# Electroactive poly(vinylidene fluoride) based materials: recent progress, challenges and opportunities

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**Abstract:** A poly(vinylidene fluoride) (PVDF) and its copolymers are polymers that, in specific crystalline phases, show high dielectric and piezoelectric values, excellent mechanical behavior and good thermal and chemical stability, suitable for many applications from the biomedical area to energy devices. This chapter introduces the main properties, processability and polymorphism of PVDF. Further, the recent advances in the applications based on those materials are presented and discussed. Thus, it shown the key role of PVDF and its copolymers as smart and multifunctional material, expanding the limits of polymer-based technologies.

**Keywords**: PVDF; copolymers; properties; polymorphism; applications

1. **Introduction**

The dramatic growth and densification in the modern cities require smart solutions to address critical demands such as mobility, healthcare, energy, and infrastructure. The Internet of Things (IoT) is one of the most promising enabling technologies for tackling these challenges by giving rise to a huge number of interconnected physical objects, sensors and networks [1]. For the effective communication to be possible between all those objects/materials, smart materials, and particularly piezoelectric and pyroelectric materials will play a relevant role, once these smart materials will provide the base for strain and vibration sensors, among others [2].

Even knowing that PVDF's piezoelectric/pyroelectric coefficients (including those found in its copolymers) are lower than those reported on ferroelectric ceramics (Table 1), PVDF, its copolymers (poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and poly(vinylidene fluoride-cochlorotrifluoroethylene) (PVDF-CTFE)), and PVDF-based composites have some key advantages for sensing applications such as the high softness and flexibility, the light weight, the low electrical permittivity and thermal conductivity, together with the impedance matching to air and water [3].

**Table 1.** Piezoelectric and pyroelectric properties of PVDF, P(VDF-TrFE) 70/30 and Lead zirconate titanate (PZT).

| Coefficient | Unit | PVDF | P(VDF-TrFE) 70/30 | PZT |
|---|---|---|---|---|
| Piezoelectric ($d_{31}$) | $pCN^{-1}$ | 8 to 22[4] | 12[3] | -123[5] |
| Piezoelectric ($d_{33}$) | | −24 to −34[6] | -38[7] | 289[5] |
| Pyroelectric ($p_3$) | $\mu Cm^{-2}K^{-1}$ | 25[5] | 31[4, 5] | 289[5] |

For those reasons PVDF's piezoelectric effect has been widely used in technological applications that require the detection of mechanical excitations such as pressure, force, strain (both compressive and tensile), vibrational, tactile awareness, acceleration and acoustic signals, among others [3]. This strong interest is also intimately related to the PVDF's broad frequency bandwidth, high sensitivity, strong robustness, easy processing, high environmental and chemical stability, and reliability. However, the most enviable

feature of PVDF-based sensors is that, as intrinsic charge generators, are self-powered [8, 9].

This particular attribute is an important milestone for sustainability, processability and integrability in mobile, wearable and hard-to-access devices and objects, over competing sensor technologies such as capacitive or resistive [8, 10].

This chapter presents the main properties and processability of poly(vinylidene fluoride) (PVDF). In addition, an overview of the main applications of this polymer, which stands out from other polymers due to its electro-activity, are described.

## 2. PVDF and copolymer: processing, polymorphism and main properties

Polyvinylidene fluoride (PVDF) is a fluorocarbon polymer, which results from the polymerization of vinylidene fluoride (VDF) monomers with a chemical formula $(-CH_2-CF_2-)_n$ [11]. It presents chemical and thermal stability (glass temperature ~ -34 ºC and melting temperature between 160 to 189 ºC) [12] and excellent mechanical properties [13] (tensile modulus: > 1.5 GPa depending of the thickness) [14, 15].

Polyvinylidene fluoride (PVDF) is known for its piezo, pyro and ferroelectric properties, related to its semi-crystallinity. It shows a typically radial symmetric spherulitic structure, where crystalline lamellar crystals are incorporated into an amorphous region of the polymer matrix [16, 17]. The difference in electronegativity between the atoms of carbon and fluorine give rise to the dipolar moments [18].

PVDF can crystallize in different polymorphs known as: α, β, γ and δ, the the most common phases being the α-phase and β-phase: the α- phase is thermodynamically more stable when processing from the melt and the β-phase has the highest electroactive properties. The unit cell for theses phase is presented in figure 1 [19].

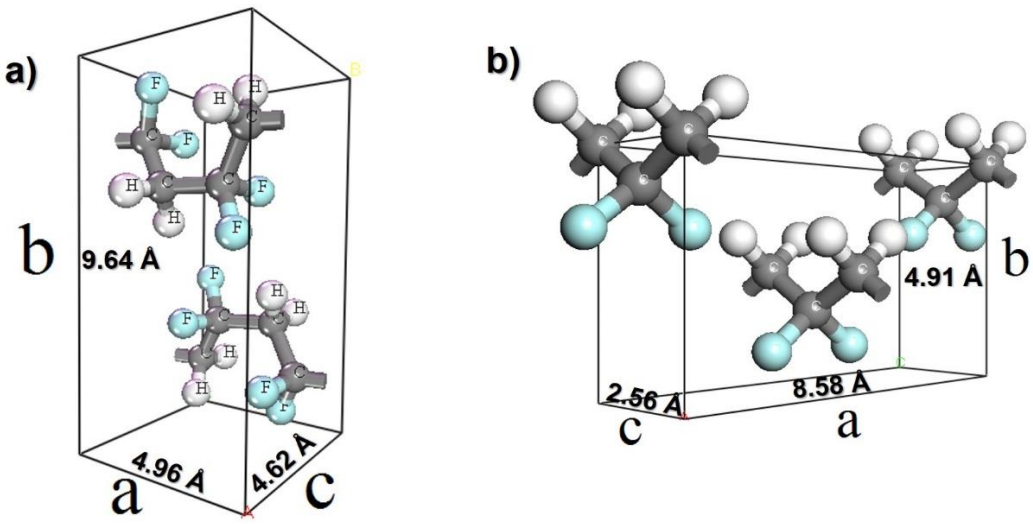



**Figure 1.** Unit cell for α-phase (a) and β-phase (b).

The α-phase unit cell is formed by two macromolecules and is nonpolar, showing a trans-cis conformational structure ($TCTC^-$) as represented in figure 1 a). A β-phase unit cell shows a polar structure, belonging to the space group Cm2m (C2V) and displaying a planar zigzag (TT) conformation with a deflection of 7 ° between the carbon-fluorine bonds (figure 1b) with the electric moment of $7.0x10^{-30}$ Cm approximately perpendicular to the direction of the chains [20]. The different crystalline phases of PVDF can be obtained through different thermal, mechanical and electrical treatments.

The α-phase of the PVDF is obtained from solution casting when solvent evaporation occurs above 120 ° C [21].

The β-phase of PVDF can be obtained through different procedures, including solution casting and crystallization at temperatures below 70ºC regardless of solvents (leading generally to a porous morphology), mechanical stretching of α-phase at temperatures below 100 º C and stretch ratio higher than or equal to 2 or with addition of different fillers ($CoFe_2O_4$, $BaTiO_3$, clay, or ionic liquids, among others) [3].

In relation to their solubility, PVDF can be dissolved in different polar solvents, such as Tetrahydrofuran (THF), Methyl Ethyl Ketone (MEK), Dimethyl Formamide (DMF), Dimethyl Acetamide (DMA), Tetramethyl Urea (TMU), Dimethyl Sulfoxide (DMSO), Trimethyl Phosphate (TMP) and N-Methyl-2-Pyrrolidone (NMP), the solubility depending on the molecular weight [22]- PVDF is not soluble in alcohols or acids [23].

With respect to the processing techniques, PVDF can be produced by doctor blade, spin coating, printing technologies, electrospinning, or electrospraying, in many different

morphologies: from film to membranes or patterned structures [24]. Further, it can be also processed by the conventional processing methods of thermoplastics, such as extrusion or injection molding.

PVDF piezoelectric characteristics are related to the crystalline part of the polymer and, in order to maximize its behavior and apply in some technologies, the poling process is required [13].

Poling is basically the application of electric field (MV/m) through the corona process or parallel plates configuration for the orientation of the dipolar moments of PVDF [25].

With respect to its copolymers, the addition of trifluoroethylene (TrFE), hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE) on vinylidene fluoride (VDF) reduces the degree of crystallinity which, for some applications is suitable (e.g. battery applications) and increases flexibility [26].

For sensor and actuator applications, the most widely used copolymer is PVDF-TrFE ad for specific molar ratios of VDF and TrFE, the polymer crystallizes in all transplanar chains, TT, similar to the β-phase of PVDF, regardless of processing conditions and techniques.

For energy storage applications, PVDF-HFP is widely used as a separator because of its low degree of crystallinity, which allows high lithium mobility, good electrolyte solution affinity and excellent mechanical properties.

Thus, PVDF and its copolymers are characterized by their electroactive properties, chemical, thermal and mechanical stability and for being processable in different shapes and formats, allowing a wide range of applications, as it will be presented in the following.

## 3. Applications

PVDF is used in many applications including sensors, actuators, environmental, biomedical and energy applications.

### *3.1.Sensors*

For PVDF sensor applications, it is essential its sensitivity and electromechanical coupling coefficient k, being the sensitivity highly dependent on the piezoelectric voltage coefficient g. In practice, the generated voltage signal is very small and has to be enhanced by an electronic amplifier [27]. The electromechanical coupling coefficient k is used to describe the conversion efficiency between electrical and mechanical energy, according to Eq. 1 and Eq. 2 [27]; where d refers to piezoelectric coefficient, K refers to dielectric constant, $\varepsilon_0$ refers the permittivity of free space, and s to the compliance. Thus, larger g and k require larger d and smaller ε. Though, a higher ε is still necessary to overcome dielectric losses.

$$g = \frac{d}{K\varepsilon_0} \tag{1}$$

$$k^2 = \frac{d^2}{K\varepsilon_0 s} \tag{2}$$

From the pioneer theoretical study of S. Lang *et al.*[28] reporting the development of a piezoelectric palpation system composed by an array of PVDF-based sensors that are pressed with a uniform stress against a soft biological tissue that has on its composition embedded hardened regions, and the first PVDF insole multisensor for pedobarography (study of the pressure distribution under the foot in standing and walking animals) report from A. Pedotti *el al.*[29], both in the beginning of the 1980's decade, almost 16000 papers have been devoted to the topic «*PVDF for sensor applications*». For comparison, a total of 55000 papers have included PVDF in their topic (SCOPUS database, 18/09/2019). The key innovations are new structures or preparation technologies for improved performances, or new application areas that have rarely employed PVDF-based sensors[27], being widely-used in tactile sensors for detecting dynamic tactile parameter such as contact forces.

Pressure sensors are the main application area of PVDF-based materials, being the work of A. Shirionov *et al.*[30] a good example of this, once it was reported a new pressure sensor with a PVDF foil, that is a low-cost alternative for the accurate measurement (≈3V output for a ≈200 kPa input) of pressure changes in chemically aggressive media with a

limited need for accuracy. This type of sensor can be used in the biomedical area, namely in endoscopic graspers with high sensitivity (50V/N), a large dynamic range (near static up to a few megahertz), and a high signal-to-noise ratio[31].

On the cases when sensors are needed to measure small deformations such as wearable cardiorespiratory signal sensor devices for monitoring sleep conditions, electronic components (amplifiers) can magnify the signal to a certain levels[32]. The applicability range of PVDF sensors for vital signal measurements was improved by Y. Wang *et al.* [33] opening new directions such as sensing garment pressure, blood pressure, heartbeat rate, respiration rate and accidental impacts on the human bodies. In this sense, PVDF nanofibrous fabrics were prepared by using electrospinning technique and exhibited excellent sensitivity (42.00 $mV.N^{-1}$) and response to external mechanical forces (≈4N).

