Evaluation of the Physico-Chemical Properties And Active Response of Piezoelectric Poly(Vinylidene Fluoride-co-trifluoroethylene) As a Function of Its Microstructure

Renato Gonçalves^{†,‡}, Vanessa F. Cardoso^{†,‡}, Nelson Pereira[†], Juliana Oliveira[†], João Nunes-Pereira^{†,‡}, Carlos M. Costa^{†,‡,} and S. Lanceros-Méndez^{‡,‡*}*

[†]Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal.

[‡]CMEMS-UMinho, Universidade do Minho, DEI, Campus de Azurém, Guimarães 4800-058, Portugal

[‡]C-MAST – Centre for Mechanical and Aerospace Science and Technologies, Universidade da Beira Interior, 6200-001 Covilhã, Portugal

[‡]Centro de Química, Universidade do Minho, 4710-057 Braga, Portugal.

[‡]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

[‡]IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

#equal contribution

* **Corresponding Authors** Email: C. M. Costa (cmscosta@fisica.uminho.pt); S. Lanceros-Méndez senentxu.lanceros@bcmaterials.net

ABSTRACT: Poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE), microstructures have been produced using different solvents, including green ones, by different techniques, such as solvent casting, screen-printing, replica molding, electropay and electrospinning. . The obtained microstructures span from simple porous and dense films, to spheres, fibers and patterned three-dimensional architectures, with no significant variation in their physico-chemical and electrical properties. The simplicity, low cost and reproducibility of the processing techniques allied to their versatility to adapt to other materials in order to produce controlled and tailored microstructures with specific properties demonstrate their potential in a wide range of technological applications, including biomedical, energy storage, sensors and actuators and filtration.

1. INTRODUCTION

In the last decades, electroactive polymers (EAPs) have demonstrated high potential as active and functional elements in a wide range of technological applications due to their ability to detect and respond to external stimuli. They have been used as scaffolds for tissue engineering ¹⁻², membranes for energy storage ³ and harvesting ⁴, sensor and actuator systems ⁵, for the development of microelectromechanical (MEMS) systems ⁶, for the development of filtration membranes ⁷, among others.

According to their activation mechanism, EAPs can be divided into electronic and ionic ⁸. While the electromechanical response is originated by the Coulomb forces produced by an electric field in the electronic group, the activation mechanism of the ionic group involves transport or diffusion of ions ⁸.

Piezoelectric polymers are electronic EAP materials that are particularly interesting and useful once they can show relevant electromechanical response, lightweight, excellent mechanical properties, high chemical and thermal stability, low production cost and easy processing in a wide range of design and structures ⁹, which constitutes a key factor for many (bio)technological applications ¹⁰.

Poly(vinylidene fluoride) - PVDF, and its copolymers poly(vinylidene fluoride-trifluoroethylene) - P(VDF-TrFE), poly(vinylidene fluoride-hexafluoropropylene) - P(VDF-HFP) and poly(vinylidene fluoride-chlorotrifluoroethylene) - P(VDF-CTFE) are the most used piezoelectric (co)polymers due to their largest electromechanical response in comparison to others piezoelectric polymers, such as polyimide, polyamides and nylon ¹¹.

PVDF is a semi-crystalline polymer that can exhibit five distinct crystalline phases, known as α , β , γ , δ and ϵ , depending on the processing conditions ¹²⁻¹³.

From a technological point of view, the most important phases are the β -phase, as it shows piezo-, pyro- and ferroelectric properties, and the α -phase, which is thermodynamically

more stable when the material is directly obtained from the melt ¹²⁻¹³. Porous and electroactive PVDF films are usually obtained by crystallization at temperatures below 70 °C, independently of the solvent being dimethylformamide (DMF) or dimethylacetamide (DMAc) ¹⁴⁻¹⁵, the most commonly used solvents for the preparation of PVDF. In turn, dense PVDF films in the β -phase are mostly obtained by applying mechanical stretching to α -phase films at temperatures below 100 °C with a stretch ratio higher than or equal to 2 or by the addition of specific fillers such as ionic liquid ¹⁶, barium titanate (BaTiO₃) ¹⁷, clays ¹⁸ or ferrite nanoparticles ¹⁹. Further, PVDF and copolymers can be processed in the electroactive phase in different morphologies, ranging from spheres and fibers to films and membranes ²⁰.

