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Piezoelectric nanofibers for multifunctional composite materials

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***Abstract*- This paper deals with the realization of 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) and their piezoelectric behavior is evaluated along the time. 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 material can be used for several application, in particular in the field of energy harvesting and mechanical sensing. Among all the piezoelectric materials, we can distinguish in ceramic piezoelectric materials, with high piezoelectric response, and polymeric ones which present lower piezoelectric characteristics. Despite this, the piezoelectric polymers are often preferable to the ceramic ones thanks to their flexibility that allows electroactive devices to be produced in the shape of thin films. Furthermore, the piezoelectric polymers can be used in the electrospinning process to create nanofibrous membranes that can be integrated in other hosting materials. For these purpose, Poly(vinylidene fluoride) (PVdF) and its co-polymers are considered the most promising candidates. If compared with the traditional piezoelectric films, the nanofibrous layers avoid the mechanical delaminations risk, thanks to the intimate contact between the nanofibers and the hosting matrix where they are immerged.

In this way, it is possible to create multifunctional materials [1], whose piezoelectric properties can be enhanced by applying a strong electric field at different stages of the manufacturing process, as will be described in the follow.

For this reason, trapped charge and electrostatic effects can be relevant during the electromechanical analysis. This paper aims at identifying the contribution of the electrostatic effect, in order to optimize the piezoelectric response.

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 electrospinning is explored; secondly, the integration process of the nanofibers in a hosting material (such as silicone rubber or epoxy resin) is described and, lastly, the poling processes are illustrated. The piezoelectric response is then analyzed over the time to observe when the contribution of the electrostatic charges injected during polarization disappears.

Electrospinning

Poly(vinylidene fluoride–trifluoroethylene) (PVdF-TrFE) Solvene (80/20 mol%, M_w=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). Such a composition is the result of a deep investigation on the stability of the electrospinning process and the analysis if the produced nanofibers. After a stirring of 24 hours at room temperature, the polymeric solution is ready to be used for the electrospinning process [2].

The electrospinning apparatus used to manufacture the nanofibers is a Spinbow Lab Unit (Spinbow S.r.l., Italy). Its working principle is shown in Figure 1 and Figure 2.

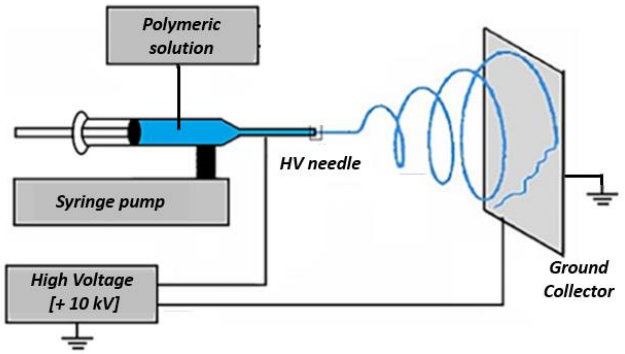

Fig. 1 Schematic view of the electrospinning unit. Positive HV needle and ground collector

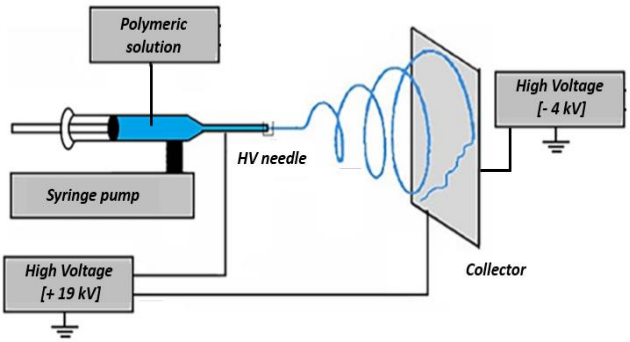

Fig. 2 Schematic view of a electrospinning unit. Positive HV needle and negative HV collector

The polymeric nanofibers are produced starting from a solution to be injected in a high electric field region. The drop coming out from the high voltage needle is stretched until the electrostatic force overcomes the surface tension, then the nanofibers deposit on the ground collector.
The quality of the nanofibers produced and the stability of the electrospinning process depend on various parameters, such as the viscosity of the polymeric solution, the distance between the high voltage needle and the ground collector, the high voltage value and the ambient conditions (e.g. air humidity and temperature).
In this work two different configurations of electrospinning setup will be considered. Firstly, the electrospinning setup depicted in Fig.1 was used, where the nanofibers are collected at the ground electrode and the high voltage applied to the needle is around 10 kV. In this configuration the electric field is relatively low in the air gap between needle and collector and the polymer dipoles could not be oriented effectively. Therefore, a post-polarization phase is needed in order to align the dipoles and detect a piezoelectric response, as will be illustrated in the next sections of this paper [3].

