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Recent progress on piezoelectric, pyroelectric and magnetoelectric polymer based energy harvesting devices

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Abstract:

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Energy harvesting from the environment based on electroactive polymers has been increasing in recent years. Ferroelectric polymers are used as mechanical to electrical energy transducers in a wide range of applications, scavenging the surrounding energy to power low power devices. These energy harvesting systems operate taking advantage of the piezoelectric, pyroelectric and magnetoelectric properties of the polymers, harvesting wasted environmental energy and converting it mainly into electrical energy. There have been developed different nano- and micro-scale power harvesters with increasing interest for powering mobile electronics and low power devices, including applications in remote access areas. Novel electronic devices are developed based on low power solutions and, therefore, polymer-based materials represent a suitable solution to power those devices. Among the different polymers, the most widely used in device application remain the poly(vinylidene fluoride) (PVDF) family, due to its higher output performance.

1. Introduction

The phenomenon of ferroelectricity was discovered by Joseph Vasalek in 1921, who investigating the dielectric properties of Rochelle salt (sodium potassium tartrate tetrahydrate – $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) stated that the permanent polarization is the natural state of the material^[1]. Ferroelectric crystals are characterized by having one or more ferroelectric phases, which present a spontaneous polarization that can be reoriented by applying an external electric field^[2]. When a ferroelectric material is under an electric field, the variation of polarization with the electric field is nonlinear, presenting ferroelectric hysteresis^[3]. Another important characteristic of ferroelectric materials is the phase transition temperature (called Curie temperature- T_C). For temperatures below T_C the crystal exhibits ferroelectricity (ferroelectric phase) and, in turn, for temperatures above T_C the crystal ceases to have ferroelectricity altering to a paraelectric phase^[2, 4]. It is typically understood that the ferroelectric phase is originated by a distortion of the paraelectric phase structure of a crystal since the lattice symmetry in the ferroelectric phase is lower^[2]. The main properties that characterize a ferroelectric material are the spontaneous and reversible polarization, the ferroelectric transition temperature and the ferroelectric hysteresis^[3]. Ferroelectric materials are a subclass of pyroelectric materials, and pyroelectric materials are also a subclass of piezoelectric ones. Thus, ferroelectric materials exhibit both pyroelectric and piezoelectric effects^[3]. The concepts of ferroelectricity, pyroelectricity and piezoelectricity are closely related with the crystalline nature of the materials^[5]. There are 32 classes of

crystals, known as point groups, and 11 of them are characterized by a centre of symmetry (centrosymmetric) and absence of polarity, so they are not ferroelectric. From the remaining 21 crystal classes, one displays no piezoelectric effect, and the other 20 classes are non-centrosymmetric. Out of these 20 classes, 10 of them show a single polar axis and are spontaneously polarized depending on temperature – they are pyroelectrics –, which vary the amplitude of the dipole moment according to the temperature. Among pyroelectric crystals, the ferroelectric ones can be distinguished as those in which the permanent dipole can be switched under the application of an external electric field^[3, 5-6]. The classification of the 32 crystal classes according to their ferroelectric, pyroelectric and piezoelectric properties are shown in Figure 1.

Figure 1. Classification of crystal classes according to their ferroelectric, pyroelectric and piezoelectric properties.

Pyroelectric materials exhibit spontaneous polarization that, by heating the material, is decreased, enabling its use as sensors for infrared radiation detection^[3]. Piezoelectric materials are non-centrosymmetric dielectric crystals that, when subjected to an electric field, origin asymmetric displacements of anions and cations causing considerable net deformation of the crystal – indirect piezoelectric effect. Another property of these materials is the generation of an electric field across the crystal when the material is subjected to an external strain by applying pressure, orienting the dipoles in a way that the crystal develops positive and negative charges on the opposite faces – direct piezoelectric effect. Both direct and indirect piezoelectric effects are used in applications as they involve conversion of mechanical energy into electrical and vice versa^[3].

The research in ferroelectric, pyroelectric and piezoelectric effects of materials has flourished on the second half of the 20th century and has found an increasing number of applications^[6].

Pyroelectric and piezoelectric materials that are also ferroelectric are generally more sensitive to environmental variations, and so most of the practical pyroelectric and piezoelectric devices use ferroelectric materials^[3].

