

CONFINED POLYMERIC NANOWIRES INTO POROUS ALUMINA MATRIX AS COMPOSITE PIEZOELECTRIC MEMBRANE FOR SENSING APPLICATIONS

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Abstract

Wet-impregnation of poly(vinylidene fluoride-tri fluoro ethylene) PVDF TrFE) was performed into commercially available porous Anodic Alumina Membrane (AAM, nominal pore size 200 nm, thickness 60 μ m), leading to an array of distributed polymeric 1D nanostructures in the AAM. The templated PVDF-TrFE) nanowires showed a diameter of about 200 nm, several microns in length and a high filling ratio of the AAM channels. X-ray diffraction and infrared spectroscopy showed the crystallization of the polymer into the ferroelectric β -phase, with crystal lamellae oriented perpendicularly to the AAM channel walls. Here ferroelectric polarization, hysteresis and displacement loops were recorded for the first time, showing a remarkable piezoelectric behavior of these 1-D polymeric nanostructures. I-V characteristics showed a consistent switching behavior of the ferroelectric polar domains, thus revealing the importance of the confined and oriented crystallization of the polymer in mono-dimensional nano-structures.

1 Introduction

Poly(Vinylidene Fluoride-Tri FluoroEthylene) [PVDF-TrFE] is a very attractive copolymer, whose remarkable piezoelectrical and pyroelectrical properties [1] gave rise to a broad range of applications, from non-volatile low-voltage memories [2, 3] to transducers, or tactile sensor devices [4].

The copolymer PVDF-TrFE readily crystallizes into the β phase, the most interesting in terms of piezoelectric properties, showing a spatial arrangement of the fluorine atoms in an *all-trans* conformation [1, 5]. A good piezoelectric response can be obtained by orienting the molecular dipoles of PVDF-TrFE in the same direction, by subjecting the material to mechanical stretching or to an intense electric field at a certain temperature (poling) [6, 7]. This polarization is mainly attributed to the spatial arrangement of the segments of the macromolecular chains, thus it was recently shown that the crystallization and consequently the polarization of PVDF-TrFE can be affected by confinement into templates [2, 8]. In particular, the confinement of polymer into porous anodic alumina membrane was reported [8, 9], thus obtaining a composite material consisting in polymeric piezoelectric 1-D nanostructures distributed throughout a porous insulating matrix.

In the present paper we show not only an effective and fast method to prepare β -crystalline piezoelectric nanowires of PVDF-TrFE into the porous alumina [9], but we study for the first time also their electromechanical response exploiting the inverse piezoelectric effect. With these highly oriented and confined polymeric nanostructures we aim to obtain a distributed array of nanometric-sized piezoelectric structures suitable both for actuators and inversely mechanical pressure sensors, i.e. for tactile sensing devices.

2 Materials and testing methods

Anodic Alumina Membranes (AAM, from Anodisc® Whatman 47 mm, nominal pore size 200 nm, thickness 60 μm) were cut in 4 pieces of about 20 x 20 mm and placed on the top of the vacuum sample holder of a spin coater (Spin150 VT BG 66-0, SPS-Europe). 100 μL (2.8%wt) of poly(vinylidene fluoride-tri fluoro ethylene) (PVDF-TrFE, molar ratio PVDF/TrFE=2.33, Piézotech) in methyl-ethyl ketone (MEK, Aldrich) were spin coated for 2' at 500 rpm and 1' at 1500 rpm on the AAM surface. In order to completely fill the pores of alumina, the wet-impregnation upon spin coating was carried out at both sides of the AAM. The samples were then dried in oven at 120 °C for 2 hours to improve the crystallization and carefully polished both mechanically and chemically with the MEK solvent in order to remove the polymer excess constituting a film on the membrane surface. 10'' etching of the alumina membrane in 4M NaOH served to improve the access to the top and bottom faces of the infiltrated nanowires. To electrically contact the polymeric wires, sputtering on both top and bottom sides of the alumina-impregnated membrane of platinum (Pt) electrodes was carried out by means of a Q150TES (Quorum Technology) sputtering system, operating at 50 mA for 180 seconds at room temperature and $8 \cdot 10^{-4}$ mbar.