Once PVDF shows not just piezoelectric properties, but also strong pyroelectric properties ones (dipolar variation in a material upon temperature variation)[30], it can be used as a pyroelectric sensor, as shown by S. Pullano *el al.* [34] by presenting a ferroelectric polymer-based temperature sensor designed for microfluidic devices. The performance of the PVDF pyroelectric sensor (0.3 V voltage variation for a temperature range of 25–65 °C) can be improved with the incorporation of microsystems such as low-noise CMOS charge amplifiers and filtering stages on a silicon platforms.

By adding 2 wt.% (weight percentage) of functionalized graphene into PVDF, V. Eswaraiah *et al.*[35] optimized the strain sensing performance (200 MPa stress for a 500 s time) on the macro-scale under tensile loads, useful for practical applications such as addressing challenges in advanced aerospace, mechanical, bionics and medical technologies. With the use of different carbonaceous nanofillers (w-layer graphene (FLG) nanoplatelets (G-NPL), graphene oxide (GO) and reduced graphene oxide (rGO) and single-walled carbon nanohorns (SWCNH)), P Costa *et al.*[36] increased the electrical conductivity nine orders of magnitude, from $\sigma \approx 5 \times 10^{-11}$ $S.m^{-1}$ from pure PVDF to $\sigma \approx 1 \times 10^{-2}$ $S.m^{-1}$ for rGO/PVDF composites, with 5 wt.% nanofillers and reaching with linearity and gauge factors≈ 11 for deformations between 0.5 and 2 mm (Figure 2), very suitable for piezoresistive strain sensing applications [36].

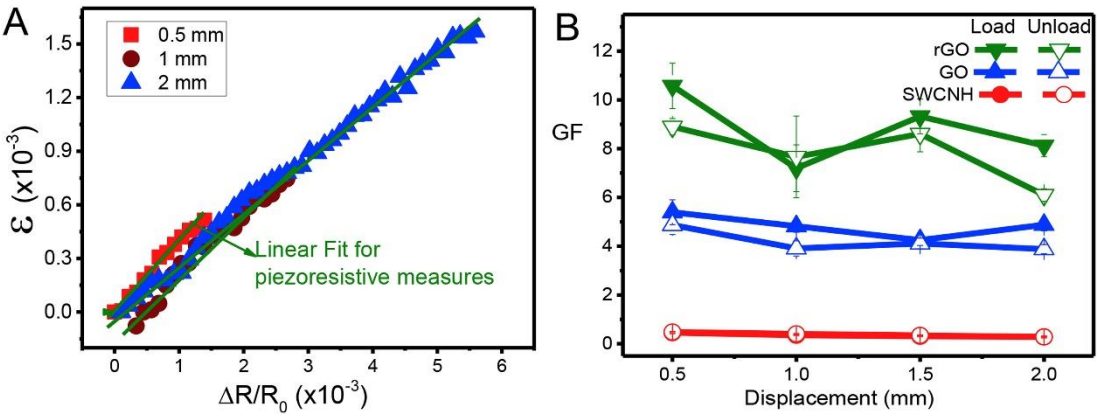



**Figure 2.** Piezoresistive sensibility (GF) measurements: a) exemplification for 0.5, 1 and mm for rGO/PVDF sample and b) for PVDF composites with 5 wt.% of different nanofillers applying 0.5–2 mm of displacement at 5 mm/min. Reprinted with permission from [36].

Changing from a resistive technology to a capacitive one, A. Hartono *et al.* [37] sandwiched a PVDF film between two electrodes in order to develop a glucose capacitive biosensors that measured the dielectric properties of the dielectric layers at the interface between the electrolyte and the electrode. It was found that the sensor output increased (up to 6.04 µV) with increasing glucose concentration up to 5.85 M.

The addition of fillers into the PVDF matrix brings added value to the use of PVDF for technological applications [3], in particular when transparency, softness and flexibility are required [38-40]. PVDF-based composites find applications as actuators [41], in vibration control [42], ultrasonic transducers [43], batteries [44], filters [45], chemical warfare protection [46] and in the biological field [47]. Further, there is an increasing impact on magnetic sensing applications, based no the magnetoelectric effect of PVDF nanocomposites [38]. The addition of magnetostrictive fillers into the PVDF matrix allows the fabrication of multilayer magnetic-responsive materials with improved magnetoelectric response suitable for sensing devices, some of them being fully printable [48]. Further, transparent magnetoelectric materials for “invisible electronics” sensing applications[49] and anisotropic magnetoelectric sensors with good linearity ($r^2$ value = 0.995) and with application potential on digital compasses, GPS devices and biomedical sensing (Figure 3) have been presented [50].

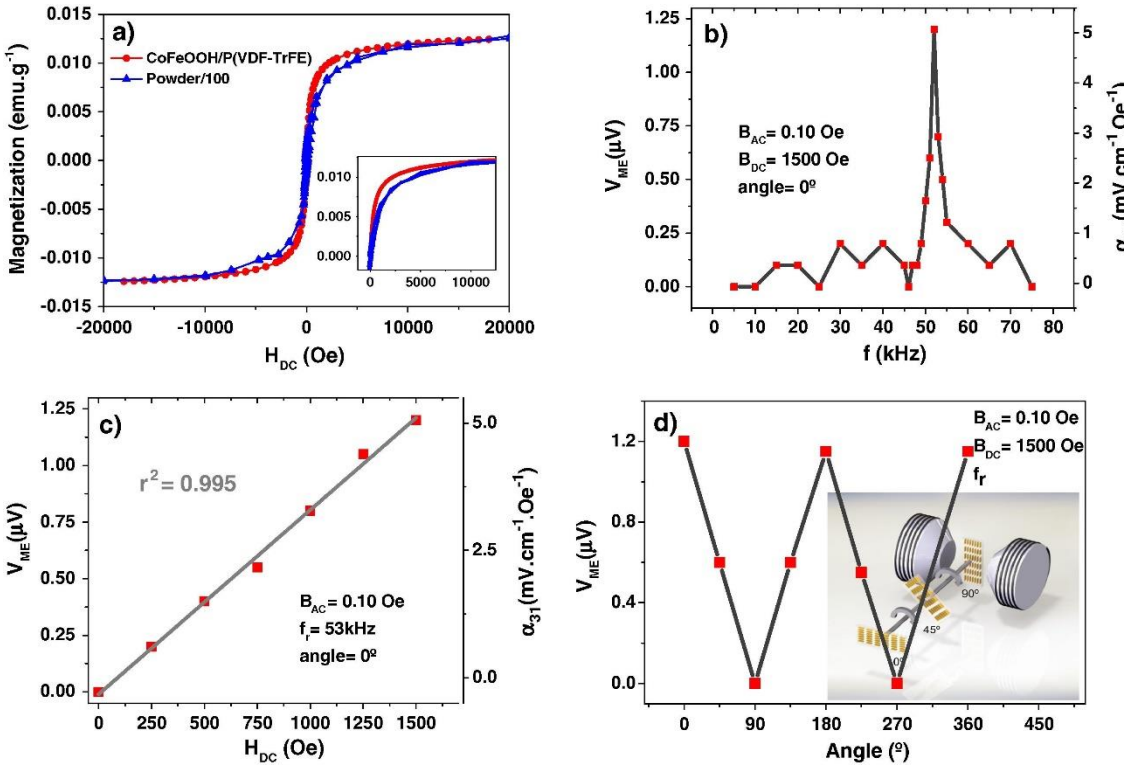



**Figure 3.** a) Room temperature magnetic hysteresis loops for the composite in comparison with the pure powder form; b) Room temperature magnetoelectric (ME) voltage ($V_{ME}$) and ME coefficient ($\alpha_{31}$) as a function of the frequency; c) Room temperature magnetoelectric voltage ($V_{ME}$) and ME coefficient ($\alpha_{31}$) as a function of the $H_{DC}$; d) Room temperature ME response as a function of the angle between $H_{DC}$ and the composite length direction. Reprinted with permission of [50]

New visions in the application of PVDF sensors in the biomedical area such as the use of the large aspect ratio PVDF fibers, allows the accurately measurement of pressure and flow in very small blood vessels and acoustic microscopy inside acoustically opaque organs can make these kind of applications totally disruptive [51, 52], for that all the requirements for the certification of this type of materials as biomaterial need to be addressed [38].

After more than a century and 55000 papers of development, PVDF-based materials have become one of the most significant multifunctional materials, particularly in the field of technological sensing applications such as electronics, robotics, and biomedical engineering. Although PVDF-based materials had a research climax in the last 3 years (with more than 5000 papers each year) and have been commercialized for a long time, there is still a lot of room for innovation with these materials [27]. As an example, recently a screen printable formulation with environmental friendlier solvent has been presented and the applicability in an all printed touch screen has been demonstrated [53].

*3.2.Actuators*

In the electromechanical actuators field, able to convert electrical signals into a mechanical force or deformation, different challenges have been addressed aiming to improve actuator speed responses, low voltage response, displacement control, frequency and current-voltage characteristics [54].

Due to its interesting properties, namely the ability to change the mechanical properties in response to an electrical stimulation, electroactive polymers (EAPs) are the most commonly used polymers for electroactive actuator's development [54, 55]. Additionally, it is also to notice that EAP materials based on piezoelectric polymers also allows the conversion of the mechanical deformation into electrical signals. Depending on the EAPs activation mechanism, they can be classified into electronic or ionic EAPs [55].

Several works have been focusing on the development of electronic EAPs actuators. However, to this type of actuators are associated several disadvantages related with the actuator performance: the actuators requires high voltages to achieve large actuation strains [56]. On the other hand, ionic EAPs are emerging as an alternative to electronic actuators due to their low driving voltages, flexibility, and lightweight [54].

These electromechanical actuators are composed by a separator, two electrode layers and a metal electrode attached to the electrode's layers. The mechanical deformation occurs after the material electrical stimulation under an applied voltage between the metal electrodes [57]. For ionic EAPs, the actuation mechanism is based on ions diffusion or mobility within the polymer matrix with the applied electrical voltage. The applied voltage allows the ionic current in the separator, resulting in a mechanical deformation, supported by the lowest potential barrier between the electrode and separator layer, occurring the migration of the cations to the negative side and the anions to the positive side close to the electrodes [58, 59].

The actuator performance is generally evaluated by the bending response resulting from an ac or dc applied voltage and can be quantified according to Figure 4 and Equation 3:

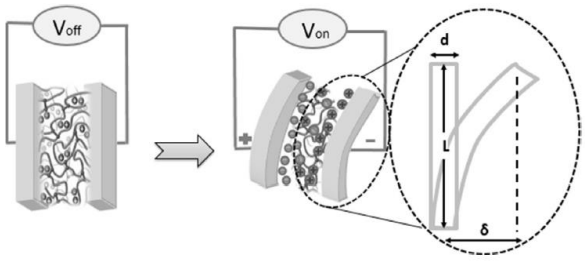


**Figure 4**. Illustration of the ion migration and bending response of the IL/PVDF composites. Reprinted with permission from [58, 60].

$$\varepsilon = \frac{2d\delta}{L^2+\delta^2} \times 100 \quad (3)$$

where L is the sample free length, d the thickness of the samples and δ the displacement of the tip of the actuator measured along the x axes, depending the bending response from the electrode area and sample strain [60].