PVDF copolymer, such as P(VDF-TrFE) with molar ratios of vinylidene fluoride between 50 and 80 %, have been developed in order to crystallize in the polar β -phase, independently of the experimental conditions ²¹. Further, and contrary to PVDF, this copolymer exhibits the ferroelectric (FE) to paraelectric (PE) phase transition at a Curie temperature, $T_c \sim 105$ °C, below the melting temperature, $T_m \sim 150$ °C ²²⁻²³.

Different processing techniques have been used to tailor the microstructure and morphology of these electroactive polymers in order to meet specific application requirements ²⁰. For example, solvent casting ²⁴, screen-printing ²⁵, inkjet-printing ²⁶, electrodeposition ²⁷ and extrusion ²⁸ techniques have been used to process dense films for sensor and actuator applications, while electrospinning ²⁹ and electrospraying ³⁰ allow to obtain fiber mats and sphere for tissue engineering purposes. Also the dip-pen nanolithography technique has already been used for the fabrication of highly oriented microstructures and nanostructures of P(VDF-TrFE) ³¹.

In relation to printing technologies, one of the most relevant printing techniques for the development of applications is the screen-printing due to its simplicity, low cost, reproducibility and versatility ³².

Moreover, thermally induced phase separation ³³ has been also applied for the processing of porous films (membranes) for battery separators and replica molding ³⁴ was employed to obtain complex patterned microstructures to be used in a wide range of (bio)technological applications.

Due to the disperse and diverse information found in the literature and the increasing interest of the aforementioned materials, the present paper shows and summarize the processing of relevant microstructures such as films, membranes, patterned microstructures, spheres and fibers using different processing methods in order to properly assess processing-properties relationships. In order to achieve these objectives, piezoelectric P(VDF-TrFE) copolymer and three different solvents with different boiling points, the commonly used DMF, a “green” solvents 1,3-dioxolane – DXL and N,N’-dimethylpropyleneurea – DMPU, were used. The latter constitutes the base of the present research since it allows minimizing the environmental impact and improve the safety and health issues related to the processing of the materials, without losing their key functional properties ³⁵⁻³⁶. It is important to notice that, beyond P(VDF-TrFE), the processing methods are adaptable not just to PVDF and related copolymers and nanocomposites, but also to others materials including biodegradable polymers, such as poly(L-lactic acid) – PLLA and poly(lactide-co-glycolide) – PLGA polymers, among others.

2. EXPERIMENTAL SECTION

Different processing techniques, including solvent casting, screen-printing, replica molding, electrospray and electrospinning were used in order to process microstructures that fulfill specific applications requirements²⁰. Table 1 illustrates those processing techniques with the corresponding structures and typical dimensions.

Table 1. Representative illustration of the processing techniques and the corresponding microstructures and typical dimensions of the obtained materials.

Processing techniques	Representative image	Structures	Typical dimensions (length × width × thickness)
Solvent coating		Porous and dense films	100 × 50 × 0.028 mm
Screen printing		Dense films	100 × 100 × 0.025 mm
Replica molding		Porous and dense complex patterned structures	76 × 26 × 0.1 mm
Electrospray/ Electrospinning		Semi-spheres, Spheres, Bead fibers, Fibers	Spheres diameter: 0.8 to 5.5 μm Fiber diameter: 120 nm to 2 μm

2.1. Materials

P(VDF-TrFE) (Solvene 250, molecular weight of 150–400 kg.mol⁻¹; 70 wt% VDF content) was supplied by Solvay. The solvents N,N-dimethylformamide (DMF, 99.5%), 1,3-dioxolane (DXL, 99.9%) and N,N' - dimethyl propylene urea (DMPU, 99.0%) were purchased from Fluka, LaborSpirit and Carlo Erba, respectively. SU-8 100 and Sylgard® 184 Silicone Elastomer (PDMS) were purchased from Microchem and Dow Corning, respectively.

