between the output voltage V_{pk-pk} and the applied force F_{pk-pk}, is about 0.8 mV/N.

A further analysis has been performed in order to evaluate the piezoelectric response over a wider range of mechanical stress. The frequency of the sinusoidal stress applied to the piezoelectric device is 2 Hz and the amplitude is varied from 20 N to 150 N, as shown in Figure 10.

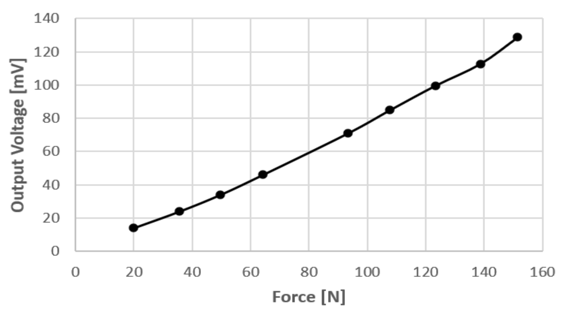

Fig. 10 Piezoelectric response at different sinusoidal stress, f=2 Hz.

The effectiveness of the sensor is verified as the transducing coefficient presents a stable value of about 0.8 mV/N all along the force range and the output voltage of the sensor increases linearly with the applied mechanical stress.

IV. Conclusion

The electrospinning process is a simple technique for the production of nanofibrous layers, that can be integrated in a soft hosting matrix, producing a self-sensing material without any delamination risk, that could occur in the case of piezoelectric polymeric film. In the case of flexible application, a further cause of mechanical damages could be the presence of thin metallic film as electrodes. Flexible and conductive electrodes were manufactured by adding conductive carbon nanopowders to the same material where the nanofibers were integrated (epoxy resin and polyurethane rubber), creating a compact system able to perform as flexible sensor without any mechanical delamination risk. Electromechanical tests were carried out to characterize the piezoelectric response of the sensor, which showed to be suitable also for measuring quasi static loads. Low frequencies test are performed to make the sensor suitable for biomedical applications, such as Gait cycle in prosthesis systems.

Further improvements to the structure of the described flexible piezoelectric sensor will be the integration of shield electrodes, with the purpose to reduce external electric noise which worsens signal-to-noise ratio, thus improving the sensitivity of the piezoelectric sensor.

V. Aknowledgments

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