Different polymer matrixes and polymer composites containing conductive fillers within the polymer matrix have been developed for this application, including, shape memory polymers, electroactive polymers and shape memory alloys [61, 62]. Regarding the use of EAPs, piezoelectric polymers are among the most interesting materials class as a polymer matrix [55], being PVDF among the most commonly used polymer matrix for electromechanical actuator's development.

Different PVDF based electromechanical actuators have been developed in order to achieve better strain responses at lower voltages. The main studies have been focusing on the development of PVDF based ionic actuators, particularly in ionic actuators comprising ionic liquids (ILs) within the PVDF polymer matrix [57-60]. The ILs, commonly defined as salts composed entirely by cations and anions [63, 64] gained a special attention to the actuator's development due to the high ILs ionic conductivity, excellent chemical and electrochemical stability [65-67] and window stability between 4 and 6 V [68, 69]. Additionally, ILs are considered non-flammability and non-volatile solvents.

Apart from the ionic conductivity, the actuator performance of an IL/PVDF actuator also depends both from the cation and anion type, chain length and IL concentration within the polymer matrix. Further, it is important to state the importance of the PVDF electroactive β phase content into the actuator performance [58]. The introduction of ILs into the PVDF polymer matrix, favors the PVDF crystallization into the electroactive phase, as a result of the interaction of the $CH_2$ and $CF_2$ groups with the negative and positive charges of the IL [58-60]. This ion-dipole interactions and the decrease in the Young Modulus as a result of the IL plasticizing effect, are the main responsible for the bending of these ionic actuators [58-60].

IL/PVDF actuators based on the ILs (N,N,N-trimethyl-N-(2-hydroxyethyl) ammonium bis(trifluoromethylsulfonyl)imide ($[N_{1112}(OH)][NTf_2]$) and 1-Ethyl-3-methylimidazolium ethylsulfate ($[Emim][C_2SO_4]$)) were developed by Dias, J.C. et al., [56]. The bending strain displacement and bending response was evaluated at different voltages (2.0, 5.0 and 10.0 V) at 10 mHz of frequency. The bending response is more dependent on the IL content, developing the $[N_{1112}(OH)][NTf_2]$/PVDF composites the highest bending motion displacement (10.5 mm) at an applied voltage of 5V (Figure 5). The authors also indicated the interesting potential applicability of the $[Emim][C_2SO_4]$ composites for biomedical applications due to its non-citotocixity [56].

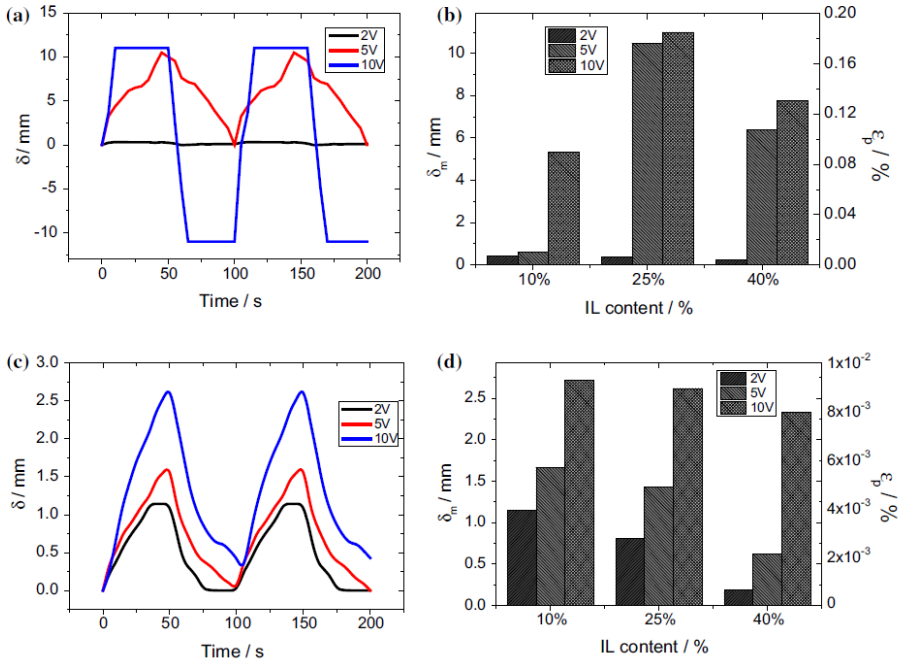



**Figure 5.** Displacement of the IL/PVDF composites as a function of time at different voltages at a frequency of 10 mHz for: (a) 25 wt% of $[N_{1112}(OH)][NTf_2]$ and (c) 10 wt% of $[C_2mim][C_2SO_4]$ within the PVDF polymer matrix. Maximum displacement and bending of the PVDF/IL as a function of IL content and voltage for (b) $[N_{1112}(OH)][NTf_2]$ and (d) $[C_2mim][C_2SO_4]$ composites. Reprinted with permission from [56].

The effect of anion type and cation chain size in the bending response was accessed, using ILs comprising the same cations, and anions, respectively. ILs sharing the same cation, the hexyl-3-methylimidazolium ($[C_6mim]^+$) and different anions (bis(trifluoromethylsulfonyl)imide ($[Ntf_2]^{-}$) and chloride ($[Cl]^-$)) were incorporated within the PVDF matrix. Results demonstrated that the actuator performance depends both on the anion and IL content, being the maximum bending response (0.53%) obtained at an

applied voltage of 10 V square signal observed for the [$C_6$mim][Cl]/PVDF composites containing 40 % wt. of the IL (Figure 6) [59]. The bending response is also cation and anion size dependent, being obtained a maximum response (0.3%) for a 10 V square signal for the IL/PVDF composite with 40 wt% content of [$C_2$mim][$NTf_2$] [60].

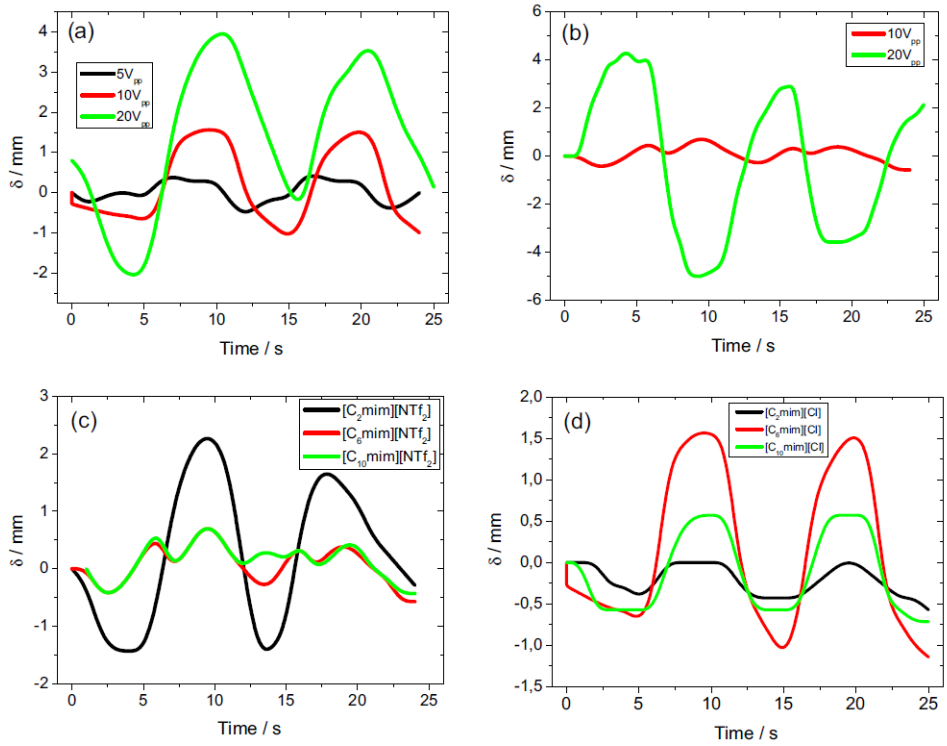



**Figure 6**. Displacement of the IL/PVDF composite actuators as a function of time under an applied voltage of 5, 10 and 20 V at a frequency of 0.1 Hz for: (a) [C6mim][Cl] and (b) [C6mim][NTf2]. Bending response at 0.1 Hz and 10 Vpp for the PVDF composites containing IL with: (c) $[NTf_2]^-$ and (d) $[Cl]^-$. Reprinted with permission from [60].

The effect of the alkyl side cation chains with variable length and family type in the electromechanical response was also accessed. Different ILs sharing the same anion, $[TFSI]^-$ and different IL cations, (families of pyridinium, imidazolium, and ammonium ions). It was observed a decrease in the electrical conductivity with the cation alkyl chain size increase, being the highest bending response observed for the composites propylimidazolium ([Pmim])[TFSI]/PVDF (5.7 mm) (Figure 7a and 7b) and propylmethylpiperidinium ([Pmpip]) [TFSI] (6.0 mm) at 5 V and 100 mHz [58].

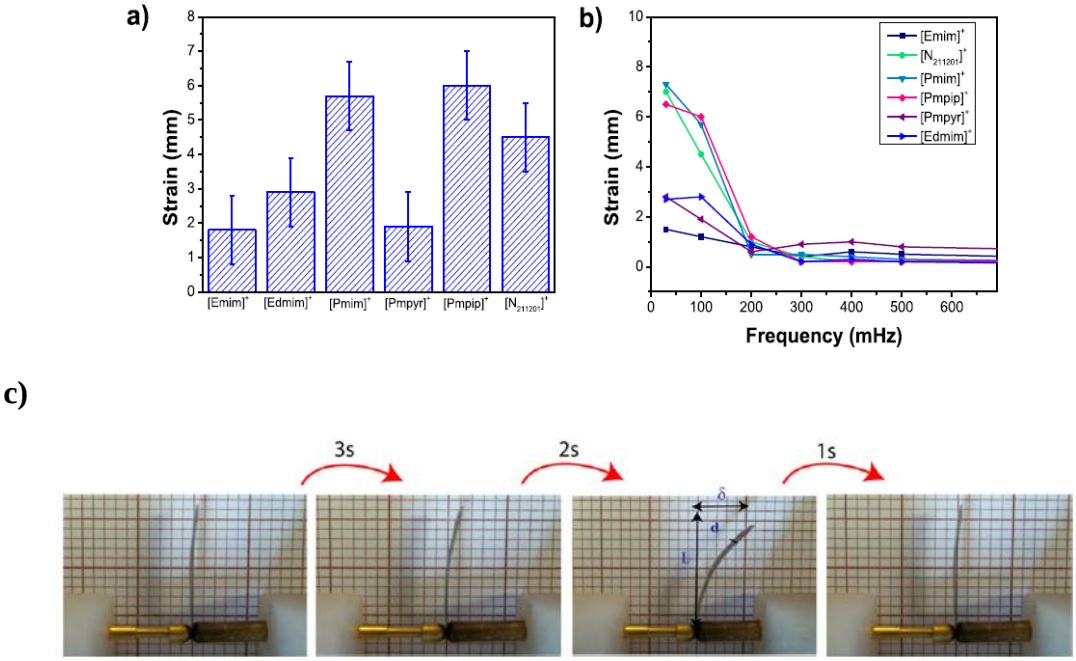



**Figure 7.** Displacement of the composites for an applied voltage of 5 V and a frequency of 100 mHz (a) and as a function of frequency (b). c) Schematic representation of the ion migration and bending response and (b) bending motion as a function of time for the [PVDF]/[Pmim][TFSI] composite at a 100 mHz frequency and 5 V. Reprinted with permission from [58].

