

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Comparison between AC and DC polarization methods of piezoelectric nanofibrous layers

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Selleri G., Gasperini L., Piddu L., Fabiani D. (2022). Comparison between AC and DC polarization methods of piezoelectric nanofibrous layers. Institute of Electrical and Electronics Engineers Inc. [10.1109/ICD53806.2022.9863546].

Availability:

This version is available at: <https://hdl.handle.net/11585/897524> since: 2022-10-26

Published:

DOI: <http://doi.org/10.1109/ICD53806.2022.9863546>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

G. Selleri, L. Gasperini, L. Piddu and D. Fabiani, "Comparison between AC and DC polarization methods of piezoelectric nanofibrous layers," *2022 IEEE 4th International Conference on Dielectrics (ICD)*, 2022, pp. 90-93.

The final published version is available online at:

<https://doi.org/10.1109/ICD53806.2022.9863546>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Comparison between AC and DC polarization methods of piezoelectric nanofibrous layers

G. Selleri, L. Gasperini, L. Piddiu, D. Fabiani
*DEI-LIMES –Department of Electrical Engineering
University of Bologna, Bologna, Italy*

Abstract- In this paper a comparison between two different polarization mechanisms of piezoelectric nanofibers of poly(vinylidene fluoride-trifluoroethylene) (PVdF-TrFE) are presented. The direct current (DC) traditional polarization method is compared with the alternate current polarization (ACP) one. The results showed a remarkable enhancement of the piezoelectric strain coefficient d_{33} of the nanofibrous mats when polarized with ACP if compared with DC polarization.

I. INTRODUCTION

The transducing mechanism of the piezoelectric materials is attracting great interest in the last period, as their self-powering capability makes them suitable for a variety of fields. According to their mechanical properties and piezoelectric performances, they can be used for different applications. For instance, ceramic piezoelectric materials, such as lead zirconate titanate (PZT), have been widely used for energy harvesting purposes, thanks to their high piezoelectric coefficients [1]. On the other hand, flexible piezo-polymers such as polyvinylidene fluoride (PVDF) and its copolymers (PVDF-TrFE) – which present lower piezoelectric performances if compared with the PZT ones – are promising candidates for wearable applications. Nanogenerators, based on PVDF, have been deeply studied and various wearable devices have been proposed based on the direct piezoelectric effect [2]. Moreover, the easy processability of the piezo-polymers is an important aspect for application fields like Structural Health Monitoring (SHM), robotic or the development of multifunctional materials. Thin films can be manufactured and integrated in remote location or curvilinear geometries for the mechanical stress monitoring of composite structures. However, the interface strength between the composite material and the fluorinated polymer can easily lead to adhesion problems, resulting in delamination and mechanical failure of the component.

In this context, PVDF-TrFE nanofibers represent a promising solution, as they can be easily embedded in a hosting material, such as epoxy resin or silicon rubber. The intimate contact between the hosting material and the nanofibers not only reduces the delamination risk, but even increases the impact strength of the composite laminate [3]. A simple way to produce nanofibers is electrospinning, during which the nanofibers are stretched and the formation of the β phase is favored [4]. Despite this, to fully align the ferroelectric domains and enhance the macroscale piezoelectric behavior of

the membrane, a poling process is required. Typically, permanent polarization is induced by applying a strong DC external electric field. Recently, investigations have been made to enhance the electromechanical response of the piezoelectric materials by applying an alternate current polarization (ACP) method. Results report enhanced piezoelectric strain coefficients d_{33} if compared with those obtained with traditional DC polarization. Various kind of bulky piezoelectric materials were investigated, such as lead zirconate titanate (PZT) and relaxor-PT crystals such as PMN-PT [5], [6] and PIN-PMN-PT [7]. Luo et al. found that the d_{33} value of PIMN-0.30PT single crystals obtained with ACP was improved up to 29% if compared with the one of DC polarization [8]. Ma et al. investigated the PZT-5H ceramic piezoelectric response under various poling conditions. An increase of the d_{33} value from 619 pC/N (obtained under DC poling conditions) to 685 pC/N (under ACP conditions) was measured [9]. Recently, Yamamoto suggested that the enhancement of the electromechanical performance of the piezoelectric materials polarized with ACP is attributable to an increase of the domain wall density [10]. Moreover, Xiong et al. studied the effects of alternate current polarization on PIN-PT crystals. The enhancement of the piezoelectric and dielectric properties were correlated to an intrinsic contribution – which originates from lattice distortion – and an extrinsic contribution, which is related to domain wall and boundary motion [11].

