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Corona poling for polarization of nanofibrous mats: advantages and open issues

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Abstract- **This paper deals with the polarization process of piezoelectric nanofibrous mats of PVdF-TrFE by using a corona discharge process. With respect to traditional contact poling this process reduces the electrical breakdown risk which could easily occur when a highly porous mat is placed between two solid electrodes. Different set-up configurations were investigated by varying the applied voltage and the distance between the needle and the sample. The polarized nanofibers show a piezoelectric strain coefficients (d_{33}) comparable with the values of a commercial stiff film.**

I. Introduction

The polarization of piezoelectric materials has attracted more and more interest in the last period thanks to the possibility of using these materials for sensing and energy harvesting applications. As a matter of fact, piezoelectric polymeric materials, such as polyvinylidenefluoride (PVdF) and its copolymers, e.g., polyvinylidenefluoride-trifluoroethylene (PVdF-TrFE), are suitable for these applications since mechanical deformations can be converted into electrical signals. To enhance the piezoelectric properties of these polymers a polarization process is needed, which aligns the electric dipoles of the crystalline structure. Traditional techniques are based on the use of a strong external DC electric field to induce a permanent polarization to the piezoelectric element [1].

The easy processability of the piezoelectric polymers allows to produce them in different shapes. In particular, via electrospinning, it is possible to manufacture highly porous nanofiber membranes, which can be embedded in hosting materials (i.e. silicon rubber or epoxy resin) in order to confer them self-sensing capabilities [2]. If compared with traditional stiff piezoelectric films, the use of nanofiber presents various advantages. In the case of a bulky PVDF-TrFE film integrated in composite materials, the interface between the epoxy matrix and the fluorinated polymer could lead to delamination, whereas the intimate contact between the nanofibers and the surroundings matrix prevents this risk and even increases mechanical strength of the host material [3]. Moreover, since the piezoelectricity is a superficial phenomenon, the nanofiber morphology maximizes the surface-to-volume ratio representing a promising way to achieve higher piezoelectric coefficient.

However, the traditional contact polarization can easily induce electrical breakdown due to the presence of air gaps between the nanofibers. Therefore, the polarization of nanofibers usually takes place in embedding materials, whose electrical properties strongly affect the success of the polarization process [4].

In this context, corona poling represents a reasonable method to avoid electrical breakdowns. In literature many works have been done on this field by directly exposing the piezo-polymeric sample to a corona wire discharge. Even if a high piezoelectric response can be obtained with this technique [5], it is difficult to achieve a uniform surface charge distribution. Therefore, an important improvement has been reached with the so called corona triode, by adding a metallic grid between the needle and the sample to ensure that the charged ions are evenly distributed and to control the potential at the surface of the samples [5]. For instance, Yadong et al. found that the piezoelectric coefficient d_{33} and the remnant polarization P_r of PVdF films treated by two polarized methods, the corona triode and a thermal contact poling in silicon oil, provided similar results, i.e. d_{33} of ~28 pC/N [6]. Moreover, an enhancement of the d_{33} values was observed by increasing the exposure time of the sample to the corona poling discharge (d_{33} of 25.3 ± 5 pC/N for 15 min and d_{33} of 34.3 ± 7.2 pC/N for 45 min) [7]. Another possible solution was presented by Li et al., where, rather than using a metal grid to uniform the ion distribution, the high voltage needle was moved thanks to a robotic arm which allowed to cover homogenously the area to be polarized [8].

With reference to the corona poling of PVdF-TrFE nanofibrous layer, Barique et al. took into account the surface electric charge density, that was found to be 2.7 times higher (0.64 nC/cm^2) than those of the as-spun nanofibers [9], while Ke et al. achieved a good sensitivity (110.37 pC/Pa) of the piezoeolectret-fiber pressure sensor [10].

In this work, polymeric nanofibers of PVdF-TrFE 80/20 are manufactured by means of an electrospinning machine and both the corona gridless and the corona triode techniques are explored to evaluated residual polarization and piezoelectric response.

II. Materials and Methods

The manufacturing process of PVdF-TrFE nanofibrous mats via electrospinning is firstly described in this section. Two type of corona poling process are investigated and the electromechanical characterization of the piezoelectric nanofibers is then presented.