Secondly, an improved electrospinning configuration has been explored whose setup is represented in Fig.2.
In this case, the collector of the nanofibers is not connected to the ground as before, but to a negative potential. Moreover, the voltage at the needle is much higher than the previous case and the distance between the high voltage needle and the negative collector is reduced. Under such configuration the electric field is enhanced and the dipoles are able to be oriented during the electrospinning process thus the piezoelectric response can be observed even without a further polarization [4].
The specific parameters of the two electrospinning processes are summed up in Table I.

TABLE I
MAIN PARAMETER OF THE ELECTROSPINNING CONFIGURATIONS

	First configuration	Second configuration
Distance (HV needle – collector)	20 cm	8 cm
HV needle potential	+ 10 kV	+ 19 kV
Collector potential	Ground	-4 kV

For the purpose of this work, the nanofibers layers have been electrospun for 1 hour, in order to collect a homogeneous sample of 70 µm thickness and 5 cm diameter.
The nanofibrous layer and the SEM view of the nanofibers can be observed in Fig.3a and Fig.3b.

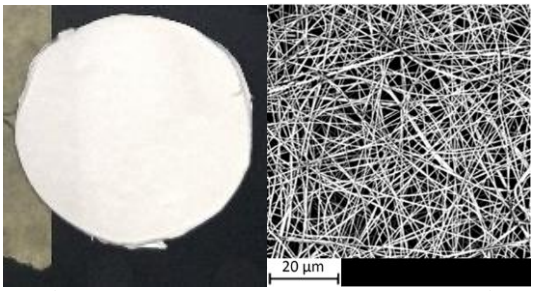

Fig. 3 Nanofiber layer, 5 cm diameter (a); SEM view of electrospun nanofibers (b).

Integration process
Once the nanofibers have been collected and the layers are produced, the integration of the samples in a hosting material is the following step. Indeed, once electrospun, the nanofibers are not handable, so a proper hosting matrix is important for the specific applications.
In order to guarantee the flexibility proper of PVDF-TrFE, a flexible silicone matrix has been chosen as hosting material. In particular, this material is polydimethylsiloxane (PDMS).
The integration process has been carried out by means of a spin coating process, whose working principle is described in Fig.4.

Fig. 4 Schematic principle of the spin coating process.

In particular, 0.5 g of PDMS has been deposited on the nanofibers substrate and the sample is fixed on the support. The angular speed in then increased up to 500 rpm for 5 minutes, reducing by 30% the amount the deposited PDMS. At the end of the process, a uniform thickness is obtained and a perfect PDMS penetration in the nanofibers layer has occurred.
In the end, the curing process of the PDMS is carried out at 80°C for 1 hour.
The final sample and an SEM view of the cross section is reported in Fig.5.

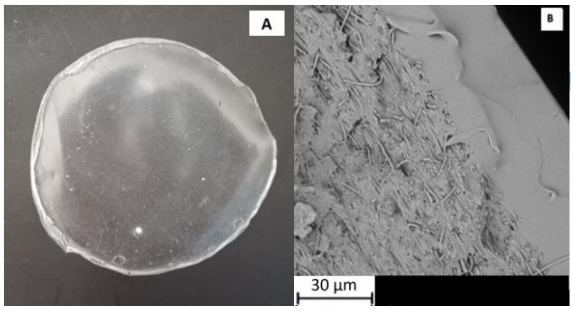

Fig. 5 Nanofiber integrated in PDMS, 5 cm diameter (a)SEM cross section view of the nanofibers integrated in PDMS (b).

The cross section of the sample has been obtained by applying a fragile cut in nitrogen. In this way, in Fig.5b it is possible to appreciate the intimate contact between the PDMS and the nanofibers, without any appreciable air cavity. The total absence of air inside the sample is an important feature to avoid the discharge phenomenon during the polarization process.
Moreover, the presence of the nanofibers inside the material makes it a multifunctional material that is able to detect the mechanical stress applied on it. It is noteworthy that, the good integration of the nanofibers in the hosting matrix avoid any delamination risk which can occur with traditional piezoelectric films even increasing mechanical properties of the hosting material.

