Energy harvesting performance of piezoelectric electrospun polymer fibers and polymer/ceramic composites

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ABSTRACT

The energy harvesting efficiency of electrospun poly(vinylidene fluoride), its copolymer vinylidene fluoride-trifluoroethylene and composites of the later with piezoelectric BaTiO₃ on interdigitated electrodes has been investigated. Further, a study of the influence of the electrospinning processing parameters on the size and distribution of
the composites fibers has been performed. It is found that the best energy harvesting performance is obtained for the pure poly(vinylidene fluoride) fibers, with power outputs up to 0.03 $\mu$W and 25 $\mu$W under low and high mechanical deformation. The copolymer and the composites show reduced power output due to increased mechanical stiffness. The obtained values, among the largest found in the literature, the easy processing and the low cost and robustness of the polymer, demonstrate the applicability of the developed system.

INTRODUCTION

Energy harvesting from mechanical vibrations has become increasingly important over the last years [1-3] mainly due to the low power requirement of small electronic components, such as wireless sensor networks used in monitoring applications. Powering small electronics using the vibrational energy available in their environment could reduce the requirement of external power sources, like batteries, and thus avoiding the associated maintenance costs [1-3].

There are three basic vibration-to-electrical conversion mechanisms: electromagnetic, electrostatic and piezoelectric transductions [3, 4]. Piezoelectric transduction has received the largest attention when compared to the other transductions systems due to its main advantages, such as large power density, easy application (piezoelectric devices could be fabricated both in macro and micro scale due to well established production techniques), and that the output voltage is obtained directly from piezoelectric material itself, that suppresses the requirement of an external voltage input [1].

The energy conversion in piezoelectric materials is based on variations in the dipolar moment when a strain is applied and therefore the formation of a potential difference that can be used to power devices [3].

In recent years a large effort has been developed focus in improving the efficiency of piezoelectric power harvesting systems. The most common type of piezoelectrics used for power harvesting are ceramics like lead zirconate titanate (PZT) or barium titanate (BaTiO$_3$) [3]. Nevertheless, piezoceramics are susceptible to fatigue crack when
subjected to high frequency cyclic loading, which created the need to search for other alternatives as poly(vinylidene fluoride) (PVDF), a piezoelectric polymer with high flexibility when compared with ceramics materials [5-7].

PVDF and vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymers have attracted scientific and technological interest due to their chemical resistance, good mechanical properties and excellent electroactive properties. (VDF-TrFE) has a ferroelectric – paraelectric (FE-PE) phase transition at a transition temperature, $T_c$, that occurs in the bulk material at temperatures below the melting temperature, $T_m$, and has large electromechanical coupling coefficient at room temperature [8, 9].

PVDF and VDF copolymers crystalline structure in the ferroelectric phase is packed in an “all-trans”, TT, planar zigzag polymer chain configuration [8]. In (VDF-TrFE), the paraelectric crystalline structure above $T_c$ is hexagonal, essentially consisting in a statistical configuration of TT, TG and TG’ rotational isomers [10]. The FE-PE transition temperature is highly dependent upon VDF content, but other factors such as heat treatments, electrical poling and processing history can also affect the transition [11-13].

New research fields are emerging based on the exploration of the nanoscale properties of such materials improving the possibilities of piezoelectric materials become a real choice for energy harvesting devices [14]. In this sense, a nanogenerator based on PZT aligned nanofibers on a silicon substrate with interdigitated electrodes has been reported which reaches an output voltage peak of 1.63 V and a power generation of 0.03 $\mu$W [15] and another piezoelectric nanogenerator based on BaTiO$_3$ on plastic substrate connected by interdigitated electrodes [16] with an output voltage up to 1.0 V and a power density of $\sim$7 mW/cm$^3$. This later nanogenerator needs extra poling treatment after processing in order to enhance the piezoelectric properties of the materials. Output voltages of nearly 40 V after poling has been reported for micropower harvesters based on PZT/PVDF and PZT/PP (polypropylene), [17] but the generated power was not reported.