Conductive polymers have been also explored for electromechanical actuator's development. Guo, D. et al.,[70] developed PVDF/ polyvinyl pyrrolidone (PVP) films with inner channels after the IL [Emim][$BF_4$] removal. The inner channels promote the adsorption of polar water and IL to develop either water- or IL-driven ion-exchange polymer metal composites (IPMC) actuators. Both water-driven and IL-driven PVDF-based IPMCs exhibit high ion migration rates, improving the actuation frequency and higher levels of actuation force and displacement. This films are a promising strategy in the design of artificial muscles with tunable electromechanical performance for flexible actuators or displacement/vibration sensors [70]. It was observed that for an ac applied field, the control and IL−IPMC resulted in a continuous electromechanical response and this IPMCs are promising in the design of artificial muscles, for flexible actuators or displacement/vibration sensors [70].

*3.3.Tissue engineering*

Tissue engineering (TE) is a multidisciplinary science that combines the principles of materials and cells in order to substitute tissues and/or to promote tissue repair/regeneration impaired by disease and/or trauma. This technique emerged as alternative to conventional methods and to overcome the gap between the growing list of patients waiting for organ transplantation and the limited number of donated organs available for such procedures [71].

One of the first paradigms of TE was the employment of supportive materials/matrices capable to provide an appropriate environment for cell adhesion, growth and differentiation toward the desired tissue [72]. In this way, different materials from natural or synthetic origin and different morphologies, were evaluated in order to determine the most prone to replace the cell environment. Natural materials began to be attractive for biomedical and TE applications as they exhibited similar properties to the tissue to replace and can be obtained from natural sources [73]. However, natural polymers can be difficult to process and usually present poor mechanical and electrical properties [74]. Therefore, a wide range of synthetic polymers have been used to construct different materials/matrices for TE.

Although an extensive list of polymer has been studied regarding TE applications, the majority of the developed materials have been used in a passive way, i.e. just as support for the cells/tissues. However, many of the major functions in cells and organs of the human body are controlled by electrical signals. For example, electrical fields influence the metabolism and growth at different stages; can guided the migration and movement of different cell types such as, epidermal, epithelial and corneal cells [75-78]; and can modulate the phenotypes of vascular endothelial cells, regenerate nerve fibres and influence ligament healing [79-81]. Also, among the different clues that determine the tissue development, cells/organs repair and/or regeneration and also the cell behaviour and function, electrical and electromechanical ones are crucial for tissues such as bone, cartilage, skeletal and cardiac muscle, skin and neural [73, 82, 83].

In this way, physical signals are particularly relevant parameters to be considered for the development of active materials/scaffolds in order to mimic the body microenvironment, providing the appropriate environment for specific cell responses. Therefore, a new paradigm for TE emerged, where the use of active/smart biomaterials with appropriate forms and geometries in order to properly regenerate specific tissues demonstrated strong

potential for novel TE strategies. This approach allows the induction of these stimuli more naturally, taking advantage of the presence of electrical or mechanical signals within the body. Therefore, multifunctional biomaterials based on smart materials have been applied in several TE fields, including bone, cartilage, skeletal and cardiac muscle and neural regeneration. Among the different smart materials, piezoelectric polymers have already shown strong potential for novel TE, once they can induce mechanical and/or electrical stimuli (Figure 8a and 8b).

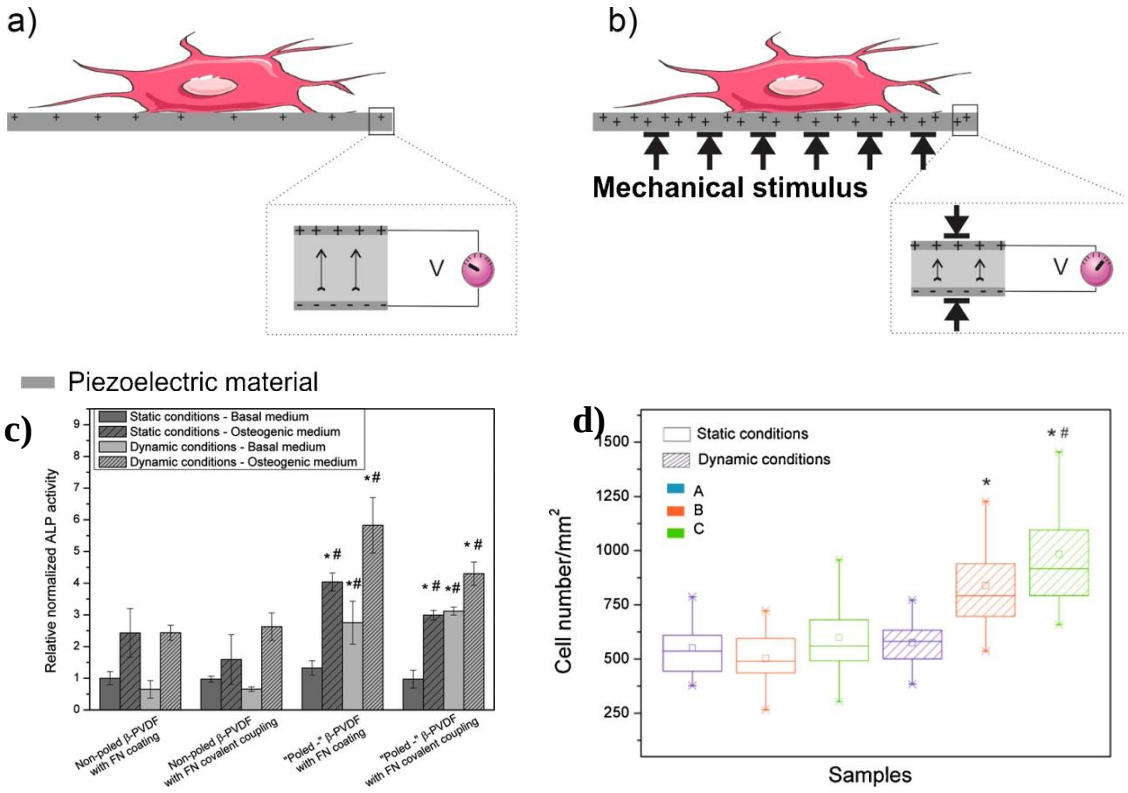



**Figure 8.** Schematic representation of the piezoelectric effect (piezoelectric material representation at the bottom of the image) and corresponding cell culture on piezoelectric supports (a) without and (b) with mechanical stimulus, the later leading to an electrical potential variation of the materials which is, in turn, influences cell response. Reprinted with permission from [73]. c) hASCs differentiation on different PVDF films determined by relative qALP expression after 15 days of culture using regular and osteogenic medium under static and dynamic conditions. Reprinted with permission from [84]; and d) Pre-osteoblast cell density obtained in the different samples (A- P(VDF-TrFE) non poled film, B - TD/P(VDF-TrFE) non poled film and C- TD/P(VDF-TrFE) "poled +" film) under static and dynamic conditions after 72 h of cell culture. Reprinted with permission from [85].

Thus, the electromechanical stimulation can be effectively conducted by PVDF. It has been demonstrated its biocompatibility as well as its influence on the cellular response [86, 87]. Firstly, PVDF biomaterials have been used to study their influence on bone regeneration, once bone itself is also piezoelectric. The influence of surface charge of the PVDF biomaterials on the adsorption of fibronectin was also investigated, demonstrating higher adsorption on charged surface rather on non-charged. After that, their influence with MC3T3-E1 pre-osteoblasts cultivated under static and dynamic conditions [86] was studied, verifying that positive surface charge promote higher osteoblast adhesion and proliferation, being still higher in dynamic conditions, i.e, with the application of the mechano-electrical stimuli. Also, the same approach was performed with human adipose stem cells, verifying that the mechano-electrical stimuli enhances osteogenic differentiation (Figure 8c) [84]. *In vivo* studies were also carried out with β-PVDF films after implantation in a bone defect. In this case, the mechanical solicitations are obtained by the rat movements and it was verified that these films lead to more defect closure and bone remodelling [88]. A piezoelectric actuator was also implanted in ostomy cuts in sheep femur and tibia in order to mechanically stimulate bone and it was observed that the total bone area and new bone area were significantly higher around actuators [89]. Another related approach that has been explored for bone TE is the use of magnetoelectric biomaterials. This kind of biomaterials can be useful, for example, in case of patient immobilization, where the natural mechanical stimulus is not fully available [90], allowing the use of an external magnetic field to remotely control tissue stimulation. Terfenol-D/PVDF-TrFe magnetoelectric composites have been used in order to study the proliferation of MC3T3-E1 pre-osteoblast cells, verifying that when the cells are cultured under mechanical and electrical stimulation, with the application of a magnetic field, the cell proliferation was enhanced (Figure 8d) [85].

In relation to neural TE applications, PVDF and its copolymer (PVDF-TrFE) have been also used under dynamic conditions. It was demonstrated that the percentage of differentiated neurons of mouse neuroblastoma cells was increased by the use of poled PVDF substrates [91]. PVDF membranes have been stimulated by acoustic stimulation in order to study the influence of electrical charges on neuritogenesis of PC12 cells. The results demonstrated that the calcium channels were activated, generating neurites via a cyclic adenosine monophosphate (cAMP)-dependent pathway [92].

PVDF was also combined with polyurethane (PU) in form of fibres for wound healing applications. The results demonstrated that when the electrospun composites were

subjected to a mechanical deformation, the scaffolds enhance fibroblast activities *in vitro* and *in vivo*, showing their potential for wound healing applications [93].

For muscle regeneration, until now, no studies with piezoelectric biomaterials under dynamic conditions were performed. Nonetheless, PVDF films are used in static conditions, where it was shown that the surface charged enhanced the cell proliferation [94] and differentiation [95].

Thus, it is possible to say that the function of piezoelectricity has begun to be understood for bone TE, but that for the others tissues that respond to mechano-electrical stimuli far more work is still needed.

### *3.4.Microfluidic applications*

Microfluidic platforms have experienced a marked evolution particularly in the last decade with new and technologically relevant applications in areas including biomedicine, environmental monitoring, food control, electronics and pharmaceutics[96-99]. Microfluidic platforms enable advanced devices capable to incorporate in a single platform all elements for an increasingly accurate (bio)chemical analysis with higher reliability when compared to traditional methods [100].

The search and integration of new materials and systems to be applied in these devices is one of the main focuses of research in the area, in order to precisely handle fluids at the microscale with a real-time detection of the microfluidic environment in the microchannels, which is essential to develop fully functional systems [101].

The use of active materials is a promising approach to achieve a new generation of active microfluidic devices. Some electroactive polymers (EAPs) proved their suitability to be used instead of ceramics as piezoelectric actuators in microfluidic systems in order to improve mixing and reaction efficiency [102]. While piezoceramics are characterized by higher piezoelectric coefficients, their high acoustic impedance compared to liquids or plastics leads to reflection at the boundary layer in almost 90 % [103]. In turn, the low acoustic impedance of polymer based EAP's allied to their excellent mechanical and optical properties [103], low-cost and easy integration turns them suitable materials for microfluidic applications [104].

One of the most suitable electroactive polymers for microfluidic applications are PVDF, along with its copolymers, that present the highest dielectric constants and electroactive

responses [24] among polymers, as well as low acoustic impedance, good mechanical and optical properties, easy integration and low-cost [24].

To precisely handle fluids at the microscale, real-time detection or actuation of the microfluidic environment in the microchannels is needed, PVDF-TrFE copolymer films allowing to be integrated as piezoelectric sensors or actuators into the devices [105].