A. Electrospinning process

The piezoelectric nanofibrous mat was produced via electrospinning starting from a polymeric solution, prepared by dissolving 7 wt% of copolymer PVdF-TrFE (80/20 mol%, Curie temperature, Tc = 130 °C, kindly provided by Solvay S.p.A. Milan) in dimethylformamide (DMF) (23 wt%) and acetone (AC) (70 wt%). The electrospinning process was carried out in a Spinbow Lab Unit (Spinbow S.r.l., Italy) by applying 12 kV at the needle and collecting the nanofibers in a low-speed rotating drum, placed at 15 cm from the needle.
The process was carried out for 6 hours in order to collect a 100 µm thick electrospun mat.

B. Gridless corona poling

The corona discharge can be classified as a glow discharge in which the ionize area is restricted to a region close to the high field electrode and the drift region extending towards the plane [5] (Fig. 1).

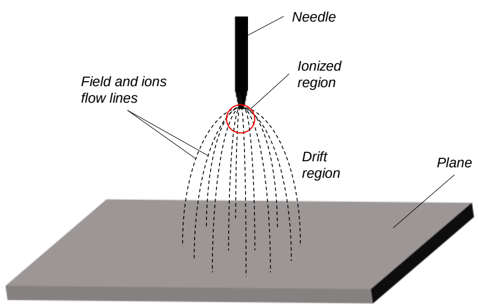

Fig. 1. Corona discharge in the point-to-plane geometry

As schematically represented in Fig.1, the electric field lines are distributed in a cone-like shape and affects a limited region of the ground plane. Therefore, with the aim to increase the polarization area for 3x3 cm^2 sample dimensions, a multiple-needle device was developed during the experimental campaign.
The gridless corona poling cell comprises a high voltage needle holder and a grounded aluminium base where the samples are placed. A PTFE structure was used to isolate the high voltage electrode and the ground plate. The needle holder was attached to a brass rod so that the distance between the tip and the sample can be regulated for obtaining different poling conditions.
The polarization process was carried out in an oven set at 130 °C, close to the Curie temperature of the PVdF-TrFE nanofibrous mat (133 °C). At this temperature, the coercive field is considerably decreased if compared with that at room temperature and the dipoles can be aligned also for low electric field values [2]. A DC voltage generator (Glassman High Voltage) was connected to the needle holder and the distance between the tips and the below plate, connected to the ground, was set at 35 mm as shown in Fig. 2. In addition, a foil of poly-coated paper was placed between the nanofiber mat and the ground plate so as to facilitate the removal of the sample.

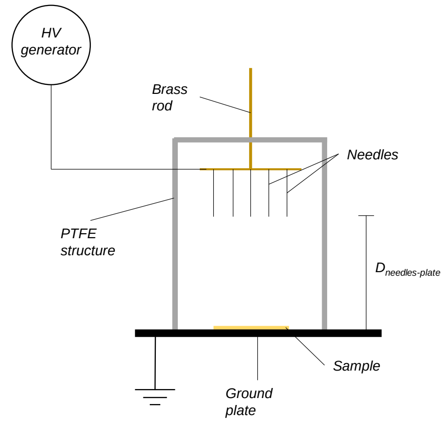

Fig. 2. Gridless corona poling set-up

As reported in Table I, four different tests were carried out varying the applied voltage between -16 kV to -22 kV. Higher HV values of the needles resulted in strong air discharges which could damage the sample. The polarization process took place at Curie temperature (130 °C) for 60 minutes. Afterwards, the high voltage was kept constant while the temperature was decreased down to room temperature and, once it was reached, the electric field was finally switched off.

TABLE I
GRIDLESS POLING CONDITION

Specimen	**$V_{Needles}$ (kV)**
1	-16
2	-18
3	-20
4	-22

C. Corona triode polarization

The experimental tests on the corona triode poling were performed with the same cell described in the previous section by adding a metallic grid between the high voltage needles and the ground base (Fig. 3). The interposed grid was connected to a DC high voltage generator (Spellman PCM3N120), with the aim to homogenize the ions distribution on the surface of the sample. The distance between the tip and the grid was set to 30 mm, while the distance between the grid and the sample was set to 5 mm so as to keep the total distance constant to 35 mm as for the gridless polarization process. The experimental campaign was completed by changing the applied voltage to the needle and to the grid as reported in Table II.
The voltage applied to the needles was set from -16 kV to -28 kV firstly with a grid voltage of -2 kV (from 1G to 7G sample) and later with -3 kV (from 8G to 14G sample).