To summarize, a general increase of the piezoelectric properties is reported in literature in case of ACP process, and particular focus has been placed on ceramic piezo-materials.

In this work, polymeric nanofibers of PVdF-TrFE are produced via electrospinning and the polarization process then carried out. The traditional DC poling process is compared with an alternate current poling (ACP) method, which is investigated in terms of frequency and number of cycles. After the polarization process, the piezoelectric response is evaluated for each manufactured specimen.

II. MATERIALS AND METHODS

The manufacturing process of the PVdF-TrFE nanofibrous layers is based on the electrospinning technique and their piezoelectric behavior is optimized by means of a polarization process, as described in this section. Moreover, the

electromechanical characterization of the piezoelectric membranes is reported.

A. Electrospinning process

The piezoelectric copolymer (PVdF-TrFE 80/20 mol%, Curie temperature $T_c=133^\circ\text{C}$, kindly provided by Solvay S.p.A. Milan) was dissolved in dimethylformamide (DMF) and acetone (AC), according to the weight percentages reported in Table I.

TABLE I
POLYMERIC SOLUTION COMPOSITION

% wt		
PVdF-TrFE	AC	DMF
7	70	23

The polymeric solution was magnetically stirred for 2 hours at 50°C before electrospinning. The electrospinning apparatus (Spinbow Lab Unit, Spinbow S.r.l., Italy) consists of a high voltage needle and a rotating drum collector connected to the ground. The use of a low-speed rotating drum has the aim to uniform the nanofibers distribution along the rotating direction. The polymeric solution was pumped into a syringe with a flow rate set at 0.8 ml/h and the high voltage applied to the metallic needle was equal to 15 kV. The distance between the high voltage needle and the drum collector was set at 15 cm and the electrospinning process took place for 4 hours. The morphology of the electrospun nanofibers was investigated through a Phenom Pro X Scanning Electron Microscope (SEM) and the samples were sputter-coated with gold before examination. The average diameter of the nanofibers was measured by means of an image analysis software (ImageJ).

B. DC Polarization process

The DC polarization process was carried out by applying an external electric field perpendicularly to the nanofibrous layer, as shown in Figure 1. Considering the high porosity grade of the nanofibrous mats, the polarization process in air is not recommended as the air gaps between the fibers would lead to electric breakdown for low values of electric field. Therefore, the whole polarization process was carried out in an ester oil bath (FR3 natural ester, Cargill), which penetrates the air pores between the fibers, allowing higher values of poling electric field (oil electrical breakdown equal to 70 kV/mm). Moreover, such a oil was chosen as result of a deep investigation over a wide range of embedding mediums where the nanofibers can be immersed in during the poling process [12]. Indeed, in the case of DC polarization, the electric field distributes unevenly between the two phases (PVDF-TrFE nanofibers and oil) accordingly to their electrical conductivity (σ). In particular, by using an embedding medium with a conductivity higher than the PVdF-TrFE one, the electric field would mainly distribute on the nanofibers and, consequently, a stronger polarization would be induced on the piezoelectric phase.

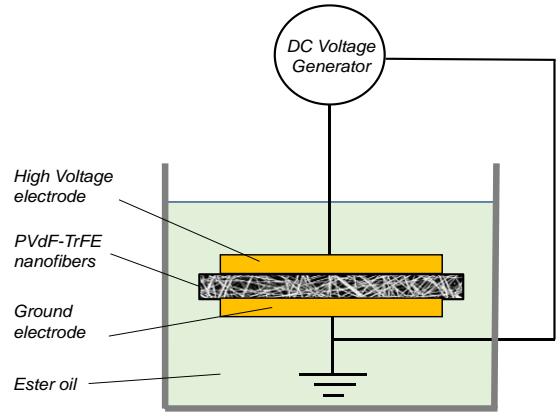


Figure 1 DC poling setup.

With the aim to induce permanent polarization on the nanofibers, the temperature of the process was set close to the Curie temperature (130°C) and an electric field of 15 kV/mm was applied on the nanofibrous mat for 10 minutes. Afterwards, the temperature was decreased down to ambient temperature, and the DC voltage generator was switched off. Finally, the nanofibrous layer was soaked in cyclohexane for one hour in order to fully remove the oil.

C. AC Polarization process

The experimental campaign on the alternate current polarization was carried out by exploring different conditions, such as the frequency of the applied electric field and the number of cycles. In Table II, each tested specimen is named and the correspondent polarization conditions are reported.