Microfluidic actuators based on PVDF-TrFE have been developed and used as micropumps in microfluidic devices, the deformation of the PVDF-TrFE film under electrical stimulation leading to a volume modification of the microfluidic chamber and subsequently drive the fluid flow [106]. Consequently this PVDF-TrFE based piezoelectric micropump is able to provide a varied range of flow rates within the range of 0–300 μl/min and a stable production of droplets with decreasing size with increasing Vpp (1.1 mm for 1.2 kV; 0.8 mm for 1.5 kV and 0.5 mm for 2.0 kV) [106]. These promising results and the potential for allowing the complete integration of several pumps into one microfluidic chip hold great potential for applications in microfluidic areas including analysis, delivery, mixture or detection [106, 107].

Piezoelectric PVDF-TrFE nanofibers have been also used as microfluidic flow sensor, able to measure flow rates ranging from 13 μl/h to 301 μl/h with a sensitivity of 0.36 mV per 1 μl/h. Further, this simple and highly sensitive sensor exhibits good linearity with the low flow rates and viscosities [108]. When compared with traditional liquid measurements using fluorescence methods, this sensor is non-intrusive, and can be simply integrated in a microchannel even if the channel is not completely transparent[108].

PVDF polymer-based temperature sensor fabricated by combining a thin PVDF pyroelectric film together with an infrared source, which stimulates the active element located on the top of the microfluidic channel, has been presented, the integration of the sensor into a system-on-a-chip platform allowing a fast monitoring of localized temperature within a biological fluid, avoiding errors in the evaluation of the thermal evolution of the fluid during analysis [109].

Finally, a transparent piezoelectric PVDF-TrFE actuator with electrodes of aluminium zinc oxide (AZO) placed underneath the reaction chamber of a PDMS microfluidic system has been developed to allow the rapid quantification of nitrite and uric acid in blood [110] where the Figure 9a) shows a photograph of the optimized piezoelectric PVDF-TrFE transducer placed underneath the PDMS microfluidic structure and Figure 9b) demonstrates the nitrile reaction times for the assays by diffusion (Vpp of 0 V)..

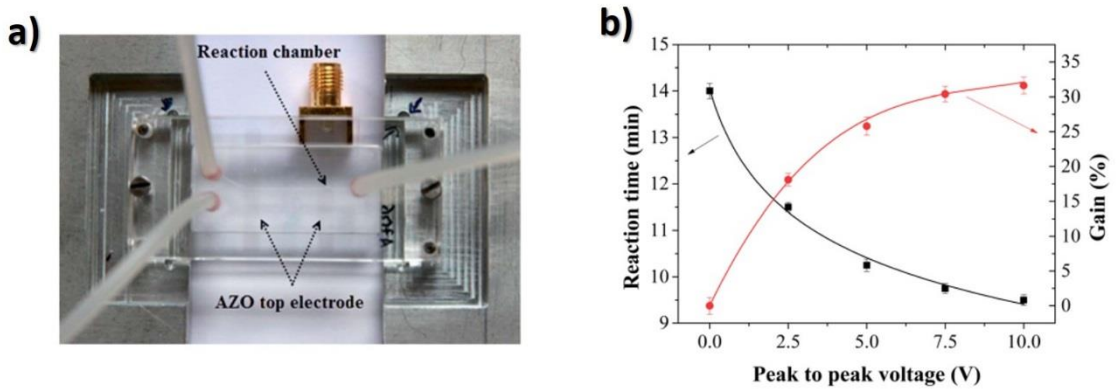



**Figure 9**. a) Photograph of the microfluidic system with the P(VDF-TrFE) piezoelectric transducer placed underneath the PDMS structure and b) Nitrite reaction time by diffusion (0 V) and acoustic streaming. Reproduced with permission from [110] of the Royal Society of Chemistry.

The acoustic streaming phenomenon within the reaction chamber is a result of the piezoelectric actuation of the polymer, decreasing the reaction time by approximately 24 % and 32 % for the uric acid and nitrite assays, respectively [111].

The aforementioned effects and devices show the versatility and multifunctionality of PVDF based materials for microfluidic applications, mainly based on the piezo- and pyroelectricity of the polymer.

*3.5.Environmental membranes*

Water pollution is a global problem that has been increasingly investigated in the last decades. Population growth together with the improvement of social wellbeing and medical care has contributed to the increasing production, use and disposal of chemicals such as pharmaceuticals, personal care products, pesticides, and endocrine disruptors, among many others [112]. All these compounds are ultimately discharged in an effluent – with or without previous treatment. The majority of these chemicals, known as emergent pollutants or micropollutants, are present in very low concentrations (ng/L to mg/L) in contaminated and treated waters [113]. They are very stable chemical compounds (usually a requirement for their applications), which makes them resilient to the conventional water treatments (e.g. physical and biological processes). Despite the low concentration of these pollutants, many reports show its toxicity to aquatic organisms as well as putative bioaccumulation of many deleterious compounds [112, 114]. Novel treatments are thus demanded to face this problem, and among many others, advanced

oxidation processes (e.g. photocatalysis), adsorption, and membrane treatments stand out from the rest owing to their simplicity and efficiency against a wide range of pollutants.

These new techniques claim for new materials, and as mentioned, fluorinated polymers such as PVDF and its copolymers (PVDF-TrFE and PVDF-HFP) possess advantageous physical-chemical properties that make them attractive for many applications, including water remediation. Moreover, such polymers can be easily processed into thin films, membranes, and fibres, among other morphologies, enlarging the range of possible applications. Also, these polymers show excellent chemical, mechanical, thermal and UV radiation resistance, related to the stable C–F bonds of the polymer chain [3, 115]. The ability to control porosity and pore size is also paramount for these applications [116, 117].

In this context, during the last decade, there was increasing production of reports on photocatalytic [118-120] or adsorptive [121, 122] membranes for water remediation. For instance, Anran Zhou and colleagues have produced a PVDF- polyvinylpyrrolidone (PVP) –titanium dioxide ($TiO_2$) - dopamine (DA) (PPTD) modified ultrafiltration membrane. The incorporation of $TiO_2$, PVP, and DA into the PVDF matrix, allowed to increase the system hydrophilicity, pore size and porosity, favouring water flux. The authors were able to remove approximately 91 % of sulfadiazine (SD) after 120 minutes of UV irradiation over the PPTD membrane, corresponding to an increase of approximately 20 % regarding SD removal without UV irradiation [123].

Another interesting work focused on the immobilisation of $TiO_2$ nanoparticles in PVDF-TrFE to degrade atrazine (azoic dye) in a solar photoreactor. The authors produced an 8 %wt $TiO_2$/PVDF–TrFE nanocomposite by solvent casting, obtaining a highly porous structure (≈ 75%) with interconnected pores (Figure 10).

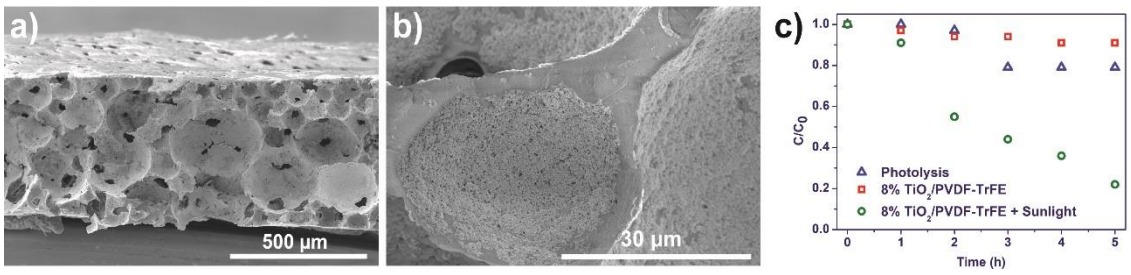



**Figure 10.** SEM images of 8 wt% $TiO_2$/P(VDF–TrFE) membranes: cross-section (a,b); Photocatalytic degradation of tartrazine (10 mg $l^{-1}$) with the 8 wt% TiO2/PVDF–TrFE nanocomposite, over 5 h of sunlight irradiation. Controls: irradiation of tartrazine solution

without the nanocomposite (photolysis); the nanocomposite in tartrazine solution with no irradiation (adsorption). Reprinted with permission from [124].

The photocatalytic results show the degradation of approximately 78% of tartrazine in a solar photoreactor after 5 hours of solar irradiation (Figure 10c). The reusability of the nanocomposites proved to be effective – with just 10% efficiency loss after three uses. The results indicate that the nanoparticles are efficiently attached to the porous structure, which allows a remarkable photocatalytic efficiency and reusability [124].

Further, different amounts of $TiO_2$ and $TiO_2$/graphene oxide (GO) (0, 3, 5, 8, and 20 wt%) were incorporated into a PVD-TrFE electrospun membranes (Figure 11a), produced by electrospinning, and the photocatalytic efficiency was tested against methylene blue (MB), both under UV and visible radiation [125]. Under UV radiation, the photocatalytic efficiencies are similar for the pristine $TiO_2$ and the $TiO_2$/GO nanocomposite (≈ 93% of MB degradation after 110 minutes). However, under visible radiation, the efficiencies are significantly different, with the 8% $TiO_2$/GO nanocomposite completely degrading MB in 90 minutes (Figure 11b-11c), against a 63 % of degradation obtained with the highest concentration of pristine $TiO_2$ (20 wt%).

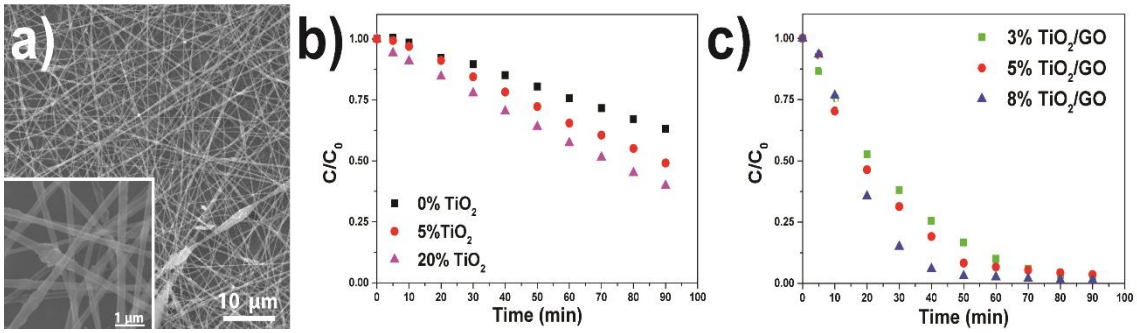



**Figure 11.** SEM micrographs of P(VDF-TrFE)/$TiO_2$/GO electrospun membranes with 20 % of GO/$TiO_2$ (a) - the inset corresponds to a higher magnification of the sample; photocatalytic degradation of MB under visible radiation for P(VDF-TrFE) fiber membranes prepared with pure TiO2 (b), and membranes prepared with TiO2/GO nanocomposite (c) reproduced with permission from [125].

The high surface area and porosity of the electrospun membranes together with the advantageous electrical and structural properties of GO are at the base of the observed performance. Also, the electric properties of the polymer, such as high polarisation and dielectric constant combined with low dielectric loss, contributed to a remarkable photocatalytic performance [125].

In agreement with the mentioned easy processability of PVDF and co-polymers, it was reported the production of a photocatalytic coating based on 50 wt% $TiO_2$/PVDF over Poly(methyl methacrylate) (PMMA) optical fibres, by dip coating [126]. This technique allowed to produce coatings with different thicknesses (ranging between 66 to 887 µm), Figure 12.