Field Emission Scanning Electron Microscopy (FESEM) images were performed on a Dual-Beam Auriga Carl Zeiss equipped with a Focused Ion Beam (FIB) to perform cross sections of the samples and an Energy Dispersive X-rays detector (EDX). In particular top- and cross-section views of the on the PVDF-TrFE-filled AAM membranes were imaged, as well as free-nanowires after the alumina dissolution in a water solution of NaOH (4 M) for 4 hours, after protecting one side of the membrane with a PVC tape. Wide-angle X-ray diffraction patterns were collected on a X'Pert Philips Diffractometer with Cu- K_{α} radiation at $\lambda = 1.5418 \text{ \AA}$. Infrared spectroscopy was carried out in absorption with a Bruker Equinox 55.

Current-voltage (I-V) curves, ferroelectric polarization hysteresis loops and piezoelectric displacement measurements were recorded simultaneously by a Piezo Evaluation System (PES, TFAalyzer 2000HS, Aixacct) coupled to a single point laser vibrometer (Polytec OVF-505).

3. Results and discussion

The wet-impregnation process leads in one step to a one-dimensional (1D) nanostructures with a diameter of about 200 nm and vertically distributed in a 60 μm thick insulating matrix, thus a polymeric-ceramic composite membrane (Figure 1). The polymeric nanowires are several micrometers long and, upon cross sectioning the alumina membrane by FIB, they showed a good filling ratio of the alumina pores. However, in some cases it is possible to see empty pores (Figure 1.a) resulting from empty or only partially filled channels by the polymer (Figure 1.c and d). This fact should be taken into account when evaluating the ferroelectric properties of the materials as a function of the working electrode area.