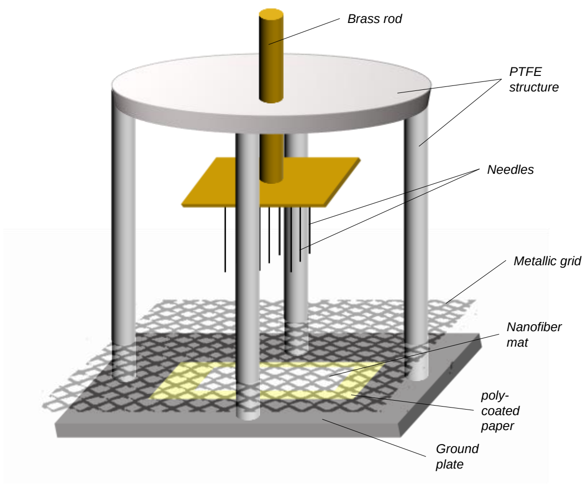

Fig. 3. Cell for corona triode poling

TABLE II
CORONA TRIODE POLING CONDITION

Specimen	**$V_{Needles}$ (kV)**	**V_{Grid} (kV)**
1G	-16	-2
2G	-18	-2
3G	-20	-2
4G	-22	-2
5G	-24	-2
6G	-26	-2
7G	-28	-2
8G	-16	-3
9G	-18	-3
10G	-20	-3
11G	-22	-3
12G	-24	-3
13G	-26	-3
14G	-28	-3

D. Electromechanical characterization

Before electromechanical tests were performed, the two opposite surfaces of the nanofibrous mats were connected to the ground for 24 hours at room temperature so as to remove any residual electrostatic charges that could have been generated during the electrospinning and poling procedures [11]. The piezoelectric strain coefficient d_{33} (pC/N) of all the polarized samples was measured by means of a piezometer (PiezoMeter PM300, Piezotest, Singapore, www.piezotest.com). The d_{33} is defined as the ratio of the collected charge generated on the two opposite surfaces of the nanofibrous mats (Q) and the applied force (F):

$$d_{33} = Q/F \qquad [pC/N] \qquad (1)$$

The sample was placed between two electrodes closed by a screw clamp and the d_{33} was measured by stressing the specimen with a compressive sinusoidal force of 0.25 N at 110 Hz. As the piezometer electrodes have a smaller surface than the nanofibrous layer, five different points of the same sample surface were measured for a complete investigation of the uniformity of the piezoelectric response.

III. RESULTS AND DISCUSSION

The electromechanical response of each polarized samples was evaluated by analyzing the piezoelectric strain coefficient d_{33}. The measured d_{33} values of the tested specimens for the gridless corona poling are reported in Fig. 4.

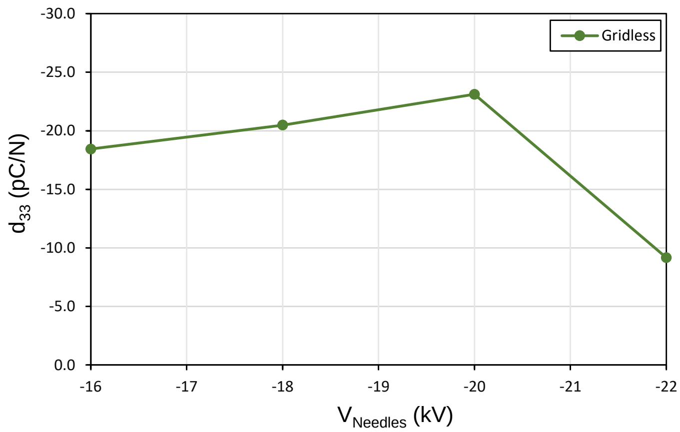

Fig. 4. d_{33} value of the specimens for gridless corona poling configurations as a function of the voltage applied on the needles

As can be evidenced from Fig. 4, the piezoelectric response increases with the voltage (absolute value) applied to the needle, with a maximum of about -23.1 ± 3.5 pC/N for $V_{Needles}$ = -20 kV. A further voltage increase results in electrical breakdowns that damage the specimen causing a considerable drop of the d_{33} value (d_{33} = -9.2 ± 3.6 pC/N).
The piezoelectric strain coefficients evaluated on the specimens polarized with the corona triode configuration are presented in Fig.5. The introduction of a metallic grid interposed between the needles and the sample allowed to apply higher HV values to the needles without any breakdown problems, while keeping the same distance between the tips and the sample adopted for the gridless configurations.