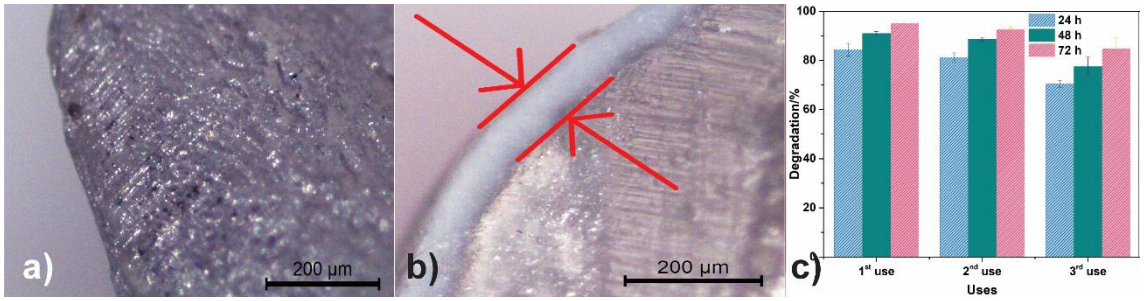



**Figure 12.** Microscope images (amplification of 50×) of a commercial PMMA optical fibre (a); coated with 50% w/w $TiO_2$/PVDF by one dip (b); Photocatalytic degradation versus number of uses (c), of 5 mg $L^{-1}$ of CIP for 72 h under artificial sunlight using the 50 w/w% $TiO_2$/PVDF-coated polymeric optical fibers. Reprinted with permission from [126].

The robustness of the PVDF coating was tested with a tape test, and the sample showing the more stable coating was able to degrade 95% of ciprofloxacin (5 mg $L^{-1}$) after 72 h under visible radiation. After three cycles, the efficiency loss was approximately 11%, confirming the effective attachment of the $TiO_2$ nanoparticle to the PVDF matrix. The optical fibres play a dual role, as a light transport and as a substrate to immobilise $TiO_2$. In this work, it was highlighted the ability of this new hybrid material to bring photocatalysis to environments deprived of sunlight (e.g. turbid, deep or underground water).

Besides photocatalytic materials, fluorinated polymers have also been employed in adsorption processes. In this way, a PVDF-HFP/bayerite composite membrane was produced for arsenic (As) removal from water [127]. Theses membranes possess porous structures with a degree of porosity between 65 and 75% (Figure 13a and 13b), a compressive strength higher than 100 kPa and water flux between 65 and 215 $Lh^{-1}$ $m^2$.

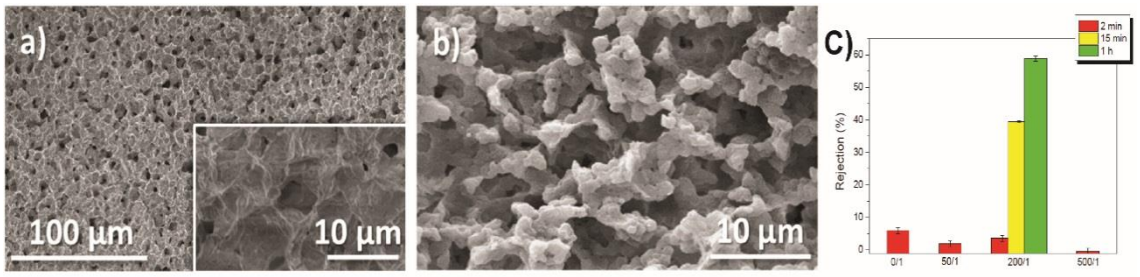



**Figure 13.** Cross-section SEM micrographs of PVDF-HFP/bayerite composite membranes with different nanofiller content a) 0/1; b) 50/1; and c) arsenic rejection of the PVDF-HFP/bayerite membranes. Reprinted with permission from [127].

The adsorption assays indicated that membrane with bayrite/As ratio of 200/1 rejected about 60 % (40% of As removal) of arsenic species present in the solution after 1 h of operation (Figure 13c).

Similarly focused on the adsorption processes, a novel type of metallic organic framework (MOF)/polymer matrix, MIL-68(Al)/PVDF was manufactured trough solvent casting (Figure 14) [128].

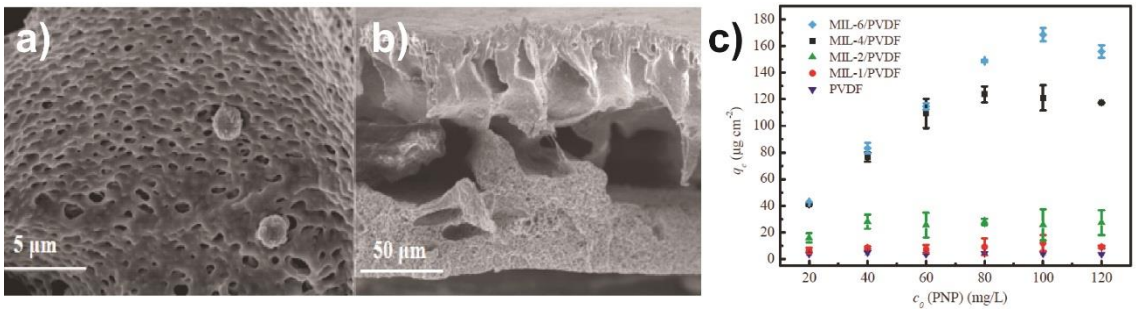



**Figure 14.** SEM images of MIL-1/PVDF (a, b); adsorption isotherms for PNP (c) on MIL-68(Al)/PVDF hybrid membranes with different adding amounts of MIL-68(Al), which are 1 wt%, 2 wt%, 4 wt% and 6 wt% respectively. Reprinted with permission from [128].

The adsorption properties of these new nanocomposites were tested against p-nitrophenol (PNP), and the results indicate that all MIL-68(Al)/PVDF samples show significantly higher adsorption capacities compared to pristine PVDF. The maximum adsorption capacity was 183.49 µg cm$^{-2}$, which value is almost as 49.9 higher than the pristine PVDF.

The future regarding environmental applications will lie on polymeric materials but with further controls over their morphology, such as porosity/pore size (control over flux and perculation), and wettability (interaction with pollutant), to match specific pollutants

requirements. Additionally, multifunctional materials such as photocatalytic and antimicrobial membranes, will endow membranes with wider water treatment (pollutants removal and disinfection). To avoid or minimise secondary pollution, caused by the detachment and discharge of active materials like nanoparticles into the treated water it is paramount to develop reusable materials. Particularly on this aspect, fluorinated polymers still present the more attractive properties when compared with natural polymers owing to their physical-chemical stability.

### *3.6.Energy harvesting*

By improving CMOS technology and electronic circuits manufacturing process, together with the high integration capacity [129], it allows, on the one hand, to reduce the energy consumption of the end devices and, on the other, to reduce the final size of the systems. Considering the emergence of hybrid solutions such as photonic and CMOS technology [130] that enable high rates of communication between subsystem, it is observe the emergence of new and more efficient devices with nA to mA consumptions (depending of μC system execution state), faster and more compact. These are the new generations of systems that aim to revolutionize our future. All of these combined developments have led to a reduction in the energy requirements for sensing, micro-actuation and communication devices, and correspond to the basic solutions for implementation of IoT solutions in the fields of biomedicine, regenerative medicine, defence, interactivity, aeronautics, smart industry and agriculture. However, the power supplies of these devices remain a major challenge for the scientific community and the industry itself, making numerous applications impracticable to date.

A device without batteries, which draws energy directly from its surroundings, is a promising way to provide continuous and inexhaustible power. The power source may be solar radiation, thermal gradient and mechanical motion. Much research focuses on mechanical movement, especially vibration, due to the vibration widely distributed in objects and in the environment.

Thus piezoelectric materials (PZE), and in particular PVDF and its copolymers, correspond to the most widely studied polymeric material to integrate as a generator element, given its high piezoelectric response (when compared to other PZE polymers) and being a flexible material with high resistance to force and deformation, which can

generate energy simultaneously by three ways: piezoelectric, pyroelectric and triboelectric when correctly combined the energy sources.

Due to strong research in this area, the energy efficiency of piezoelectric nanogenerator (PENG) and triboelectric nanogenerator (TENG) is expected to increase from the order of micro-watt (μW) to the order of several milliwatts (mW) [131, 132].

This increase in energetic transduction efficiency is based, on the one hand, on optimizing the manufacture of PVDF films and their copolymers, and on the other, on design factors such as resonance frequency, structural configuration and resonance tension. Based on the adjustment of these parameters, it allows a perfect transduction between the generator and the power source, which reduces system losses, where, depending on the application, the frequency and acceleration may have different values, hence the need to adjust the generator to power source or ensure that the generator has the widest possible response range, for systems where these values are quite dynamic, as shown in table 2:

**Table 2**: Peak frequency and acceleration for various energy sources [133, 134].

| Source | **Frequency (Hz)** | **Acceleration (m/s)** |
|---|---|---|
| Human walking | 2-3 | 2-3 |
| Car engine compartment | 200 | 12 |
| Door Closing | 125 | 3 |
| Induction motor | 10-300 | 500 |
| Disel motor | 10 to 10000 | 500 |
| Industrial break | 10 to 100 | 0 - 100 |
| Washing and drying machine | 121 | 3.5 |

At an early stage in the development of PENG solutions, they were based on the traditional single element cantilever format [134]. Then new architectures have been developed that promote the optimization of the generated energy, such as stacked cantlilevers, circular diaphragm, cymbal configuration [135] and capillary format [136], among others.

Based on advanced material manufacturing processes, allowing the production of nano-fibers (Figure 15a), nano-spheres and thin-film based nanocomposites (Figure 15b), it is possible to obtain an increase in energy efficiency, where it is already possible to verify responses in the order of $100mW.cm^{-2}$ of power density [137], Table 3 shows a summary of the generated power according to the material manufacturing technology and the applied geometry.

**Table 3**. Compilation of power output of the PENG based on PVDF l.

| Material | Type | Power density | Ref. |
|---|---|---|---|
| PVDF-HFP-TEA-$BF_4$ | Yarn | 43 μW.h.$cm^{-2}$ | [138] |
| PVDF | 3D spacer yarn | 5.1 μW.$cm^{-2}$ | [139] |
| PVDF-TrFE | Electrospun webs | 5.9 mW.$cm^{-3}$ | [140] |
| PVDF | FILM | 65 nW.$cm^{-2}$ | [141] |
| PVDF-$NaNbO_3$ | Nanofilm | 16.2 μW.$cm^{-3}$ | [142] |
| P(VDF-TrFE) and $BaTiO_3$ | Electrospun film | 16 μW.$cm^{-2}$ | [143] |
| PVDF + ZnO | Film | 16 μW.$cm^{-3}$ | [144] |
| PVDF + ZnO | Film and nanowires | 170 μW.$cm^{-3}$ | [145] |
| PVDF + BTZO | Film | 2.5 nW.$cm^{-2}$ | [146] |
| PVDF-niobate-based | Film | 11.7 μW.$cm^{-2}$ | [147] |
| PVDF + activated carbon | Film | 63.1 mW.$cm^{-2}$ | [148] |
| PVDF + GO-ALO | Nanocomposite film | 28 μW.$cm^{-3}$ | [149] |
| PVDF | Triaxial braided fibers | 29.6 μW.$cm^{-3}$ | [149] |

In the current quest for higher power generation, given the characteristics of PVDF and its copolymers, high dipolar momentum and flexibility [150], it is pointed as a good candidate for an effective dielectric in the development of TENGs, based on the processability. From this polymer, several approaches have been adopted to improve the performance of TENGs, such as: work function, dielectric constant, friction coefficient, surface resistivity, carrier density, or intrinsic density. The most diverse formats have been e applied, as well as the response to multiple effects.