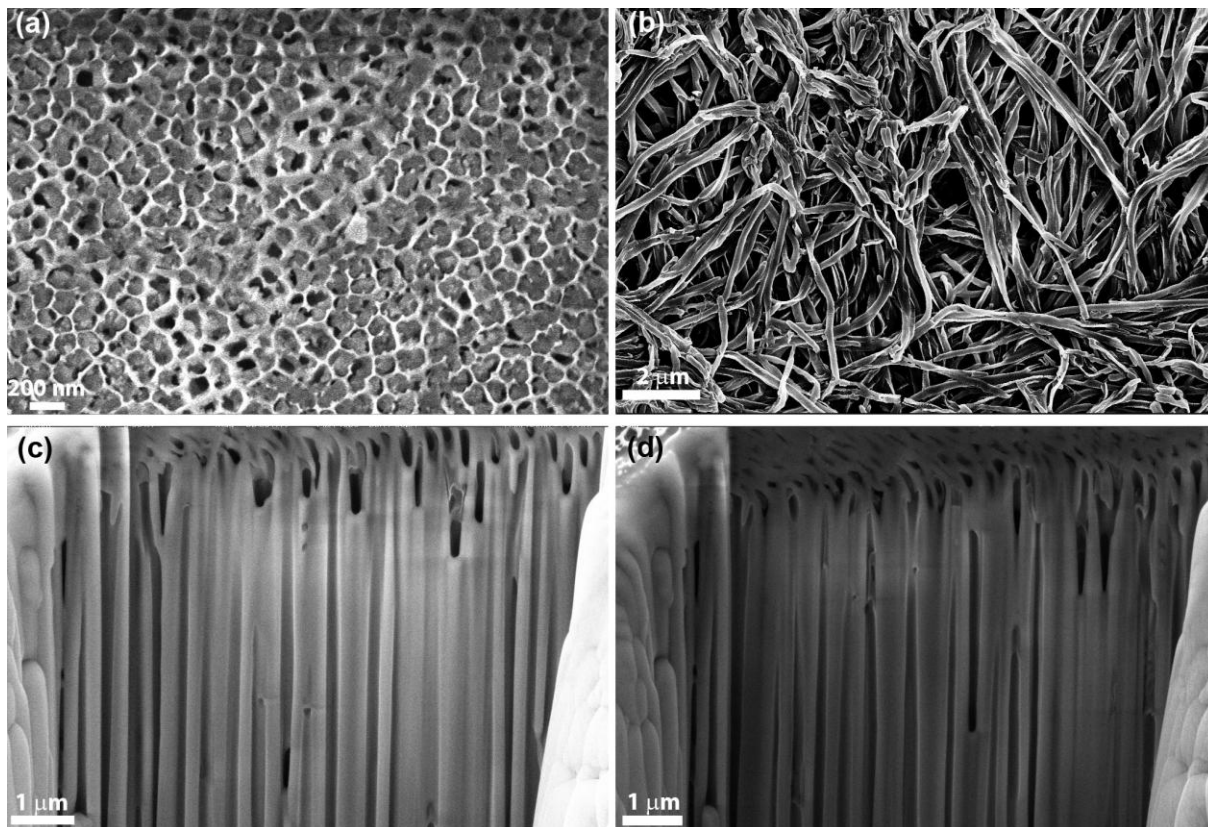


Figure 1. Field Emission Scanning Electron Microscopy (FESEM) images obtained on the polymer-impregnated alumina composites. (a) top-view showing the alumina channels filled with the polymer; (b) PVDF-TrFE polymeric nanowires upon the complete dissolution of alumina; (c) and (d) Cross-section of the alumina matrix by Focused Ion Beam (FIB) showing the pores filled or partially filled by the polymer.

The polymer crystallinity into the alumina restricted geometry was studied by X-ray diffraction (Figure 2.a), where the experiment setup was in θ - 2θ mode, having the scattering vector perpendicular to the alumina membrane surface (as schematically depicted in the inset of Figure 2.a). Both the bulk copolymer (trace C) and the PVDF-TrFE-AAM composite (trace B) show the reflections at 19.9° , corresponding to the overlapping of (110) and (200) reflections, at 34.8° , which is the (001), and at 40.7° , overlapping of (111) and (201) reflections, all ascribable to the β ferroelectric phase. Evidences of the crystalline structure of the polymer is observed at higher magnification in the FESEM image acquired in cross-section upon FIB processing (Figure 2.b). The crystal stacking along the polymeric nanowires is arranged perpendicularly to the alumina channels axis, confirming what previously reported in the literature [10, 11]. A comparison at the same magnification with a PVDF-TrFE film, similarly obtained by spin coating from a solvent solution, shows similar crystals in size, with a random orientation due to the absence of nano-confinement.