Polymer nanofibers offer the possibility to tailor materials properties and increase performance for a number of applications, including energy generation and storage. Micro and nanofibers can be produced by several techniques such as drawing, template
synthesis, phase separation self-assembly and electrospinning, [18] the latter being the most straightforward, convenient and scalable technique for nanomaterials production, [18, 19] allowing the production of continuum fibers with diameters of a hundreds of nanometers up to few micrometers [20]. Electrospinning is process for producing nanofibers by forcing a viscous solution through a spinneret subjected to an electric field. Crossing the spinneret the solution drips and the high applied voltage leads the drop into an elongated cone; with appropriated viscosity and surface tension a stable solution jet erupts from the solution droplet. The process makes use of fluid applied charges to provide a stretching force to a collector where is a potential gradient. This mechanism ensures the fibers polarization [18, 21].

Several parameters have influence in electrospun fibers morphology and properties and can be divided in three main groups: initial polymer solution, jet formation and finally the collection procedure [18].

Electrospun piezoelectric nanofibers offers excellent flexibility and improved strength, so it is expected their exploitation in a wide variety of applications [22]. Generators based on randomly electrospun PVDF fibers have been developed [23] that when submitted to periodic oscillations between 1 and 10 Hz achieved output voltages between 0.43 and 6.3 V. The reported current, around 5 μA, seems to be too high for an insulating material such as PVDF. Even so, the output power generated was around 0.03 μW [24].

PZT and BaTiO₃ are known to be excellent piezoelectric materials, with high dielectric and piezoelectric values [25, 26]. It seems interesting in this way to explore the possibility to prepare electrospun composite fibers of PVDF and P(VDF-TrFE) with BaTiO₃ on top of an interdigitated circuit in a single step process (no poling of the fibers is further needed) in order to study the influence of the ceramic filler in the energy harvesting efficiency of the polymer. In this way, both the influence of the processing parameters on the fiber characteristics and the nanogenerator performances will be addressed.

EXPERIMENTAL
Pure polymer samples of poly(vinylidene fluoride) (PVDF, from Solef 1010) and composites of poly(vinylidene fluoride trifluorethylene) ((P(VDF-TrFE) (70/30), from Solvay) with barium titanate (BaTiO$_3$ nanoparticles with average size of 10, 100 and 500 nm, from Nanoamor) were prepared by dispersing the ceramic powder in a solution of polymer with N,N-dimethylformamide (DMF, from Merck) and methylethylketone (MEK, from Panreac) (7.0/3.0 vol/vol) to in a polymer plus ceramic concentration of 15 % (w/w) of the total solution. The polymer to ceramic relative concentration ranged from 0 up to 20 % ceramic content (w/w). The final solution was dissolved at room temperature with the help of a magnetic stirrer until complete polymer dissolution.

The polymer solution was placed in a commercial plastic syringe (10 mL) fitted with a steel needle with inner diameter ranging from 0.5 to 1.7 mm. Electrospinning was conducted in a range between 20 and 35 kV with a high voltage power supply from Glassman (model PS/FC30P04). A syringe pump (from Syringe pump) was used to feed the polymer solutions into the needle tip at rate between 0.5 and 8 mL/h. The electrospun fibers were collected in a grounded collecting plate (random fibers) or in a rotating drum (oriented fibers), placed at a distance between 10 to 30 cm from the needle, and in interdigitated electrode plates (fig.1).

Electrospun fibers were coated with a thin gold layer using a sputter coating (Polaron, model SC502 sputter coater) and their morphology was analyzed using a Scanning Electron Microscope (SEM) (Cambridge, Leica) with an accelerating voltage of 15 kV. The fiber average diameter and its distribution was calculated over approximately 40 fibers using de SEM images at 2000X magnification and the Image J software.

Infrared measurements (FTIR) were performed at room temperature, in order to evaluate the phase of the polymer, in a Perkin-Elmer Spectrum 100 apparatus in ATR mode from 4000 to 650 cm$^{-1}$. FTIR spectra were collected with 32 scans and a resolution of 4 cm$^{-1}$.