The performance of a triboelectric harvester is strongly defined by the selected material pair, based on the experimental “triboelectric series” tables [151], preferably choosing a pair composed of the opposite ends of the table, such as the case of PVDF that are located at one end of the series.

At the moment, there are two representative operating modes in the TENGs, vertical separation and side sliding contacts [152]. Nowadays instantaneous power density is reported in the order of tens of mW.$cm^{-2}$ [152], however a good energy transduction efficiency has not been demonstrated, being necessary a lot of input energy in the system, when compared with the output energy, hence the weak or non-existent applicability. Similar to PENGs, to increase transduction efficiency, the materials manufacturing process has been optimized, increasing the surface area with the insertion of nano-pores or non-surface structures, as well as surface coating by PVDF nanofibers [132, 153],

where there is already a power reference in the order of 10mW.cm$^{-2}$ [132, 153] (Figure 15c). This is clearly the way forward in the area of TENGs and PENGs.

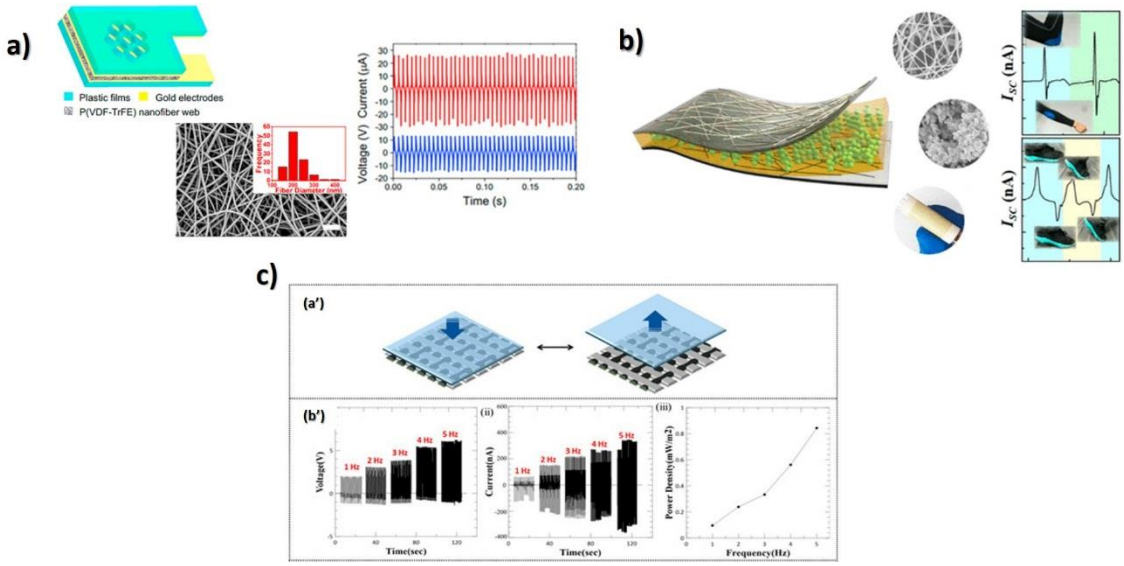
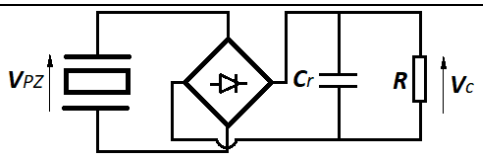
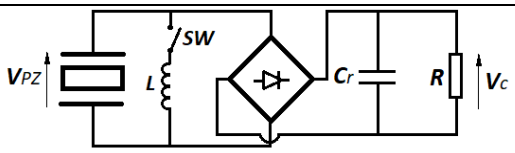
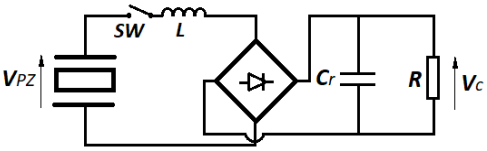
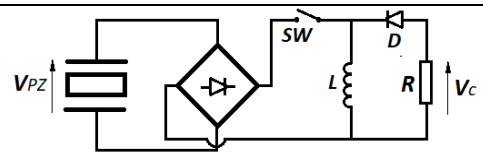
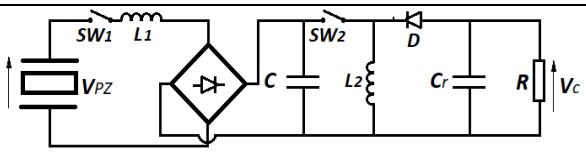
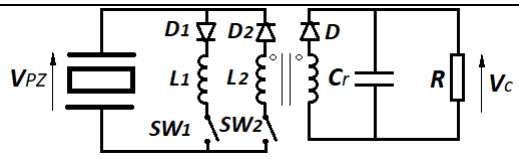



**Figure 15**. a) Schematic structure of the acoustoelectric power nanogenerator with microstructure and power generation of nanogenerators. Reprinted with permission from [140]. b) Fully rollable nanocomposite-based nanogenerator (NCG). Reprinted with permission from [147]. c) (a') Schematic of WTENG working mechanism under non-deformation mode where PDMS is chosen as the freestanding triboelectric layer. (b') The measured (i) voltage (ii) current and (iii) power density when the WTENG is contacted by the freestanding PDMS layer. Reprinted with permission from [153].

Over the past decade there has been an exponential growth of TENGs and PENGs architectures, but one of the biggest challenges for the true technological revolution in the area of self-power sensor and self-power devices is the energy storage circuit, and its ability to acquire power from the generator/transductor. There are currently six main circuit topologies which are the focus of the investigation as shown in the following table:

**Table 4:** Compilation of work principle energy harvesting circuit: Standard technique DC mode (STD) [154], Parallel Synchronized Switch Harvesting on Inductor (p-SSHI) [155], Parallel Synchronized Switch Harvesting on Inductor (s-SSHI) [156], Synchronous Electric Charge Extraction (SECE) [157], Double Synchronized Switch Harvesting (DSSH) [158] and Optimized Synchronous Electric Charge Extraction (OSECE) [159].

| | Circuit | Advantage | Drawback | Relative Efficiency |
|---|---|---|---|---|
| **STD** |  | Simple | Load matching<br>Low power | 0 |
| **p-SSHI** |  | High Power | Load matching,<br>Switch device | 800% |
| **s-SSHI** |  | High Power | Load matching,<br>Switch device | 700% |
| **SECE** |  | Good Power,<br>Load independent | Inductor, Switch device | 400% |
| **DSSH** |  | Good Power,<br>Load independent | Complex circuit switch strategy | 600% |
| **OSECE** |  | Wide bandwidth | 3-port transformer, complex circuit | 400% |

However, it is important to note that despite the good results already achieved when these systems are subjected to conditions in the real environment and not in the laboratory, the generated voltages and currents still low, which makes coupling of the electronic harvesting circuit very difficult, given the minimum operating conditions of the electronic components used. This is a major challenge in transposing this technology.

3.7.*Energy storage systems*

Electrochemical energy storage devices are increasingly needed and are related to the efficient use of energy in a highly technological society that requires high demand of energy [160].

Energy storage devices are essential because, as electricity is generated, it must be stored efficiently during periods of demand and for the use in portable applications and electric vehicles. In this area, batteries and / or super capacitors stand out [161, 162] as key elements for energy storage. The most widely used energy storage systems are Lithium-ion batteries considering their characteristics of being light, cheap, showing high energy density, low self-discharge, higher number of charge/discharge cycles and no memory effect [163]. These batteries are composed by different components: electrodes and separator/electrolyte [164]. The cathode material (positive electrode) is responsible for the cell capacity and cycle life and the anode material (negative electrode) should have a low potential in order to provide a high cell voltage with the cathode [165]. Independently of the type, anode and cathode are composites composed by a polymer binder, a conductive additive and the corresponding active material [165].

Each constituent of the cathode has a specific function and the polymer binder has the role of binding the active material and conductive additive and strongly affects the battery performance [165].

Poly(vinylidene fluoride), PVDF, is widely used as a polymer binder due to its excellent properties: high electrochemical, thermal, and chemical stability, ease of processing, proper swelling properties with excellent mechanical strength, low impedance at high discharge rates and excellent coherence within electrodes..

Recently, poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, was also proposed as a polymer binder for C-LiFePO4 based cathodes and their electrochemical behavior was compared to PVDF and PVDF-HFP as it is shown Figure 16 [166].

In this work it is shown that cathode morphology and electrical conductivity are similar, independently of the polymer binders, but that the swelling values depend on the selected binder.

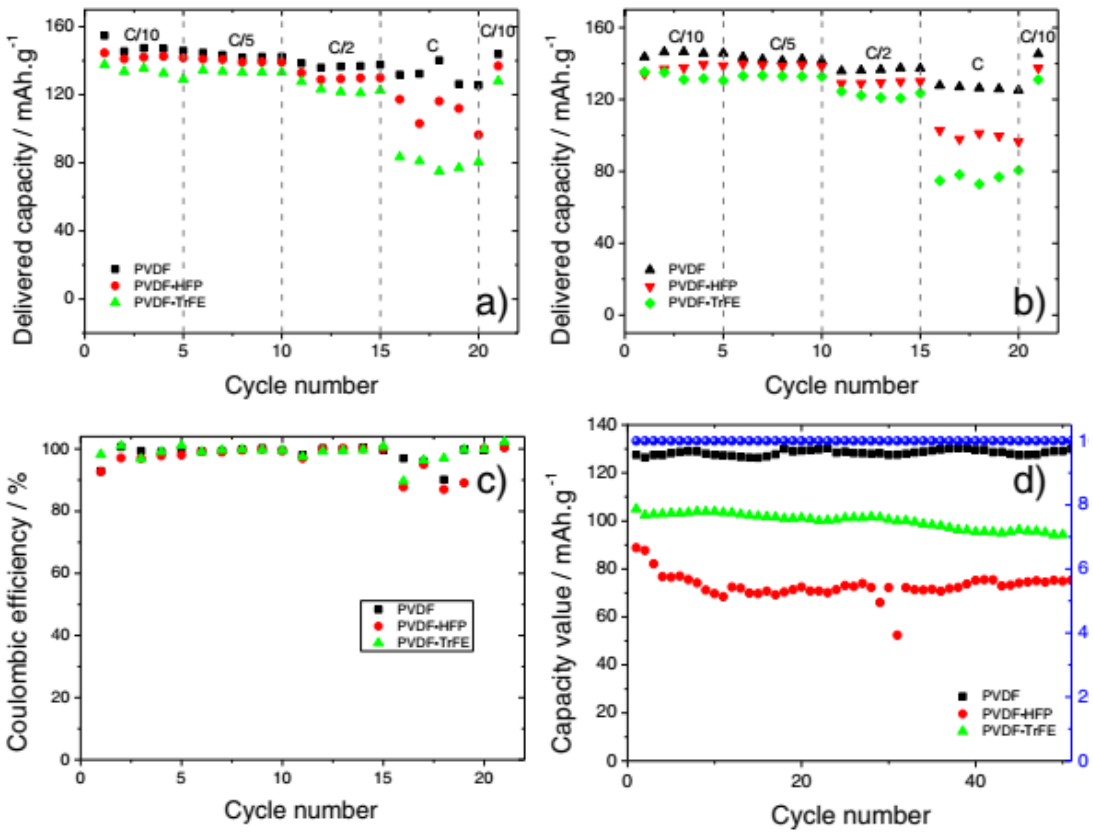



**Figure 16**. Rate performances of the samples during the charge process a) and discharge process b). c) Coulombic efficiency of the samples determined from b) and d) Cycling performance and coulombic efficiency of LFP cathodes films with PVDF, PVDF-HFP and PVDF-TrFE at C-rate in the voltage range from 2.5 to 4.2 V. Reprinted with permission from [166].