Nanofibers polarization
To enhance the piezoelectric properties of the PVDF-TrFE nanofibers, a polarization process is needed. A DC electric field is applied across the two opposite surfaces of the samples and the temperature is increased above the Curie temperature. The Curie temperature of the PVDF-TrFE used for this work is 133°C, so the polarization process is conducted at 135°C. As the right temperature is reached, electric field is applied and is hold at the set value for 5 minutes. Then, the temperature is decreased up to the ambient temperature and the electric field is removed, in order to fix the dipoles of the material in the electric field direction. The polarization setup is represented in Fig.6.

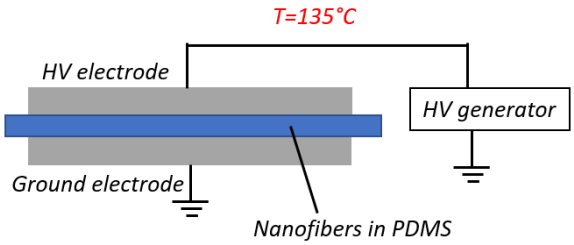

Fig. 6 Schematic representation of the polarization process

The polarization process has been carried out for all the samples where the nanofibers were electrospun with the first configuration (Fig.1), so with the grounded collector and lower electric fields. In particular, two samples have been polarized with an electric field value of 20 kV/mm (samples 1a and 1b) and two samples at 25 kV/mm (samples 2a and 2b). The samples with the nanofibers electrospun with the second configuration (samples 3a and 3b, Fig.2) have not been post-polarized, in order to analyze the piezoelectric response and the effectiveness of that process [4].
During the electrospinning and polarization process there is a high amount of trapped charges inside the produced samples, because of the high electric fields the polymer nanofibers are subjected. Electrostatic tests underline a contribution of about 4 $\mu C/m^2$. If an electromechanical test is carried out immediately after the realization of the samples, the piezoelectric response would be probably overwhelmed by the electric charges stored in the sample. These charges may decay over time depending on to the electrical conductivity of PVdF-TrFE – PDMS sample.
Discharge process
The aim of this stage is to figure out a way to analyze the pure piezoelectric response of the produced samples. For this purpose, after the polarization process both the surfaces of the samples (1a, 2a, 3a) have been short-circuited in oven at 60°C, in order to help the trapped charges to flow out of the samples. On the other hand, the other twin three samples (1b, 2b, 3b) have not been discharged, so the electrostatic contribution is expected to last for a longer period of time.
The electrostatic charges can be accumulated both in the PDMS matrix and the PVDF-TrFE nanofibers themselves. Trapped charges, however, are not supposed to stay for a long time in the PVDF-TrFE because of its relatively high conductivity, whereas it is reasonable to think that the charges trapped in PDMS matrix could take more time to flow out, due to its lower conductivity.
With the purpose to observe the effect of discharge process over the time, the samples have been periodically tested for a long period of time, trying to identify the transient period where the electrostatic contribution is relevant.
Table II sums up all the different samples of this work.

TABLE II
PRODUCTION STEPS OF EACH SAMPLE OF THIS WORK

	Electrospinning		Poling conditions		Discharge process	
#	1st conf.	2nd conf.	Time [min]	Electric field [kV/mm]	T [°C]	Ground connected
1a	X		5	20	60	Yes
1b	X		5	20	T_{amb}	No
2a	X		5	25	60	Yes
2b	X		5	25	T_{amb}	No
3a		X	No polarization		60	Yes
3b		X	No polarization		T_{amb}	No

The nanofibers of the samples 1a, 1b, 2a and 2b have been produced with the first configuration (Fig.1), so with relatively low electric fields (+10 kV/ground). The electrospinning process of the samples 3a and 3b is carried out with the high electric field (+19kV/-4kV) of the second configuration (Fig.2).

III. EXPERIMENTAL RESULTS

The electrical response of the multifunctional material has been evaluated by testing it with mechanical sinusoidal loads having with a max of 20 N.
The mechanical tests are weekly conducted.
The two opposite surfaces of the samples are connected to the electrometer in order to acquire the charge accumulated on the electrodes as the force is applied. Then, the d_{33} piezoelectric coefficient can be calculated as follow:

$$d_{33} = \frac{Q}{F} \qquad [\frac{pC}{N}]$$

where Q is the amount of charge accumulated on the two opposite surfaces of the material as a mechanical force F is applied on the vertical direction.
In Fig.7 and Fig.8 the d_{33} trend is graphed over a period of almost 50 days. The accuracy of the measurement is about 10%.