TABLE II
AC POLING CONDITIONS

#	Cycles	
f [Hz]	10000	100000
10	1	2
50	3	4
100	5	6

Each nanofibrous mat was polarized at 130°C in the same ester oil bath used for the DC polarization. The high voltage waveform for the application of the alternate electric field was generated according to the setup of Figure 2.

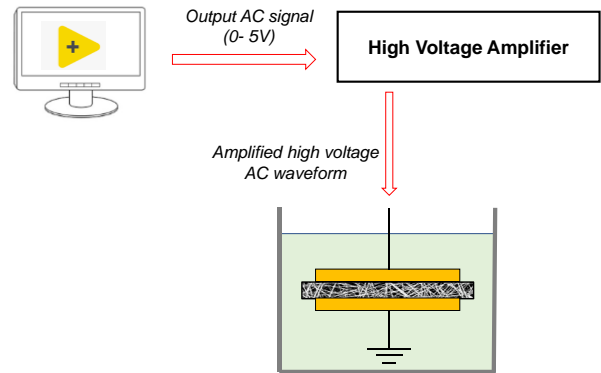


Figure 2 AC poling setup.

By means of the Labview software a signal output was generated and amplified by a high voltage amplifier (Trek, High Voltage Amplifier). The high voltage output was then connected to the high voltage electrode of the polarization cell and an electric field was consequently applied on the nanofibrous mat.

As listed in Table II, 10, 50 and 100 Hz frequencies were applied to the specimens under test. For each of them, the tests were repeated for 10000 cycles and 100000 cycles. In particular, once the temperature of the system reached 130°C, the alternated electric field started oscillating at the designed frequency with an initial amplitude equal to zero. During every cycle, the electric field amplitude was increased of a specific amplitude step in order to achieve the final value of 15 kV/mm during the last cycle of the process. Afterwards, the electric field was kept at 15 kV/mm and the temperature was decreased down to room temperature. Finally, the electric field was switched off and the nanofibrous membrane was soaked for one hour in a cyclohexane bath to remove the oil and restore the original porosity grade of the nanofibrous mat.

A representative curve of the electric field used for the ACP process is reported in Figure 3. The poling conditions illustrated in Figure 3 (frequency=10 Hz, 10 cycles) are not replicated during the experimental campaign, but they are useful to clearly illustrate the trend of the poling electric field. Tests on a broader range of the number of cycles will be investigated in future works.

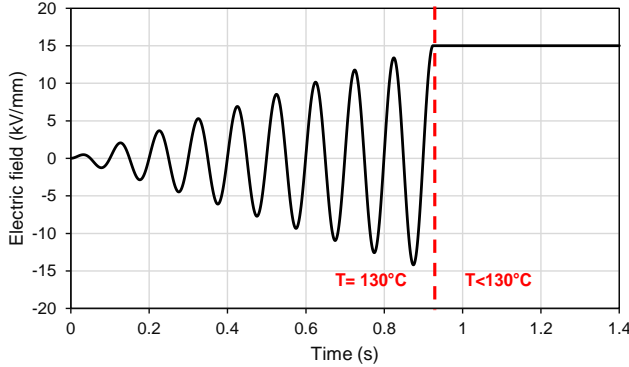


Figure 3 Representative curve of the electric field applied during the ACP.

D. Electromechanical characterization

Once the polarization processes were completed, the piezoelectric strain coefficient d_{33} (pC/N) of every nanofibrous mat was measured by means of a piezometer (d_{33} PiezoMeter System, Piezotest, Singapore, www.piezotest.com). The d_{33} is defined as the ratio of the amount of charges generated on the two opposite surface of the layer and the applied force:

$$d_{33} = \frac{Q}{F} \quad \left[\frac{pC}{N} \right]$$

In particular, the d_{33} was measured by stressing the samples with a compressive sinusoidal force oscillating between 0.25 and 0.5 N at 10 Hz.

Before to be tested, the two opposite surfaces of the nanofibrous mats were connected to the ground for 24 hours at room temperature in order to eliminate the residual electrostatic charges that could be formed during the electrospinning and the poling processes [13].

III. RESULTS AND DISCUSSION

A. Micrograph analyses

The nanofibrous membrane obtained during the electrospinning process are observable in Figure 4. The nanofibrous layers showed a randomly oriented and beads-free nanofibers. The average diameters of the nanofibers were measured to be 370 ± 90 nm.