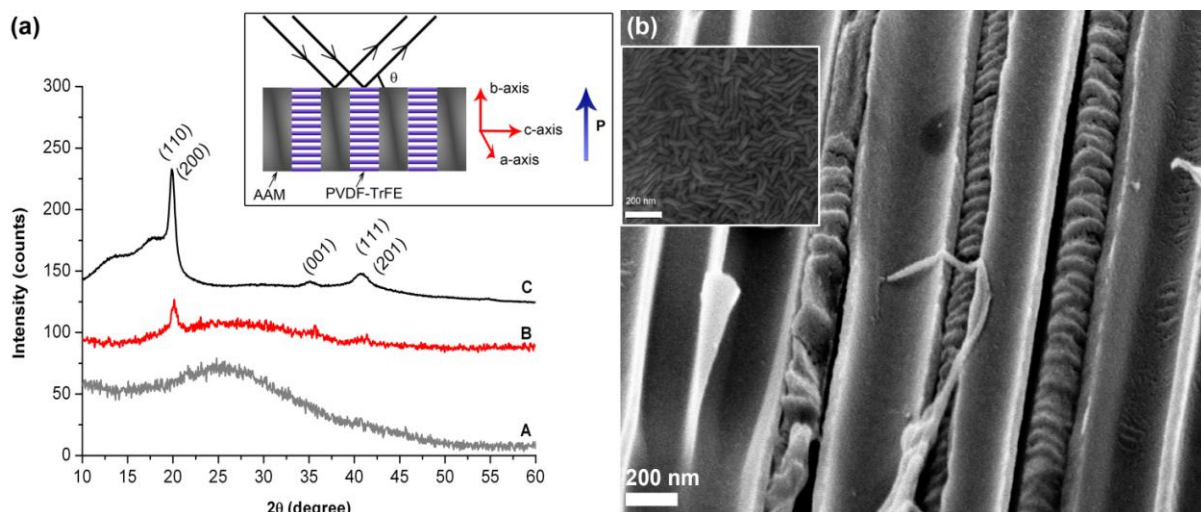


Figure 2. (a) Wide Angle X-Ray diffraction pattern of the PVDF-TrFE-alumina composite (Trace B) in comparison to the empty porous alumina (AAM, trace A) and to the semi-crystalline copolymer in powder form (Trace C), before dissolution into the solvent. Inset: Schematic representation of the incident X-ray and of the crystalline orientation of the PVDF-TrFE polymeric nanowires into the alumina channels, showing a vertical polar b -axis and in-plane a and c -axes, thus perpendicular to the AAM channels. (b) Crystal orientation, magnified by FESEM, of the polymeric PVDF-TrFE nanowires into the AAM. The crystal lamellae are perpendicular to the alumina channels axis. Inset: PVDF-TrFE film showing needle-like crystals of the β -phase.

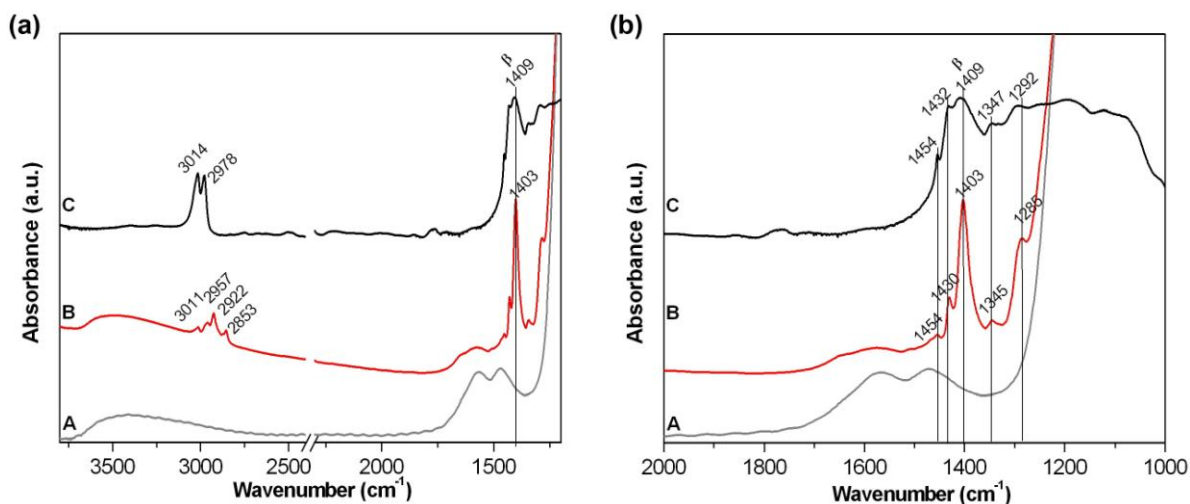


Figure 3. Infrared spectroscopy in adsorption mode, comparing the empty alumina (curve A) with the polymeric nanowires into the AAM matrix (PVDF-TrFE-AAM composite, curve B) and the pure PVDF-TRFE copolymer (curve C).

Infrared spectroscopy was recorded in absorption mode on the PVDF-TrFE nanowires confined into the alumina channels (curve B in red, Figure 3) and compared to the bulk copolymer (curve C, in black) and to the empty porous alumina (curve A, in grey). Presence of $-\text{CH}$ asymmetric and symmetric and stretching vibrations are identified in the range between 3000 and 2850 cm^{-1} in both the composite materials and the pure copolymer (Figure 3.a). The presence of the β ferroelectric phase is ascribed to the vibration peaks at 1409 cm^{-1} [2], thus also confirming the previous XRD results. At a closer magnification (Figure 3.b) one can resolve more vibration peaks ascribable to the β phase and the relative intensities between the composite materials (red curve, B) and the bulk copolymer (black curve, C). First, we observe that the 1403 cm^{-1} B1 band, corresponding to the wagging vibration of CH_2 , having the dipole moment μ_c parallel to the chain c -axis, is more intense in the PVDF-TrFE-AAM

composite with respect to the copolymer in bulk (curve C, at 1409 cm^{-1}). Secondly, the band at 1285 cm^{-1} (A_1) corresponds to the symmetric stretching vibration of CF_2 , having a transition dipole moment μ_b parallel to the polar b -axis; it is less defined with respect to the same vibration in the bulk copolymer (at 1292 cm^{-1}). These results seem to indicate that the c -axis of the polymeric nanowires confined into the alumina channels is predominant and oriented parallel to the alumina surface, thus perpendicularly to the AAM channel axis, as found with the previous results (Figure 2).