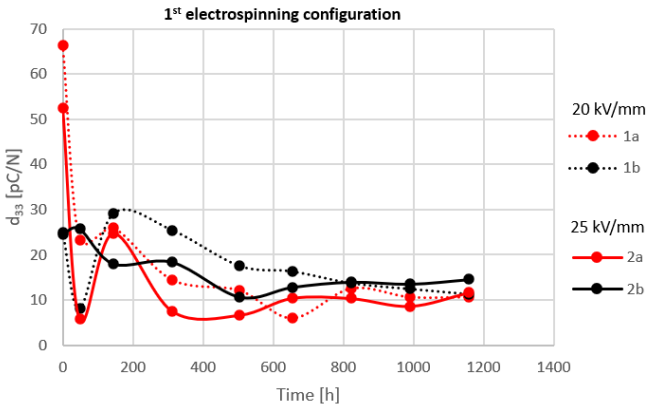

Fig. 7 D_{33} evaluation for the samples produced with the first electrospinning configuration; then polarized at 20 kV/mm and 25 kV/mm

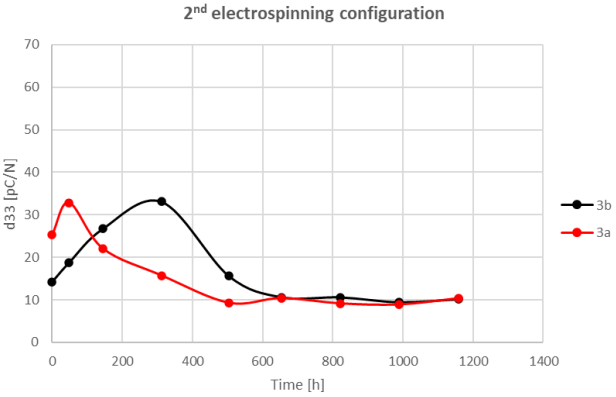

Fig. 8 D_{33} evaluation for the samples produced with the second electrospinning configuration; without a further polarization

As it is possible to observe from the plots in Fig 7, at the beginning of the discharge process all the d_{33} values are high if compared to the traditional piezoelectric polymers. As predicted, the measurements are affected by a considerable amount of electrostatic charges that influence and hide the real piezoelectric response. In the second electrospinning configuration (Fig. 8), the first peak is shifted further in the time, likely due to a charge migration from PVDF-TrFE to PDMS matrix.
After a period of time from 300 hours to 800 hours, we can observe that the samples that are not short-circuited at 60°C (1b, 2b and 3b) present a higher value if compared to the relative twin samples (1a, 2a and 3a). This behavior is probably due to the presence of residual trapped charges that still affect the real piezoelectric measurements.
In the last part of the time period considered, we can see that the d_{33} values reach almost constant values for several repeated measurements and all the trapped charges are dissipated.

A further aspect to be considered is the good piezoelectric response of the samples 3a and 3b. Even without any polarization process they present almost the same d_{33} of the other samples. This means that if the electric field used during the electrospinning process high enough, the dipoles are able to orient such in a way that a good piezoelectric response can be observed. This represent an important aspect for those applications where the curing temperature of the hosting material is lower than the Curie temperature of the nanofibers. In this case the fibers polarization would not be necessary and the second electrospinning configuration would represent a valid solution.

IV. Conclusions

The electrospinning process, starting from a polymeric solution, allows the production of nanofibers that can be integrated in a hosting material. In this work the piezoelectric nanofibers were immersed in a PDMS matrix in order to create a self-sensing material. After the electrospinning process and nanofiber polarization, the presence of trapped charges in the PVDF-TrFE nanofibers and in the PDMS matrix affect the real piezoelectric response.
A long time period study has been conducted in order to analyze the electromechanical response of the produced samples. A discharge process of 20 days is necessary to reach a stable d_{33} value that is not affected by the trapped charges. Moreover, it results convenient to use high temperature during that process because at ambient temperature the discharge takes place much slower.

V. Aknowledgments

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