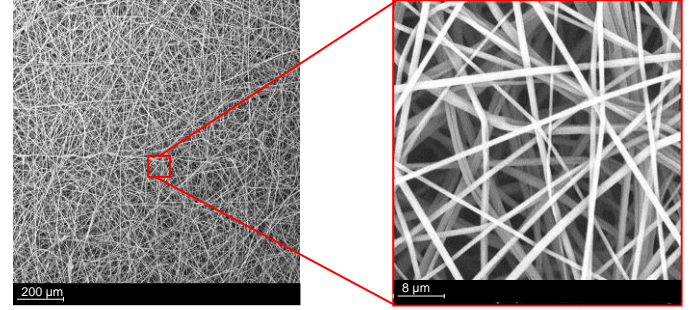


Figure 4 Micrograph analyses of the PVdF-TrFE nanofibers for different magnifications.

B. Electromechanical response

The piezoelectric strain coefficients d_{33} of the polarized specimens are reported in Table III (the specimen named “0” refers to the one poled in DC conditions) and their trend is plotted in Figure 5 as function of the frequency of the poling electric field and the number of cycles.

TABLE III
 d_{33} MEASUREMENT OF THE SPECIMENS

	Specimens						
	0	1	2	3	4	5	6
d_{33} (pC/N)	-16	-21.6	-17	-22.9	-24.7	-24.1	-28.6

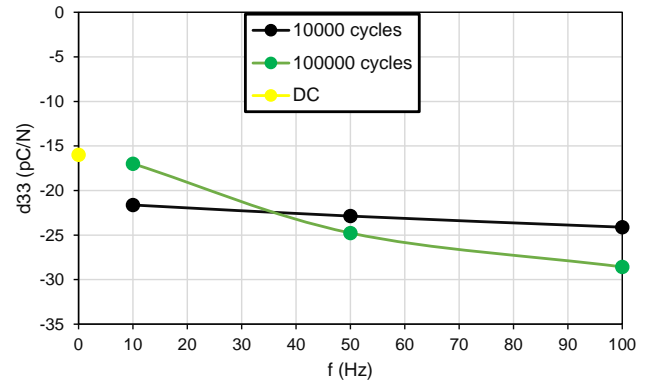


Figure 5 d_{33} value of the specimens as function of the frequency of the electric field and the number of cycles.

As observable from Table III, the lowest d_{33} value, which corresponds to the nanofibrous layer polarized in DC conditions, is equal to -16 pC/N. All the specimens polarized with the ACP method showed a higher piezoelectric coefficient than the DC one, thus demonstrating the effectiveness of such a technique. The presence of an AC polarization phase during the process facilitates the dipoles movement and favors their alignment during the subsequent DC part, which occurs when the AC electric field reaches its maximum amplitude. Overall, the higher the frequency of the applied electric field, the higher the piezoelectric coefficient. However, this trend is slightly observable when the samples are polarized for 10000 cycles, where the d_{33} increases from -21.6 pC/N (at 10 Hz) to -24.1 pC/N (at 100 Hz). On the other hand, in the case of 100000 cycles, the frequency of the applied electric field has a remarkable effect. Indeed, in the case of 10 Hz, the d_{33} value of the nanofibrous mat (-17 pC/N) is basically the same of the DC-poled one, whereas in the case of 100 Hz the d_{33} value arises up -28.6 pC/N, which corresponds to an increase of 78% and matches the performances of commercial PVdF-TrFE bulk film (d_{33} = -25÷-30 pC/N).

IV CONCLUSIONS

In this work, a comparison between two polarization methods of PVdF-TrFE nanofibrous mats is proposed. Starting from polymeric solutions, homogeneous nanofibrous layers of 100 μ m thickness were electrospun. With the aim to align the ferroelectric domains and enhance the piezoelectric response of the specimens, the traditional DC polarization was performed and compared with the AC polarization. Among the different investigated conditions, the highest d_{33} value - measured in the case of 100 Hz and 100000 cycles - was equal to -28.6 pC/N, considerably higher than the d_{33} value obtained with the traditional DC polarization (-16 pC/N). Future developments will regard investigations over a wider frequency range and number of cycles of the poling electric field. Moreover, studies on the polarization of ceramic PZT nanofibers - which typically present higher piezoelectric performance than the piezo-polymers - will be performed with the aim to develop wearable and flexible devices for energy harvesting applications.