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Pedro Costa received his graduation and master in 2007 and 2009, respectively, from Science School of Minho University. In 2013, received the PhD in Mechanical Engineering from Engineering School of Minho University. The research interests include polymeric composites materials for sensors and actuators, using different materials as matrix and reinforcement. Large deformation sensors with piezoresistive properties is the current study field. Although the composites sensors, the elastomeric matrices are interest materials for energy harvesting or scavenging.

João Nunes-Pereira graduated in Physics and Chemistry, obtained a Master degree in Physics and a PhD in Science (Physics) at the University of Minho in 2013. Currently, he is a postdoctoral researcher working on the development of new polymer-based materials for sensor and actuator applications and advanced ceramics for aerospace structures. His research interests are in the field of advanced functional materials for application in the areas of aeronautics, energy, and environment.

Nelson Pereira received his graduation and Master in Industrial Electronics Engineering and Computers at the University of Minho. He is presently a PhD grant student at University of Minho in the Electroactive Smart Material Group (ESM), Portugal. His work has focused in the area of multifunctional inks for interactive applications.

Nelson Castro received an integrated Master degree in electronics and computing engineering from the University of Minho in 2013. He worked in the development of electronic instrumentation for polymer based printed sensors and smart materials like magnetoelectric, piezoelectric, piezoresistive and capacitive. Currently, he is working towards his PhD in optimization of polymer based magnetic composites and bioreactors for biomedical applications in tissue engineering.

Sérgio Gonçalves is a PhD student at University of Minho working on the use of electroactive smart polymers as sensors and actuators for tangible user interfaces (TUI). He completed his Master degree in 2011 in Industrial Electronics and Computer Engineering at the University of Minho with specialization in embedded systems and robotics, spending one year at Asian Institute of Technology, Thailand. His research interest in the TUI field led him to receive awards especially the prestigious World Technology Award 2013 for Entertainment, in New York.

S. Lanceros-Mendez graduated in Physics at the University of the Basque Country, Leioa, Spain. He obtained his Ph.D. degree at the Institute of Physics of the Julius-Maximilians-Universität Würzburg, Germany and was Research Scholar at Montana State University, Bozeman, MT, United States. Until 2016 he was Associate Professor at the Physics Department of the University of Minho, Portugal and since 2016 he is Ikerbasque Professor at the BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain, where he is also Scientific Director. His work is focused in the area of smart and functional materials for sensors and actuators, energy and biomedical applications.

The discovery of piezoelectricity in polymers of interest for applications was first reported by Kawai on poly(vinylidene fluoride) (PVDF) in 1969^[7], and it was followed by the discovery of the pyroelectricity of the same polymer two years later^[8]. The polymer family of PVDF are at the basis of significant scientific and technological advances in last decades. In particular, the homopolymer PVDF and its copolymer poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) have been widely used for applications^[9]. PVDF and its copolymers show the best-known electroactive properties^[10] among polymeric materials, thus being the choice of excellence for smart materials applications in areas such as sensors^[10-11], actuators^[10], ultrasonic transducers^[11], energy harvesters^[12], biomaterials^[13] and energy storage systems^[14], among others. PVDF and P(VDF TrFE) show lower piezoelectric and pyroelectric coefficients than the piezoelectric ceramic lead zirconate titanate (PZT), nonetheless they present the advantages of low permittivity and thermal conductivity, good impedance matching to air and water, flexibility, softness, processability^[15] and relatively low cost^[9b, 10].

Since Pierre and Jacques Curie in 1880 discovered the effect of generating electrical charge from pressure on single crystal materials that piezoelectric effect is being studied to transform mechanical energy into electrical energy for low-power devices. There are various materials with ferroelectric properties, ranging from single crystals to ceramic materials, from amorphous to semicrystalline polymers as well as composites using combinations of the aforementioned materials. In general, literature reports these types of materials as promising materials in generators or harvesters for nano- and micro-devices and systems.

Polymers with electroactive properties represent the most interesting class of polymers used as smart materials in various applications including sensors, actuators or energy harvesting devices, among others^[10]. Ferroelectric polymers have attracted considerable importance in the scientific community due to their potential in the next generation of electronic devices and energy applications. The discovery of the ferroelectric phenomenon in polymers (Kawai 1969)^[16] stimulated strong research activity and interest in soft materials and led to a broad range of applications.

2. Ferroelectric polymers

Ferroelectric polymers are a group of materials that show spontaneous electric polarization, which is reversible upon the application of an electric field to the material^[17].