2.2. Processing of porous and dense films by solvent casting

P(VDF-TrFE) was dissolved in DXL or DMF solvents with a weight fraction of 9 % under magnetic stirring at a temperature of 50 °C until a transparent and homogeneous solution was obtained. After cooling to room temperature (RT, approximately 25 °C), the copolymer solution was placed on a clean glass substrate, spread using a casting knife with a 50 µm gap and introduced in an air oven (Binder, ED23) at temperatures of 25 °C and 80 °C for DXL and 210 °C for DMF, until complete evaporation of the solvent, in order to prepare porous and dense films, respectively ³⁶.

2.3. Processing of dense films by screen-printing

P(VDF-TrFE) was dissolved in DMPU with a weight fraction of 17 % under magnetic stirring at a temperature of ~ 30 °C until a transparent and homogeneous solution was obtained. The copolymer solution was pressed using a squeegee over the screen (polyester mesh with 62 monofilament by cm) placed at a 100 mm distance from the glass substrate and introduced in an air oven (Binder, ED 23) at 210 °C during 10 minutes.

2.4. Processing of patterned microstructures by replica molding

In order to fabricate patterned P(VDF-TrFE) microstructures, SU-8 and PDMS molds were fabricated adapting a previous protocol³⁴. These two materials are typically used in microfluidic technology and allow developing structures in the micro- and even nanoscale dimension with a wide range of patterned architectures. SU-8 molds were first fabricated through a low-cost photolithography process and used to obtain the PDMS molds by replica molding. PDMS has the advantage of being flexible, transparent, mechanically stable and highly resistant to temperature and to the solvents generally used in the manufacture of polymers such as PVDF. Moreover, SU-8 and PDMS molds can be used repeatedly without losing their properties, making this technique adequate to process patterned polymer microstructures in an effective, inexpensive and reproducible way. In this specific processing technique, DMF was preferably used as solvent due to its lower evaporation rate (boiling point of 153 °C and vapor pressure of 516 Pa) comparatively to DXL (boiling point of 75 °C and vapor pressure of 9333 Pa)³⁷. Therefore, P(VDF-TrFE) with a weight fraction of 15 % was prepared similarly to the procedure described in the previous section. After cooling to RT, the P(VDF-TrFE) solution was transferred to the PDMS mold and placed in an air oven at 25 °C during 1 week in order to obtain a porous patterned microstructure. Dense microstructures can be obtained in a similar way rising the evaporation rate by increasing the solvent evaporation temperature to values higher than 70 °C³⁴. Finally, the patterned P(VDF-TrFE) microstructures were gently removed from the PDMS molds.

2.5. Processing of electrospun fiber mats and electrosprayed spheres

Solutions of P(VDF-TrFE) were prepared with weight fractions of 3, 7, 15 and 18 %, using DXL as solvent. The solutions were kept under magnetic stirring for 2 h at RT to ensure the complete dissolution of the copolymer, and then introduced into a plastic syringe connected to a flux regulator. In order to create a jet, high voltage was applied between the syringe needle and an aluminum foil (collector), where the different structures were collected forming a mat. The deposition conditions used were 10 kV bias with a PS/FC30P04 power source from Glassman, 0.5 mm needle inner diameter, 0.4 ml.h⁻¹ flow rate and 20 cm needle-collector distance.

2.6. Sample characterization

Surface and cross section of the P(VDF-TrFE) microstructures was obtained by scanning electron microscopy (SEM) (NanoSEM – FEI Nova 200) with an accelerating voltage of 10 kV. Fourier transformed infrared spectroscopy (FTIR) was used to identify the copolymer crystalline phase. Measurements were performed with a Jasco FT/IR-4100 system in attenuated total reflectance (ATR) mode from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹ and 64 scans. Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851e Mettler Toledo apparatus under a high purity nitrogen atmosphere (99.99 % minimum purity) and a flow rate of 50 mL.min⁻¹. Samples of approximately 4 mg were placed in an aluminum oxide crucible and heated from 25 to 800 °C at 10 °C.min⁻¹. Differential scanning calorimetry (DSC) was used to measure the melting temperature and the degree of crystallinity of the copolymer. These measurements were performed in a DSC 822e Mettler Toledo, using samples of 4 mg, under a nitrogen atmosphere in aluminum pans. Measurements were carried out from 25 to 200 °C at a heating rate of 10 °C.min⁻¹.