The thermal behavior of the electrospun fiber mats was analyzed by differential scanning calorimetry measurements (DSC) with a Pyris apparatus from Perkin-Elmer. The samples were cut into small pieces from the middle region of the electrospun membranes, placed into 50 µL aluminum pans and heated between 30 and 220 ºC at a heating rate of 10 ºC/min. All experiments were performed under a nitrogen purge.
Energy harvesting performance of the electrospun samples was evaluated by periodic bending tests (low deformation) in a electromechanical generator (Frederiksen 2185.00) excited from 1 Hz to 1 MHz using a signal generator (Circuitmate GF2) (fig.1). The maximum vertical displacement of the samples was about 10 mm from initial position, corresponding to displacements between -10 and 10 mm. The voltage output was measured using an oscilloscope (Axo 4005) and the data collected with the Picoscope software. Samples were also submitted to bending tests with high deformation, where the mechanical stress was applied by a finger.

![Figure 1](http://dx.doi.org/10.1016/j.sna.2013.03.023)

**Figure 1:**

RESULTS AND DISCUSSION

The influence of the electrospun processing parameters on average fiber size and characteristics such as electroactive phase content and degree of crystallinity of PVDF [27] and P(VDF-TrFE) [28] have been study previously, and this section will focus on the composite fibers. The influence of the applied electric field in the BaTiO$_3$/P(VDF-TrFE) electrospun fibers nanocomposites has been evaluated keeping constant the needle inner diameter of 0.5 mm and the flow rate of 0.5 mL/h. In general, BaTiO$_3$/P(VDF-TrFE) electrospun membranes show a random distribution of and smooth fibers with diameters of 450 ± 100 nm with absence of beads (figure 2). A histogram of the fiber diameter distribution was determined from the SEM images and a
fiber average was obtained. The histograms of figure 2 (a, b and c) were acquired from 40 measurements of the nanofibers present in the image.

Following a similar procedure, from the systematic variation of the other main parameters affecting the electrospinning process their influence on the average fiber diameter has been obtained (fig.3).

It was observed that the applied electric field does not have influence on the fiber diameter and distribution (figure 3a). On other hand, for a fixed applied electric field, inner diameter, flow rate and for the same polymer/ceramic concentration an increase of the average fiber diameter was observed (figure 3b). Fiber average diameter and its distribution are strongly affected by the flow rate, demonstrated by an increase of the mean fiber diameter from 422 ± 27 nm to 649 ± 127 nm by increasing the flow rate from 0.5 mL/h to 8 mL/h (figure 3c). Feed rate determines the amount of solution available at the needle tip for electrospinning. When feed rate increases, there is a corresponding increase on the fiber diameter due to the larger volume of solution that is drawn away from the needle tip [18].

It was interesting to note that the inclusion of ceramic BaTiO3 nanoparticles in the polymer solution does not influence the fiber average diameter and distribution (figure 3d). The effect of BaTiO3 particle average diameter in the fiber size and distribution was characterized for ceramic particles with 10, 100 and 500 nm (figure 4) for the fibers with 20 % BaTiO3 content. All membranes show no polymer beads but some particle clusters due to the large ceramic content for the given fiber average diameter. With respect to the particle average size, particles with a mean diameter lower than 100 nm are trapped inside the fiber (figure 4a and d), but the particles with an average diameter of 500 nm are randomly dispersed in and outside the fibers due to the fact that the fiber average diameter is smaller than the BaTiO3 single particles and clusters (figure 4b). The average fiber diameter for the BaTiO3/P(VDF-TrFE) composites with 10 nm particles diameter is 469 ± 136 nm, for the composite with 100 nm particles is 543 ± 92 nm and for the membrane with 500 nm particles size shows an mean diameter of 377 ± 70 nm, which is smaller than the particles itself making impossible entrapment of the filler inside the polymer fiber (figure 4).
The sample obtained in the drum collector (figure 4d) presents a preferential fiber orientation with an average fiber diameter of 525 ± 126 nm and with a compact structure. For randomly and aligned fibers, it was noted that composites fibers are uniformly filled with discontinuous ceramic particles that are essentially inside of the fibers giving origin to a self-assemble BaTiO$_3$ fiber morphology (figure 4c and d). This preferential arrangement of electroactive ceramic particles is probably due to the difference of density between the polymer matrix and the filler.