Additionally the band at 1430 cm^{-1} corresponds to the deformation vibration of CH. Other bands at wavenumbers lower than 1200 cm^{-1} are not visible in the PVDF-TrFE-AAM composites, due to the huge bump, arising at 1200 cm^{-1} , attributed to the alumina.

The preferred orientation of the chain c -axis upon nano-confinement into the alumina channels leads to favorable ferroelectric and piezoelectric properties in the direction perpendicular to the alumina surface. Actually, upon the application of a vertical electric field, coaxial to the alumina channels, the polarization P is maximized along the alumina channels, owing to the vertical orientation of the polar b -axis of the nanowires, as shown in the inset of Figure 2.a. This configuration is therefore strategic for piezoelectric applications, to use such composite membrane for mechanical pressure sensors or nano-actuators.

Therefore we investigated the piezoelectric properties of the PVDF-TrFE-AAM composites by a Piezo Evaluation System, a characterization instrument coupled with a laser vibrometer, exploiting the inverse piezoelectric effect. In particular, by applying an electric field along the nanowire axis, the overall electrical and electromechanical properties of these structurally oriented and distributed nanowires can be evaluated, measuring the resulting ferroelectric polarization hysteresis and mechanical displacement loops (Figures 4.a and 5). To our knowledge, such characterization is applied here for the first time to these confined polymeric nanowires. Upon varying the frequency from 1 to 10 Hz, we obtained polarization hysteresis curves which tends to be rectangular (as in ideal ferroelectric materials) as soon as the frequency increases. The remnant polarization (P_r) at 5 Hz was $15\text{ }\mu\text{C}/\text{cm}^2$ (Figure 4.a, curve in blue) and the coercitive field (E_c) of $55.3\text{ MV}/\text{cm}$ based on the thickness of $60\text{ }\mu\text{m}$, thus in line with the literature values obtained for thin films of poled PVDF-TrFE [3, 12]. In the present case, only a small percentage of the electrode area comprises the polymeric nanowires, whereas most of the remaining electrode surface covers the non-polar alumina, thus reducing the effective electrode working area. However the favourable orientation of the polar b -axis, as well as the improved crystal orientation of the confined polymer into the alumina channels, leads to a good coupling between the applied electric field and the dipole moment.

The electric current versus the applied voltage curves (Figure 4.b) show the symmetric switching peaks at both positive and negative electric field values, indicating the ferroelectric switching behaviour of the polar domains under the applied electric field.

The displacement butterfly loop deals to an averaged d_{33} constant (obtained from the linear part of the piezoelectric displacement curve) of about $4\text{ pm}/\text{V}$ (Figure 5, showing the loop recorded at 10 Hz), which is in line with the literature values (from 5 to $20\text{ pm}/\text{V}$ of poled thin film of PVDF-TrFE [13, 14]). One should take into account here that the nanowires displacement can be reduced by alumina wall constriction and also that the working electrode area in contact with the nanowires is quite inferior with respect to the overall Pt-sputtered area, due to the presence of the insulating non-polar alumina. However, this d_{33} value is still remarkable also despite the absence of poling of the PVDF-TrFE nanowires, which is in contrast usually applied to the polymeric films [15]. We attribute this effect to the high polymer crystallinity due to the confinement into the alumina templating-channels. Further

improvements of the piezoelectric response can be obtained by reducing the leakage current, appearing at high voltages with an abrupt increase of the current (see Figure 5).