It was demonstrated that PVDF-TrFE could be used as a binder for CLiFePO4 cathodes and that the molecular weight and chain structure, i.e., the number of fluorine atoms, and polarity of the fluoropolymer binders, are essential in determining the overall cathode performance [166].

In addition, the effect of the ferroelectric characteristics of PVDF ligand on the effective transport of Li ions in a LIB system was evaluated for α-phase and β-phase, as shown in Figure 17 a) -c) [167].

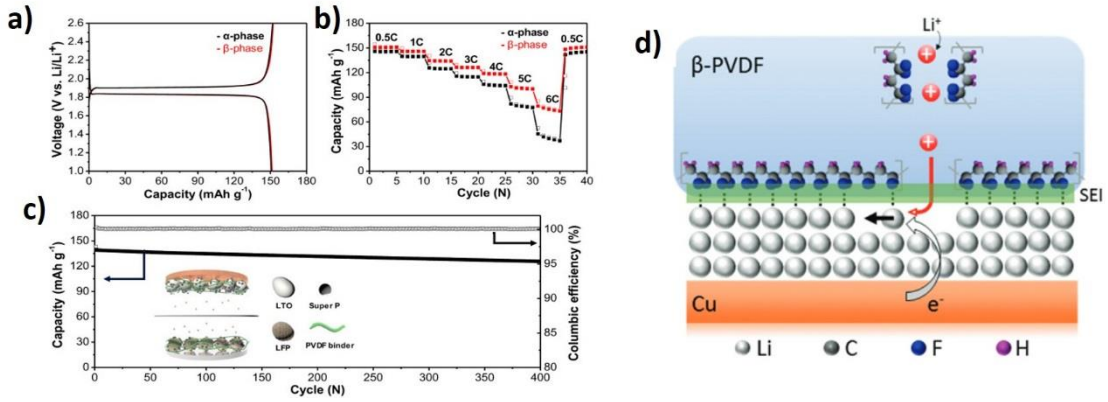



**Figure 17**. a) The first discharge–charge profiles of ferroelectric and paraelectric PVDF-incorporated LTO and LFP electrodes at constant 0.1 C rates in a potential window of 1–2.6 V, b) Rate capability of ferroelectric and paraelectric PVDF containing electrodes from 0.5 to 6 C rates, c) Long-term cycling stability and coulombic efficiency of ferroelectric PVDF containing LTO and LFP electrodes at a rate of 1 C. Reproduced with permission from [167] and d) Schematic illustration of layer by layer deposition and preferential diffusion pathways for Li ions. Reprinted with permission from [168].

It was demonstrated that the interaction energy between PVDF and LFP surface became stronger only when the polarization axis is parallel to the substrate for ferroelectric PVDF phase, facilitating Li-ion transport for both discharge and charge process [167].

In fact, it was also verified that the β-phase of PVDF is a promising artificial solid-electrolyte interphase coating on both Cu and Li metal anodes for dendrite-free Li deposition/stripping and enhanced cycling performance as shown in figure 17d) in which the dendrite suppression is attributed to the electronegative F-rich interface that favors layer-by-layer Li deposition [168].

In addition to PVDF as a binder, this polymer and its copolymers are widely used as separator component in Lithium-ion battery systems [169].

The main functions of the separator is to be a medium for ions transfer between the electrodes, prevent contact between the anode and the cathode, regulate cell kinetics and promote safety in the charge and discharge mechanism [170, 171]. It main properties are small thickness, excellent permeability, higher porosity, small pore size and interconnectivity, good wettability, excellent electrolyte absorption and retention and chemical, thermal and mechanical stability [172].

For porous polymer matrix as separator, PVDF and its co-polymers are widely used due to their good mechanical properties, high dielectric constant, wetting by the liquid

electrolyte, chemically inertness, good contact between electrode and electrolyte and being stable in cathodic environment (low value of the HOMO band) [173].

To obtain porous membranes based on PVDF and its copolymers, different processing techniques are used, such as thermally induced phase separation, template synthesis, self-assembly or electrospinning [174].

There are many works based on PVDF and its copolymers for separators and it has recently been shown for single porous membrane that the β-phase content in the membranes leads to higher polarity and facilitates faster lithium ion migration within the separator for similar microstructures as shown in figure 18a-b) [175].

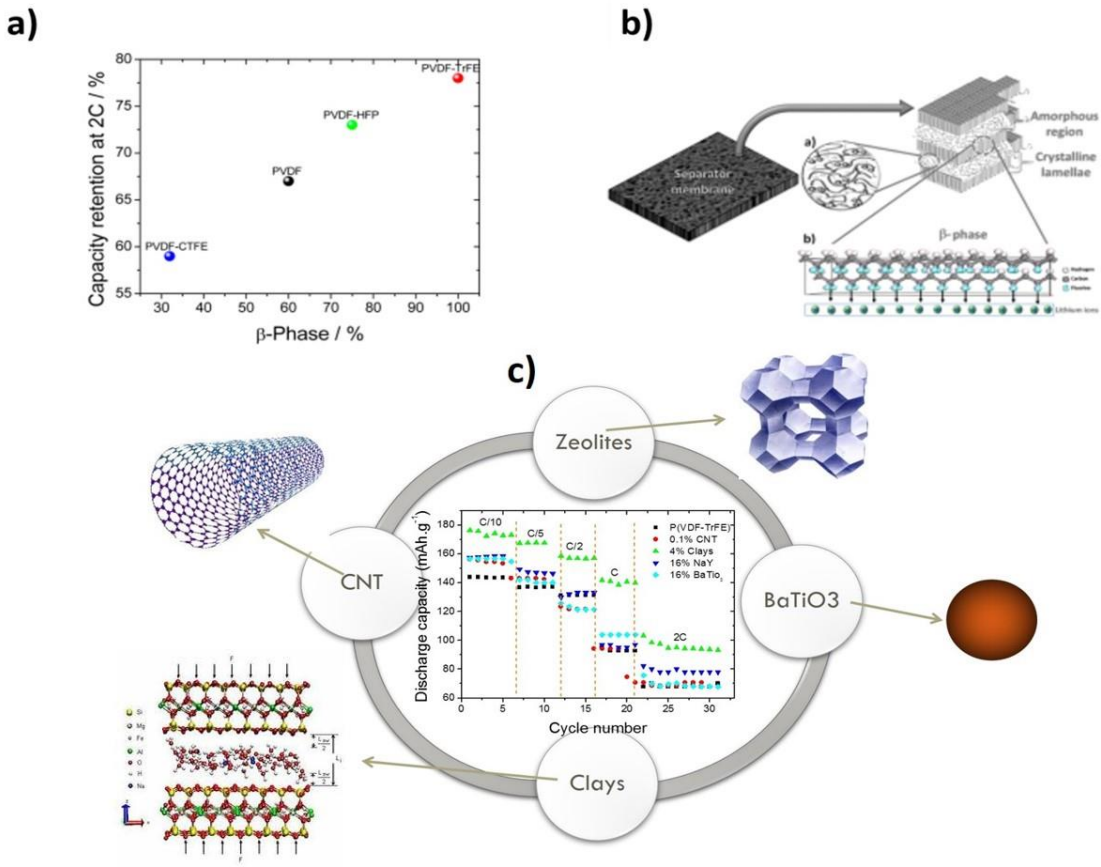



**Figure 18**. a) Capacity retention as a function of β-phase content for the different membranes and b) Schematic representation of the interaction between lithium ions and the fluorine atoms of the β-phase of PVDF. Reproduced with permission from [175]. c) Cycling performance from 0.1C to 2C of cathodic half-cells from the different composite membranes and the pristine polymer. Reproduced with permission from [176].

Another widely used separator types are composite membranes and, in another work, it was found that for PVDF-TrFE polymer, the filler type and its amount allows tuning cycling behavior, as shown in Figure 17c [176].

In conclusion, PVDF and its copolymers as binder and separator show suitable properties for their use in lithium-ion batteries, the ferroelectric phase improving lithium ions mobility which is a way to increase battery performance.

## *4. Outlook and future trends*

Poly(vinylidene fluoride) and its copolymers are semicrystalline polymers, lightweight, flexible and tough. In the electroactive β phase shows high dielectric and piezoelectric values and can be obtained in the form of ultrathin films, fibers and membranes and easily transformed into to the desired configuration. The physical properties of PVDF can be controlled in a wide range by appropriate chemical modifications or by the preparation of (nano)composites and therefore tuned to be applied in different applications.

The near future regarding the application of PVDF-based materials for the sensor industry is closely related to the production of miniaturized piezoelectric devices with low cost, low waste, low power consumption, high performance and with the fabrication of high-quality micrometer-size patterns onto a variety of hard and flexible substrates. Ink-jet printing can be a way to address these challenges.

The main limitation of PVDF-based sensors, the non-linearities and changes in the piezoelectric properties that affect the accuracy of the calibration, for strains higher than 150 μstrains, can be solved with the introduction of ceramic or polymeric fillers.

For the future, PVDF could be a fundamental tool in the development of bionic robots and in their interaction with their surroundings.

Finally, and although there is still room for more fundamental research, the progress in PVDF-based materials can open other variety of applications such as vibration isolation/dampening devices, precision engineering tools, health monitoring systems, communication and micro manipulation.

For actuator application, significant efforts need to be achieved to increase the actuator performance namely the actuator stability along the time, and actuator durability. Efforts must be also devoted to the generated force developed by the actuator. Additionally, as there is a lack of studies reporting on the actuators applicability, other interesting efforts relies on the exploration of the bending motion effect in several areas, such as, biomedical applications and robotics.

For tissue engineering, it is important to develop effective therapies for regenerative medicine. The use of piezoelectric biomaterials can be one possible solution once they

can tune the effective electric field characteristics of the natural ECM observed during development, regeneration or repair of the tissues, by the generation of electric field in response to minute mechanical vibrations.

The future regarding environmental applications will lie on polymeric materials but with further controls over their morphology, such as porosity/pore size (control over flux and perculation), and wettability (interaction with pollutant), to match specific pollutants requirements. Additionally, multifunctional materials such as photocatalytic and antimicrobial membranes, will endow membranes with wider water treatment (pollutants removal and disinfection). To avoid or minimize secondary pollution, caused by the detachment and discharge of active materials like nanoparticles into the treated water it is paramount to develop reusable materials. Particularly on this aspect, fluorinated polymers still present the more attractive properties when compared with natural polymers owing to their physical-chemical stability.

For energy harvesting applications, piezoelectric nanogenerator (PENG) will be used as standalone and portable power sources for low power electronic devices such as sensors, low power communication and micro and nano actuation systems, with particular focus on implantable sensors and actuators, precision agriculture, self-predictive monitoring in industrial, automotive and aeronautic maintenance systems. On the other hand, given the characteristics of the base material used, it can have dual function and can be used as motion, acceleration, voltage / current sensors. Due to the increase in output power and the technological advancements in electronics, the applicability of these solutions will certainly increase, allowing to meet the great challenges of the IoT and industry 4.0 era in a near future.

Finally, considering its excellent properties, PVDF will continue to be applied as binder and separator in energy storage systems but some properties must be improved, including interfacial stability with the electrodes and increased ionic conductivity value. Also, it is necessary to understand the polymer/electrolyte interaction allowing to identify the electrolyte formulation with the most favorable overall performance for porous membranes for separators and polymer binders in electrodes.

Thus, based on their outstanding characteristics in terms of electroactive properties, stability and processability, PVDF based materials will lead to an increasing number of high-performance applications, extending the limits of polymer based technologies.

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