The nature of the crystalline phase present in the electrospun BaTiO$_3$/P(VDF-TrFE) fibers can be identified by Fourier transformed infrared spectroscopy (FTIR) and by differential scanning calorimetry (DSC) (fig.5).

FTIR spectra showed that nanocomposite crystallization occurs in the polymer ferroelectric phase due to the presence of the characteristic absorption band at 840 cm$^{-1}$ [27] (figure 5a). It was observed that the changes in the electrospinning processing conditions do not affect polymer crystallization, due to the absence or suppression of absorption polymer bands.

PVDF DSC thermogram shows a peak around 160 °C which corresponds to the melting temperature of the polymer (figure 5b). The DSC thermograms of the PVDF-TrFE show two characteristic peaks: the one at lower temperatures corresponds to the ferroelectric-paraelectric transition and occurs around 117 °C, the second peak correspond to the melting of the paraelectric phase and is located around 145 °C (figure 5b). The DSC thermograms of BaTiO$_3$/P(VDF-TrFE) composites shows the same two peaks, located at the same temperatures, which confirms that the changes in the electrospinning conditions does not change the ferroelectric polymer phase. The inclusion of different filler contents also does not affect the polymer polar phase, as has been demonstrated in previous works. [29]

Piezoelectric properties are being used for sensors and actuators as well as for energy harvesting applications, taking advantage of nanoscale materials such as nanowires, nanorods and nanofibers from PZT, BaTiO$_3$ or ZnO [15, 16, 22].

It has been demonstrated the capability of PVDF film, [17] PZT [15] and BaTiO$_3$ [16] fibers as energy harvesters one the materials have been processed and poled. It was also
demonstrated that the electrospinning process gives origin to obtain electrically poled fiber in a single step production process due to the high electric field involved in the electrospinning process [30].

BaTiO$_3$/P(VDF-TrFE) composite fiber as well as pure PVDF and P(VDF-TrFE) electrospun fibers were directly spun into a interdigitated array at an electric field of 1.25 kV/cm, a needle inner diameter of 0.5 mm, a flow rate of 1 ml/h and a distance between the tip and the collector of 20 cm, without further electrical poling, and submitted to a periodic bending oscillation at different frequencies. The energy harvesting device was then subjected to mechanical excitations in the frequency range from 1 Hz to 1 MHz using a vibration generator (figure 1). The generator device is represented in figure 1, in which the polymer and polymer/ceramic fibers are working in longitudinal mode with the alternating pressure results in surface charge variations in the fibers due to their combined tensile and bending stresses. A voltage difference between two adjacent electrodes is thereby induced, the interdigitated electrodes enhances the power output of the generator as the piezoelectric fibers between each pair of adjacent electrodes results in a power generating unit connected in parallel to other units.

In order to align the fibers, the interdigitated electrodes were grounded on the two terminals in a process similar to the one suggested by Ramakrishma et al. [18]. The distance between the anode and the cathode was about 0.5, 0.2 and 0.1 mm as showed in figure 1b.

The piezoelectric fiber generators were tested under two different conditions. In the first one, the output voltage of the PVDF, P(VDF-TrFE) and BaTiO$_3$/P(VDF-TrFE) (20 % ceramic loading at the different filler average sizes) electrospun fibers was measured by applying a periodic deformation at different frequencies. As presented in figure 6, the generated voltage induced by the piezopotential reached 180 mV for the PVDF fibers. On the other hand, P(VDF-TrFE) fibers showed a piezopotential around 100 mV and the electrical output voltage measured for the BaTiO$_3$/P(VDF-TrFE) electrospun fibers decreases with increasing ceramic particle average diameter for a fixed fiber loading. An average piezopotential of ~100 mV was found for the fibers with BaTiO$_3$ particles of ~10 nm, which is close to the one found for the pure polymer matrix, the piezopotential strongly decreasing with increasing filler size (figure 6c). The negative
voltage signal observed in figure 6a is generated due to the reverse flowing carriers when the external load is removed and the piezopotential vanish. The power generated by the fibers promoted by the periodic harmonic vibration can be calculated through:

\[
P_L = \frac{1}{T} \int_0^T \frac{V_0(t)^2}{R_L} dt
\]

where \(V_0(t)\) is the real time voltage, \(R_L\) is the load resistance and \(T\) is the period of load application.