The piezoelectric phenomenon was first discovered in single crystals and ceramic materials. In polymers, Kawai discovered the piezoelectric properties in poled PVDF, followed by the

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discovery of its pyroelectricity two years later^[18]. The ferroelectric properties of PVDF were only confirmed in 1978 by Kepler and Anderson^[19]. Previously, in 1963 piezoelectric properties were already reported in two polymers, poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC), by Kocharyan^[20]. PVDF has been recognized as the “ferroelectric polymer” per excellence, showing interesting physical and chemical properties, as compact structure, chemical stability, large permanent dipole moment, ease manufacturing^[15] and low annealing temperature^[18]. Also, PVDF can be fabricated using different processing methods (including melt and solvent processes) and in polymer blends or combined with inorganic materials in the form of composites. Electroactive polymers research and application is having an important growth in recent years mainly based on PVDF and their copolymers, as P(VDF-TrFE), poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) or poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE)^[10].

Although PVDF provides the best example of ferroelectric polymers, there are other polymers with interesting ferroelectric properties which have been extensively investigated in the last decade. These polymers include polyamides, cyanopolymers, copolymers and terpolymers based in PVDF, polyureas, polythiureas, biopolymers such as polypeptides and cyanoethyl cellulose, ferroelectric liquid-crystal polymer, cellular ferroelectret polymer blends and composites^[17, 20–21].

The ferroelectric properties of polymers are achieved through their molecular structure and orientation. The mechanical properties of polymers, as flexibility and light weight, compared to single crystals or ceramics are an advantage for the manufacturing of sensors and actuators devices. Therefore, these organic ferroelectric materials allow novel possibilities in the areas of memories, capacitors, piezo- and pyroelectric sensors and actuators^[17]. The main disadvantage of the use of piezoelectric polymers is that piezoelectric coefficients ($d_{33} < 35$ pC/N) are lower than those for other piezoelectric materials, as well as the limited thermal stability at higher temperatures^[9a, 22]. From an electronic approach, ferroelectric polymers are polar and possess a non-conjugated backbone, being of lower electrical conductivity^[20].

Regarding their properties, there are two main types of piezoelectric polymers with different operating principles: amorphous and semicrystalline polymers^[23]. Semicrystalline polymers show a certain percentage of polar crystalline phase. Their mechanical orientation, thermal annealing or high voltage treatment are all effective to induce/improve the piezoelectric crystalline phase within the polymer. Amorphous polymers also present piezoelectric effects if their molecular structure contains

strong molecular dipoles. Amorphous polymers, however, usually exhibit a lower piezoelectric response than semicrystalline polymers.

Both types of piezoelectric polymers (semicrystalline and amorphous) must show structural properties that should exist for a polymer material to present piezoelectric properties. Mainly, the molecular structure of the polymer must contain dipoles, then these dipoles should be oriented within the material and kept in their favoured orientation state. This reorientation is done through a poling process method^[23].

2.1. Poly(vinylidene fluoride)

The chemical formula of PVDF ($-\text{CH}_2-\text{CF}_2-$) is transitional between the chemical structure of polyethylene ($-\text{CH}_2-\text{CH}_2-$) and polytetrafluoroethylene ($-\text{CF}_2-\text{CF}_2-$), providing both high flexibility (similar to polyethylene – PE) and some stereochemical constraint (similar to PTFE) to the main-chain structure of PVDF^[20]. Due to its structural characteristics, PVDF has different molecular and crystal structures, which depends on the processing conditions of the material^[10].

PVDF is a semicrystalline polymer and presents five distinct crystalline phases related to different chain conformations: all trans (TTT) planar zigzag for the β phase, TG^+TG^- (trans-gauche-trans-gauche) for the α and δ phases and $\text{TTTG}^+\text{TTTG}^-$ for γ and ϵ phases^[10, 17]. Figure 2 shows the different most investigated and used phases of PVDF for applications: α , β and γ phases. PVDF is readily prepared through free radical polymerization of gaseous monomers 1,1-difluoroethylene and can be crystallized with a degree of crystallinity typically between 50 and 60%^[17].

Figure 2. Schematic chain conformations of the most used phases of PVDF. The all trans planar zigzag for the β phase, TG^+TG^- for the α and δ phases and $\text{TTTG}^+\text{TTTG}^-$ for γ and ϵ phases.