Dielectric measurements were performed with a Quadtech 1929 Precision LCR meter at 25 °C in the frequency range from 20 Hz to 1 MHz with an applied voltage of 0.5 V in dense films with circular gold electrodes (5 mm diameter) deposited by magnetron sputtering (Polaron Coater SC502) to obtain the parallel plate condenser geometry. Dielectric loss and capacity were measured and the dielectric constant was obtained taking into account the geometrical characteristics of the sample.

The piezoelectric coefficients, d_{33} , were measured for dense films (d_{33} meter APC YE2730A) previously subjected to corona discharge within a home-made corona chamber, after an optimization procedure, with an applied voltage of 10 kV at a constant current of 20 μ A, constant distance of 2 cm between sample and tip, poling time of 1 hour and poling temperature of 120 °C.

3. RESULTS AND DISCUSSION

In the following sections, the obtained P(VDF-TrFE) microstructures are presented, together with their main physico-chemical properties.

3.1. P(VDF-TrFE) structures

3.1.1. Porous and dense films

Porous and dense films were obtained by solvent casting and screen-printing varying the solvent evaporation temperature and the copolymer concentration between 9 and 17 wt.%. The influence of the weight fraction in the P(VDF-TrFE) microstructure can be found in a previous work ³⁶, where it was demonstrated that the microstructure remains approximately constant, independently of using DXL, DMPU or DMF as a solvent, for the same solvent evaporation temperature. Further, as it has been reported for DMF ²³, the solvent evaporation temperature of DXL and DMPU proved to have a significant role on the final morphology of the films, as it is presented in Figure 1.

Figure 1. Representative SEM images of the surface of the P(VDF-TrFE) solvent casted and screen-printed films (with an amplified view in the inset). Films obtained by solvent casting from DXL and dried at 25 °C (a) and 80 °C (b). Films obtained by screen-printing from DMPU and dried at 210 °C (c). Films obtained by solvent casting from DMF at 210 °C (d).

In fact, while at 25 °C rough films with a porous morphology are obtained, increasing the solvent evaporation temperature to 80 °C, the porosity disappears, and smoother and dense films are obtained. In the first case, i.e. porous films, irregular pore sizes are observed with dimensions below 5 μm.

These results are explained in terms of the biphasic P(VDF-TrFE)/DXL phase diagram presented in Figure 2, where the blue stars indicate the copolymer weight fraction and solvent evaporation temperature of the processed films.

Figure 2. Phase diagram of the binary P(VDF-TrFE)/DXL system.

The phase diagram shows three main regions: stable, metastable and instable that are separated by the binodal and spinodal lines. The liquid-liquid separation process that gives rise to porous morphologies, as the one obtained at RT (Figure 1a), occurs in the metastable region, i.e., in the region between the spinodal and binodal lines, which is dominated by nucleation and growth³⁸. Further, in this section of the phase diagram, the polymer chains present a reduced mobility hindering the copolymer to occupy the free space left during the evaporation of the solvent²⁴.

Increasing the solvent evaporation temperature to 80 °C, no liquid-liquid phase separation occurs, being the samples located outside the binodal line and therefore dense P(VDF-TrFE) films are obtained (Figure 1b). This temperature was chosen considering the low

boiling point and high vapor pressure of DXL compared to DMF, as indicated previously³⁷.

Comparing to the P(VDF-TrFE)/DMF system²⁴, it is concluded that the solvent properties affects not just the phase diagram but also the porous morphology of the P(VDF-TrFE) copolymer. In fact, using DMF as solvent interconnected and well defined pores are obtained, contrarily to the heterogeneous porosity verified using DXL. Nonetheless, both of them are porous and can be used as membranes or scaffolds for a wide range of biotechnological applications³⁹⁻⁴⁰. Outside the binodal line and independently of the solvent used, smooth and dense films useful for sensors and actuators applications are obtained^{8,41}.

For the production of dense films by printing technologies, the DMPU solvent can be the ideal green solvent when compared to DXL, once it has similar physical properties to those of DMF, including dielectric constant and dipole moment⁴². The final morphology of the dense films using DMPU and DMF as solvent is shown in Figure 1c) and d), respectively. Thus, it is shown that the printing technique does not affect the morphology of the samples and that DMF can be substituted by DMPU.