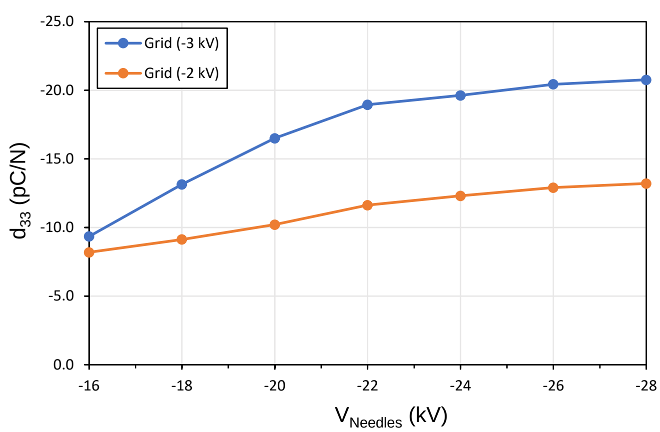

Fig. 5. d_{33} value of the specimens for the corona triode configuration as a function of the voltage applied on the needles

A general increasing trend of the d_{33} with the applied voltage (absolute value) can be observed, similarly to the gridless polarized specimens. The maximum applicable voltage to avoid disruptive discharges which may damage the specimens is about -28 kV. For this limit value, with the grid at -2 kV it is possible to reach a piezoelectric strain coefficient of -13.2 ± 2.3 pC/N, whereas with a voltage of -3 kV applied to the grid, a value of d_{33} = -20.8 ± 1.7 pC/N can be measured, which is close to those obtained with the gridless configuration.

In Table III, all the d_{33} values are reported with the corresponding standard deviation values. Indeed, five tests were performed on different points of the specimen in order to investigate the homogeneity of the charge distribution on the nanofibrous layer surface. While for corona triode polarization the standard deviation has values between ± 1.2 pC/N and ± 2.5 pC/N, for the gridless poling these values increase until ± 5.3 pC/N. Therefore, the introduction of the metallic grid, even if slightly reduces the d_{33} maximum values, is crucial for an homogeneous piezoelectric response over the sample surface.

TABLE III
PIEZOELECTRIC STRAIN COEFFICIENT OF THE SAMPLES

	Gridless						
Samples	**1**		**2**		**3**		**4**
d_{33} (pC/N)	-18.4 ± 5.3		-20.5 ± 4.6		-23.1 ± 3.5		-9.2 ± 3.6
	Grid (-2 kV)						
Samples	**1G**	**2G**	**3G**	**4G**	**5G**	**6G**	**7G**
d_{33} (pC/N)	-8.2 ± 2.5	-9.1 ± 2.2	-10.2 ± 1.7	-11.6 ± 2.0	-12.3 ± 2.1	-12.9 ± 1.8	-13.2 ± 2.3
	Grid (-3 kV)						
Samples	**8G**	**9G**	**10G**	**11G**	**12G**	**13G**	**14G**
d_{33} (pC/N)	-9.3 ± 2.3	-12.1 ± 2.2	-16.2 ± 2.5	-18.9 ± 1.2	-19.6 ± 2.5	-20.4 ± 1.9	-20.8 ± 1.7

IV. CONCLUSIONS

In this study, the electrospinning technique was used to fabricate piezoelectric polymeric nanofibers mats and a corona polarization process was adopted to enhance the piezoelectric response. Two different set-ups were examined and, among them, the best piezoelectric strain coefficient was reached without the use of a grid. On the other hand, the presence of the grid allows to obtain a uniform distribution of the piezoelectric response on the whole surface of the samples, as it can be noted by considering the lower standard deviation values. The effectiveness of such corona poling technique is demonstrated by reaching d_{33} values around 25 pC/N, which are comparable to those of commercial PVdF-TrFE bulky films.

Future developments will concern wider investigations on the corona triode polarization, for instance by increasing the applied voltage to the grid so as to reach the same value obtained with the gridless poling. Furthermore, a deeper analysis will be carried out by varying the distance between the needles and the specimen and the distance between the grid and the ground plate. Finally, the effect of variable number of needles will be evaluated to optimize the charge distribution for a uniform d_{33} value over the sample surface.

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