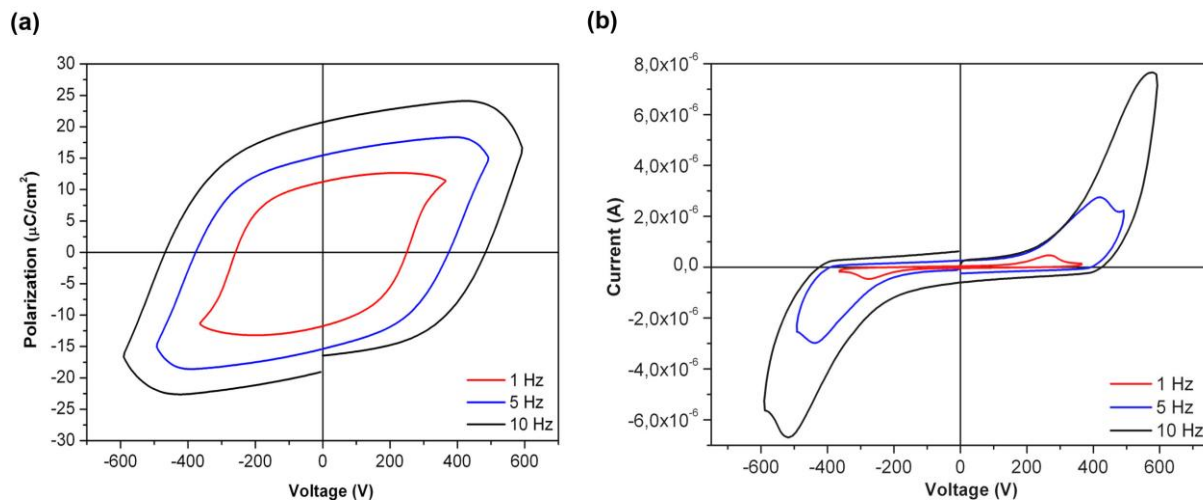


Figure 4. (a) Ferroelectric polarization hysteresis and electromechanical displacement loops obtained by applying an electric field at different frequencies to the confined polymeric nanowires into the alumina. (b) Current versus the applied voltage at different frequencies, showing the polarization domain switching peaks.

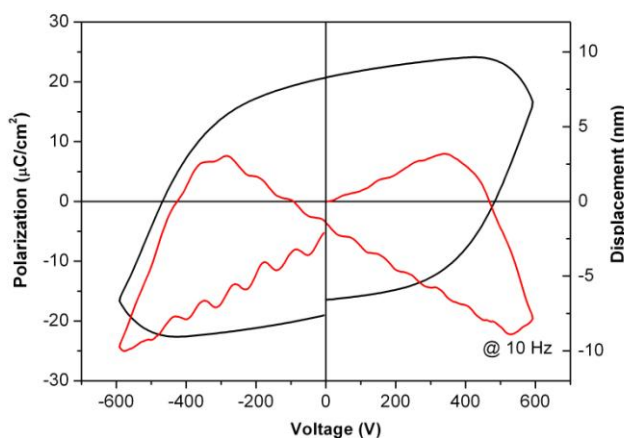


Figure 5. Polarization hysteresis (in black) and displacement butterfly (in red) loops of the PVDF-TrFE-AAM composite at 10 Hz.

4. Conclusions

We have reported on a facile method to confine a ferroelectric copolymer PVDF-TrFE into 200 nm-sized channels of a commercial porous anodic alumina membrane (AAM) of 60 μm in thickness. We have shown that the confinement leads to a preferential orientation of the crystalline β ferroelectric phase, showing the *c*-axis perpendicular to the alumina channels and the *b*-polar axis along the alumina channels. This effect induce a favorable orientation of the nanowires polarization axis, which results parallel to the alumina channels and thus perpendicular to the AAM surface. By applying an electric field across the PVDF-TrFE-AAM composite membrane, one can thus obtain crucial piezoelectric properties. The electromechanical characteristics of these ferroelectric nanowires confined into the porous alumina were measured here for the first time by a Piezo Evaluation System, obtaining ferroelectric polarization hysteresis and displacement loops, in line with the literature values for poled ferroelectric films. One can then conclude that the absence of any poling on our

nanowires do not affect the remarkable piezoelectric features, thanks to the nano-confinement. Thus we obtained in one preparation step a ready-to-use system showing piezoelectric properties, without any further processing, like poling or mechanical stretching. As a future outlook, these crystalline piezoelectric nanowires distributed in vertical array into a dielectric membrane can be engineered in a piezoelectrical MEMS device, thus potentially addressing applications like tactile sensors or nano-actuators.

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