3.1.2. Three-dimensional patterned microstructures

3D patterned P(VDF-TrFE) microstructures were fabricated using replica molding technique. As previously indicated, the procedure involves the fabrication of PDMS molds by replica molding using pre-fabricated SU-8 molds. In this work, two different P(VDF-TrFE) microstructures are presented based on arrays of wells and pillars with dimensions of 250 μm (diameter/height/depth) separated by the same dimensions.

Representative SEM images of the surface of the patterned P(VDF-TrFE) microstructures are presented in Figure 3. In the present case, DMF was preferably used as solvent instead

of DXL due to its lower vapor pressure. In order to use DXL, the PDMS molds must first be subjected to a plasma oxygen treatment in order to reduce the hydrophobicity of the surface and favour the entry of the solution into the wells ⁴³⁻⁴⁴. It is important to notice that, in any case, this technique can still be used, regardless of the polymer and solvent.

Figure 3. Representative surface SEM images and amplified views (insets) of patterned P(VDF-TrFE) microstructures obtained by replica molding: arrays of (a) wells and (b) pillars.

Patterned P(VDF-TrFE) microstructures constituted by highly porous arrays of wells and pillars were obtained at RT. Increasing the solvent evaporation temperature leads to a decrease of the degree of porosity and pore size due to faster evaporation rate. Further, solvent evaporation can occur in a region of the phase diagram (see Figure 2 for the phase diagram of P(VDF-TrFE) with DXL, which shows similar characteristics ²⁴) with no phase separation, avoiding the formation of pores and leading to arrays of dense wells and pillars ³⁴. The dimensions and architectures of the final copolymer microstructures can be adjust depending of the application requirements during the processing of the SU-8 molds, while the morphology depends mostly on the solvent evaporation temperature.

3.1.3. Microspheres and electrospun fiber mats

The influence of the P(VDF-TrFE)/DXL weight fraction in the microstructures obtained by electrospinning/electrospray was evaluated keeping the voltage, flow rate, distance between the collector and the tip of the syringe constant. The influence of the copolymer solution concentration and processing parameters, such as electric field, flow rate and inner needle diameter, on spheres and fibers size and distribution were already studied for P(VDF-TrFE) copolymer⁴⁵ and DMF solvent³⁰. Representative SEM images of the obtained microstructures are presented in Figure 4.

Figure 4. Representative SEM images of P(VDF-TrFE) microstructures obtained by electrospinning with P(VDF-TrFE)/DXL weight fractions of (a) 3 and (b) 7 wt.%, and electrospinning with weight fractions of (c) 15 and (d) 18 wt.%. Insets images show magnifications of the corresponding microstructures.

The results show that the copolymer concentration has a significant role on the final microstructure: At low copolymer concentrations, i.e. 3 and 7 wt.%, P(VDF-TrFE) semi-spheres (Figure 4a) and spheres (Figure 4b) are obtained by electrospraying, respectively. Increasing the copolymer concentration to 15 and 18 wt.%, beaded fibers (Figure 4c) and fibers (Figure 4d) are achieved by electrospinning, respectively.

The surface tension is a critical issue in order to control the copolymer microstructure. In a spherical microstructure, polymer entanglement is not achieved and the jet suffers some perturbation due to the capillary instability. This capillary instability is originated due to the low viscoelastic force, which is not able to match the electrostatic and columbic repulsion forces that stretch the electrospinning jet ⁴⁶ (Figures 4a and 4b). Therefore, for copolymer concentrations below 7 wt.%, the obtained spherical structures show an average diameter of $4.5 \pm 2 \mu\text{m}$ ⁴⁷. Moreover, at much lower concentration, i.e. 3 wt.%, it is also observed the collapse of the copolymer microstructures forming hollow semi-spheres. When the capillary force is almost stable the bead fiber is formed (Figure 4c) ⁴⁵. P(VDF-TrFE) bead fibers result when the copolymer concentration is between 7 and 15 wt.%. Further, by increasing the copolymer concentration, the density of the beads decreases changing its shape to oval form until reaching the fiber structure. Finally, by further increasing the solution concentration, the fiber diameter also increases (Figures 4c and 4d) due to the higher viscosity of the solution. The transition from beads to fibers is associated to the entanglement of the copolymer macromolecular chains in the solution when the copolymer concentration is 2 to 2.5 times the entanglement concentration (C_e) ^{46, 48}. C_e rises with increasing degree of branching due to the higher density of the branched copolymer segments hindering chain overlap. Therefore, the microstructure shown in Figure 4d is just composed by fibers with a diameter of $1.65 \pm 0.56 \mu\text{m}$.