In the present setup where the fibers are attached to each pair of adjacent electrodes, the piezoelectric coefficient that mostly contributes for the electrical output voltage is the one along the fiber longitudinal direction, commonly denominated as \(d_{31}\), where the polymer chains are stretched along the fiber and the output electrical signal is measured in the same direction.

Goldfard and Jones [31] investigated the efficiency of a piezoelectric material in a stack configuration for converting mechanical harmonic excitation into electric energy. In general, the conversion efficiency can be improved with a larger coupling coefficient and smaller damping. Table 1 shows the characteristic electroactive properties of PVDF, P(VDF-TrE) and BaTiO₃.

**Table 1.** Characteristic physical properties of electroactive PVDF, [32] P(VDF-TrFE) [33] and BaTiO₃ [26].

Table 1 shows that piezoelectric coefficients of the ceramic filler and its electromechanical coupling coefficient are larger than for the pure polymer and therefore will tend to increase electromechanical conversion and therefore power output. On the other hand, the electromechanical system can be modeled by a coupled spring-mass-damper system, [34] and in the case of the BaTiO₃/P(VDF-TrFE) the ceramic nanoparticles acts as a defect for the fibers (figure 4), contributing for the increase of the damping of the composite fibers and consequently for the decrease of the mechanical to electrical energy conversion. As observed in figure 6, the reduction of the electromechanical conversion due to increased damping is larger than positive
contribution of the larger coupling coefficient of the fillers, resulting in an overall decrease of the power output. It is to notice that, despite the larger electromechanical coupling coefficient, the output power for P(VDF-TrFE) fibers is also lower due to lower piezoelectric coefficient and larger damping due to the increase stiffness due to the (VDF) content. Additional contributions to the decrease of the output power in the composites can arise from the random orientation of the BaTiO$_3$ electroactive domains, leading to an overall reduction of the effective dipolar moment of the electroactive composite fibers when compared to the single polymer. The piezoelectric coefficients of organic and inorganic phases are opposed, which can lead to counteract effects. [35, 36]

Consequently, the maximum output power is obtained for the PVDF fibers (~0.03 μW) and a decrease of the generate power was observed for the P(VDF-TrFE) and for the BaTiO$_3$/P(VDF-TrFE) fibers (figure 6d). It is interesting to notice that the output power is nearly frequency independent in the 100 Hz to 10 MHz frequency range under study, which is interesting for a broad range of applications. The composite fibers do not show response frequencies below to 100 Hz, whereas the polymer fibers still show reasonable responses due to the lower stiffness.

In order to study the effect of larger deformations on the output voltage of the electroactive polymer fibers and fiber composites, the finger (previously protected by an insulator glove in order to prevent interferences from human bioelectricity) were used to apply a periodic dynamic loading on the top of the generator by simple tapping during which, the positive and the negative output voltage was measured (figure 7). The highest output voltage record during the finger experiment was 5.02 V, leading to conclude that amplitude of the voltage output depends on the amount of the strain imposed to the surface generator, being higher for higher mechanical deformations (figure 7b) as larger strains provide more mechanical energy available for conversion into electrical energy. The maximum output power generated by these higher strains was 25 μW, which confers such piezoelectric vibration-to-electricity converters large interest for micromechanical memory devices [37] and bioaplications in order to harvest human motion to power in-body biosensors.

Chen et al. [15] study the characteristics of a piezoelectric nanowire of only PZT on top of interdigitated electrodes obtained a power generation of ~0.03 μW for an higher deformations. In another work, but with poled BaTiO$_3$, Park et al. [16] obtained by
magnetron sputtering on top of a flexible interdigitated electrodes substrate an under mechanical higher mechanical deformation, also generated same power.