ACKNOWLEDGMENT

The research activity was supported by NATO Science for Peace and Security Programme (grant G5772) and from the European Union within the Horizon 2020 research and innovation program, under grant agreement n. 780871 (MyLeg project <http://www.myleg.eu/>).

REFERENCES

- [1] N. Sezer and M. Koç, "A comprehensive review on the state-of-the-art of piezoelectric energy harvesting," *Nano Energy*, vol. 80, no. November 2020, p. 105567, 2021, doi: 10.1016/j.nanoen.2020.105567.
- [2] X. Pu, W. Hu, and Z. L. Wang, "Toward Wearable Self-Charging Power Systems: The Integration of Energy-Harvesting and Storage Devices," *Small*, vol. 14, no. 1, pp. 1–19, 2018, doi: 10.1002/smll.201702817.
- [3] T. Brugo and R. Palazzetti, "The effect of thickness of Nylon 6,6 nanofibrous mat on Modes I–II fracture mechanics of UD and woven composite laminates," *Compos. Struct.*, vol. 154, pp. 172–178, 2016, doi: 10.1016/j.compstruct.2016.07.034.
- [4] F. Calavalle, M. Zaccaria, G. Selleri, T. Cramer, D. Fabiani, and B. Fraboni, "Piezoelectric and Electrostatic Properties of Electrospun PVDF-TrFE Nanofibers and their Role in Electromechanical Transduction in Nanogenerators and Strain Sensors," *Macromol. Mater. Eng.*, vol. 305, no. 7, pp. 1–8, 2020, doi: 10.1002/mame.202000162.
- [5] Z. Zhang *et al.*, "The performance enhancement and temperature dependence of piezoelectric properties for Pb(Mg 1/3 Nb 2/3)O 3 -0.30PbTiO 3 single crystal by alternating current polarization," *J. Appl. Phys.*, vol. 125, no. 3, pp. 0–7, 2019, doi: 10.1063/1.5052709.
- [6] C. Qiu *et al.*, "Transparent ferroelectric crystals with ultrahigh piezoelectricity," *Nature*, vol. 577, no. 7790, pp. 350–354, 2020, doi: 10.1038/s41586-019-1891-y.
- [7] J. Liu *et al.*, "Impact of alternating current electric field poling on piezoelectric and dielectric properties of Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 ferroelectric crystals," *J. Appl. Phys.*, vol. 128, no. 9, 2020, doi: 10.1063/5.0020109.
- [8] C. Luo, T. Karaki, Y. (John) Yamashita, and J. Xu, "High temperature and low voltage AC poling for 0.24Pb(In1/2Nb1/2)O3-0.46Pb(Mg1/3Nb2/3)O3-0.30PbTiO3 piezoelectric single crystals manufactured by continuous-feeding Bridgman method," *J. Mater.*, vol. 7, no. 3, pp. 621–628, 2021, doi: 10.1016/j.jmat.2020.11.003.
- [9] J. Ma, K. Zhu, D. Huo, X. Qi, E. Sun, and R. Zhang, "Performance enhancement of the piezoelectric ceramics by alternating current polarizing," *Appl. Phys. Lett.*, vol. 118, no. 2, pp. 3–8, 2021, doi: 10.1063/5.0035153.
- [10] N. Yamamoto, Y. Yamashita, Y. Hosono, K. Itsumi, and Kazuhiko Higuchi, "Ultrasonic probe, piezoelectric transducer, method of manufacturing ultrasonic probe, and method of manufacturing piezoelectric transducer US 9 , 966 , 524 B2," 2018.
- [11] J. Xiong, Z. Wang, X. Yang, R. Su, X. Long, and C. He, "Effects of alternating current poling on the dielectric and piezoelectric properties of Pb(In0.5Nb0.5)O3-PbTiO3 crystals with a high Curie temperature," *RSC Adv.*, vol. 11, no. 21, pp. 12826–12832, 2021, doi: 10.1039/d0ra10234b.
- [12] G. Selleri *et al.*, "Study on the polarization process for piezoelectric nanofibrous layers," *2021 IEEE Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2021, pp. 61–64, doi 10.1109/CEIDP50766.2021.9705470., pp. 31–34, 2021.
- [13] D. Fabiani, G. Selleri, F. Grolli, and M. Speranza, "Piezoelectric nanofibers for multifunctional composite materials," *Conf. Electr. Insul. Dielectr. Phenomena, CEIDP*, vol. 2020-October, pp. 247–250, 2020, doi: 10.1109/CEIDP49254.2020.9437547.