The influence of the copolymer concentration on the different microstructures produced by electrospray and electrospinning is summarized in Figure 5.

Figure 5. Schematic diagram of the influence of P(VDF-TrFE)/DXL solution concentration in the production of the different electrospray and electrospinning microstructures.

3.2. P(VDF-TrFE) physico-chemical properties

The crystalline phase and thermal characterization of the P(VDF-TrFE) samples were performed to verify if the main properties of the material are influenced by the different processing technique used for obtaining the different microstructures.

FTIR-ATR spectroscopy was used to identify the copolymer phases of the different P(VDF-TrFE) samples (Figure 6a).

Figure 6. Representative (a) FTIR spectra; (b) TGA thermograms; (c) DSC curves; and (d) melting temperature and degree of crystallinity of the P(VDF-TrFE) microstructures.

Independently of the processing technique and experimental conditions all samples show the same infrared spectra with the main adsorption bands corresponding to the polymer chain *all-trans* conformation²⁴. In fact, the infrared spectra show the characteristic

electroactive β -phase vibration modes at 840 cm^{-1} , 877 cm^{-1} and 1285 cm^{-1} (identified in the figure by the arrows) that represent CF_2 and CC symmetric stretching, CH_2 and CF_2 rocking and CF_2 antisymmetric stretching, and CH_2 and CC symmetric stretching and CCC scissoring, respectively ⁴⁹.

Regarding the TGA thermogram (Figure 6b), the same degradation behavior with a single degradation step between 430 and $500\text{ }^\circ\text{C}$, characteristic of the $\text{P}(\text{VDF-TrFE})$ copolymer is observed, which is explained by the chain-stripping where carbon-hydrogen scissions occur, leading to the formation of hydrogen fluoride ³⁶. The residual weights after complete degradation range from 2 to 15 %.

Further, two endothermic peaks are observed in the DSC thermograms that correspond to the ferroelectro (FE)-paraelectric (PE) phase transition at approximately $102\text{ }^\circ\text{C}$ and melting temperature of the PE phase at around $148\text{ }^\circ\text{C}$ (Figure 6c) ⁵⁰. Once again, the used processing techniques and conditions do not affect the main characteristics of the $\text{P}(\text{VDF-TrFE})$ samples. The degree of crystallinity ($\Delta\chi$) is calculated by:

$$\Delta\chi = \frac{\Delta H_f}{\Delta H_{100}} \quad (1)$$

where ΔH_f is the melting enthalpy of the sample and ΔH_{100} is the melting enthalpy for a 100 % crystalline sample ($\Delta H_{100} = 103.4\text{ J.g}^{-1}$ ¹²). The results are presented in Figure 6d. While the melting temperatures of the different $\text{P}(\text{VDF-TrFE})$ samples shows a small variation, within experimental error, between 147 and $150\text{ }^\circ\text{C}$, the degree of crystallinity shows a higher variation between 15 and 30 % certainly explained by the different copolymer concentration used in each experiment and by the use of different solvents. It can be observed that the crystallization dynamic is affected by the different copolymer concentration of polymer/solvent solution, i.e., for low concentration the crystallization process occurs faster, leading to a lower degree of crystallinity ⁵¹ for microspheres and electrospun fiber mats. For samples obtained by doctor blade and screen-printing

technique a different solvent was used, leading also to a lower degree of crystallinity, as it has been demonstrated that the degree of crystallinity is dependent of the solubility of the polymer in each solvent ⁵².

3.3.P(VDF-TrFE) electrical properties

For sensors and actuators applications, it is important to evaluate the dielectric and piezoelectric properties of the dense films produced by solvent casting (dense film) and screen-printing (printed film) techniques.

Figure 7a shows the variation of ϵ' for the dense and printed films as a function of frequency. This behavior is similar for both films with ϵ' decreasing with increasing frequency ⁵³.