CONCLUSIONS

As a conclusion, the largest energy harvesting efficiency is obtained for the pure poly(vinylidene fluoride) fibers, with power outputs up to 0.03 μW and 25 μW under low and high mechanical deformation. The copolymer and the polymer/ceramic composites show reduced power output due to increased mechanical stiffness. The obtained values, among the largest found in the literature, the easy processing and the low cost and robustness of the polymer, demonstrate the applicability of the developed system.

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Figure and table captions

**Figure 1.** a) Scheme of the experimental setup used for the periodic bending tests; b) Interdigitated electrode plate with electrospun fibers.

**Figure 2.** BaTiO$_3$/P(VDF-TrFE) electrospun membrane obtained at 15/85 polymer/solution and with 5 % BaTiO$_3$ nanoparticles with particle size of $\Theta = 100$ nm: a) 20 kV, b) 35 kV, c) 25 kV and d) backscattering image of sample obtained at 25 kV (image b). Traveling distance of 20 cm, needle inner diameter of 0.5 mm and flow rate of 0.5 mL/h.

**Figure 3.** a) Influence of applied electric field on the mean diameter of the electrospun BaTiO$_3$/P(VDF-TrFE) fibers, the flow rate was 0.5 mL/h and needle inner diameter of 0.5 mm; b) Influence of tip inner diameter on the mean diameter of the electrospun BaTiO$_3$/P(VDF-TrFE) fibers, the flow rate was 0.5 mL/h and applied electric field of 1.25 kV/cm; c) Influence of flow rate on the mean diameter of the electrospun BaTiO$_3$/P(VDF-TrFE) fibers, the tip inner diameter was 0.5 mm and the applied electric field of 1.25 kV/cm; d) Influence of BaTiO$_3$ content on the fiber mean diameter for the electrospun BaTiO$_3$/P(VDF-TrFE) membrane, the tip inner diameter was 0.5 mm, applied electric field of 1.25 kV/cm and a flow rate of 0.5 mL/h. Average filler size: $\Theta = 100$ nm; filler concentration in a), b) and c) 5 %.

**Figure 4.** Influence of BaTiO$_3$ particle average size in the composite fiber diameter: a) 10 nm, b) 500 nm, c) backscattering image of electrospun fibers with 20 % BaTiO$_3$ ($\Theta = 100$ nm) and d) electrospun BaTiO$_3$/P(VDF-TrFE) (20 % BaTiO$_3$ and $\Theta = 100$ nm) membrane obtained at 750 rpm. For all samples, tip inner diameter was 0.5 mm, applied electric field of 1.25 kV/cm and a flow rate of 0.5 mL/h.
**Figure 5.** a) Infrared measurements for the BaTiO$_3$/P(VDF-TrFE) electrospun membranes with a tip inner diameter of 0.5 mm, applied voltage of 25 kV, distance between tip and collector of 20 cm and a flow rate of 1.0 and 8.0 mL/h; b) DSC results for the BaTiO$_3$/P(VDF-TrFE) electrospun membranes with a tip inner diameter of 0.5 mm, applied voltage of 25 kV and a distance between tip and collector of 20 cm and a flow rate of 1.0 and 8.0 mL/h.

**Figure 6.** a) Voltage generated during 6 ms at a frequency of 1 kHz, of an electrospun sample of BaTiO$_3$/P(VDF-TrFE) with 20 % of ceramic; b) maximum voltage generated at different frequencies for all type of samples produced; c) piezopotential obtained at 1 kHz for P(VDF-TrFE) and BaTiO$_3$/P(VDF-TrFE) with 20 % ceramic filler and d) maximum power generated by the electrospun membranes.

**Figure 7.** a) Diagram of a bending test performed with a finger; b) positive output voltage generated during a test performed with finger deformation for the PVDF electrospun fibers.

**Table 1.** Characteristic physical properties of electroactive PVDF, $^{[32]}$ P(VDF-TrFE) $^{[33]}$ and BaTiO$_3$. $^{[26]}$