The values of the dielectric constant shown in figure 7a are similar to the ones reported in the literature for P(VDF-TrFE) polymer ⁵⁴ and the small differences are a consequence of the morphological and microstructural variations occurring due to the different processing conditions.

Figure 7. (a) Dielectric constant and (b) modulus of the piezoelectric d_{33} coefficient for the dense and printed films.

Figure 7b shows the d_{33} piezoelectric coefficient for both samples as a function of time in order to evaluate the stability of the signal. Between experiments, the samples were

stored in a dust free environment under ambient conditions. It is observed that the piezoelectric response is stable after 4 weeks. After this time, the d_{33} piezoelectric coefficient is 25 and 17 pC/N for dense and printed films, respectively, the values obtained in this work being similar to the ones reported in the literature, i.e, 23.9 pC/N⁵⁵ and 14 pC/N⁵⁶. Again, the observed differences are related to the degree of crystallinity of these samples and also variations in the microstructural features attributed to the different processing technologies and conditions and not by the technique itself. The degree of crystallinity has important role in the d_{33} piezoelectric response, which increases with increasing degree of crystallinity⁵⁷. The initial variation of the piezoelectric d_{33} coefficient as a function of time for both samples is related to relaxation phenomena in the dipolar and crystalline structure^{55,57}.

In conclusion, the main physico-chemical and electrical characteristics of the P(VDF-TrFE) microstructures, including polymer phase, degradation and melting temperature, degree of crystallinity, dielectric constant and piezoelectric responses are independent of the experimental conditions used for the preparation of the different structures and fit the requirements for the different applications that will be described in the following section.

3.4. Microstructures vs. applications

Certain devices and systems need require specific and precise microstructures and properties to meet demanding application requirements. Thus, the different microstructures produced in this work can find application in different areas, including biomedical, energy storage, sensors and actuators and filtration (Figure 8), and are prepared by simples, reproducible and low-cost technologies.

Figure 8. P(VDF-TrFE) microstructures and the corresponding application areas.

Thus, novel tissue engineering strategies require piezoelectric scaffolds with tailored microstructures for effective control of cells expansion and differentiation ^{2,40}. The same occur in pharmacology where these properties have a leading role in the controlled release of drugs ⁵⁸⁻⁵⁹. In the area of energy storage, such as in the development of lithium-ion batteries, the control of the microstructure and morphology of the separator membrane affects directly the performance of the battery ⁶⁰. The same occurs with the porosity of the films (membranes) used in filtration where pore size and degree of porosity should be determined specifically for the compounds to be filtrated ⁶¹⁻⁶². In sensors and actuators systems, the morphology and electroactive properties of the copolymer delineate their possible applications ^{13, 54}. In addition, these P(VDF-TrFE) microstructures have been proven to be suitable for related technological applications such as magnetoelectric ⁶³ and photocatalytic ⁶⁴ applications ³⁹, water purification systems ⁶¹, among others.

4. CONCLUSIONS

P(VDF-TrFE) microstructures with different architectures and morphologies were fabricated through simple, low cost and reproducible procedures involving solvent casting, screen-printing, replica molding and electrospray/electrospinning techniques. Porous and dense films were fabricated through solvent casting and screen-printing techniques using different solvent evaporation temperature. Patterned P(VDF-TrFE) microstructures were fabricated by replica molding using prefabricated molds obtained by common microfluidic processing technologies. In this case, different kind of architectures, morphologies and dimensions can be processed in order to meet specific requirements. By electrospray/electrospinning techniques microstructures ranging from semi-spheres to fibers were produced varying the copolymer concentration. Through the physico-chemical and electrical characterization, it was possible to conclude that the various microstructures obtained through the different techniques used do not significantly affect the copolymer phase, degradation and melting temperature, degree of crystallinity, dielectric constant and piezoelectric coefficient of the samples. Therefore, these structures demonstrate high potential in a wide range of (bio)technological applications from biomedical, energy storage, sensors and actuators, to filtration, among others. Moreover, all techniques used are adaptable to related PVDF copolymers and composites, among others, and demonstrate the versatility of materials, structures and properties that can be obtained.

AUTHOR INFORMATION

Corresponding Author

C. M. Costa (cmscosta@fisica.uminho.pt); S. Lanceros-Mendez
(senentxu.lanceros@bcmaterials.net)

Author Contributions

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Notes

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