The main properties of PVDF, in particular for sensor or actuator application devices, are related to the strong electrical dipole moment of the PVDF monomer unit (5 to 8×10^{-30} C·m) which is due to the large electronegativity of the carbon and fluorine atoms^[10]. The electric polarization of PVDF in crystals is then generated from the regular packing of molecular chains in a way that the internal moments are not cancelled out. The piezoelectric coefficients of PVDF films in the β -phase were reported to be as

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large as -34 pC/N , larger than the values observed in any other polymer. PVDF is a thermally stable polymer with glass transition temperature (T_g) near -40°C ^[24].

The β -phase of the PVDF shows the highest dipolar moment per unit cell ($8 \times 10^{-30} \text{ C}\cdot\text{m}$)^[10] and the largest piezoelectric being used for a wide range of applications in the areas of sensors^[10], actuators^[20], batteries and biomedical^[25] applications as well as in energy harvesting devices as nano- and microgenerators^[22] or self-powered devices^[26].

The α and ϵ -phases of PVDF are macroscopically nonpolar due to the self-cancellation of the dipolar moments between the two antiparallel chains within the unit cell^[10, 17].

To obtain the β -phase of PVDF, several processing strategies have been used^[15]. The most used method is the α to β phase transformation, achieved by mechanically stretching (at low speed and temperature between 80 and 140°C ^[10]) in order to orient the molecular chains and, then pole the samples under an electric field of few hundreds of MV/m at a controlled temperature. Other strategies used to obtain β -PVDF is the addition of fillers that can act as nucleating agents of the electroactive phase^[10].

2.2. Poly(vinylidene fluoride)-based copolymers

The PVDF molecular structure can be modified to tailor intermolecular interactions and, therefore, modify the overall properties of the PVDF polymer. Nowadays, those modifications have been adopted to produce a series of novel PVDF-based copolymers and terpolymers with distinct behaviours in response to electric fields.

2.2.1. Poly(vinylidene fluoride-co-trifluoroethylene)

Poly(vinylidene fluoride-co-trifluoroethylene) or P(VDF-TrFE), Figure 3, is the most studied and used co-polymer of PVDF. Its ferroelectric phase-transition was discovered in 1980^[20]. The introduction of trifluoroethylene (TrFE) co-monomer into vinylidene fluoride (VDF) leads the material to crystallize in the ferroelectric crystalline β -phase when the VDF content is between 50 and 80 %^[10, 27]. Thus, the copolymer crystallizes directly in the β -phase without the thermos-mechanical processes, generally applied to PVDF samples^[27].

Figure 3. Schematic chain conformations of P(VDF-TrFE).

The synthesis of P(VDF-TrFE) is through free radical polymerization of the two monomers^[11].

P(VDF-TrFE) shows higher remnant polarization when compared with PVDF due the high degree of crystallinity and the favoured orientation of well grown crystallites^[11]. The oriented crystal provides P(VDF-TrFE) with a larger electromechanical coupling factor, leading to a higher efficiency in mechanical to electrical transformation, or vice-versa.

The transition temperature of the copolymer depends on the molar ratio of TrFE, decreasing with increasing molar ratio between 55 and 88 mol% to $\approx 130^\circ\text{C}$ ^[10]. PVDF and P(VDF-TrFE) show similar mechanical properties, dielectric constant and dielectric losses, but the piezoelectric coefficient d_{33} and k_{33} are larger in the copolymer compared to pure PVDF^[23].

2.2.2. Poly(vinylidene fluoride-co-chlorotrifluoroethylene)

The copolymerization of PVDF with the introduction of chloride trifluoroethylene (CTFE) on the polymer chain leads to the P(VDF-CTFE) copolymer (Figure 4).

Figure 4. Schematic chain conformations of P(VDF-CTFE).

Its final properties depend on the polychlorotrifluoroethylene (PCTFE) contents in copolymer and the glass transition temperature of the copolymer changes from -40°C in PVDF to -45°C of PCTFE^[10]. The copolymer can be obtained in a semicrystalline state just for CTFE contents below 16 mol%, while for higher CTFE concentrations the material always remains in an amorphous state^[28]. P(VDF-CTFE) presents piezoelectric properties with optimized d_{33} around -140 pC/N ^[10, 29], larger electrostrictive strain response and higher dielectric constant when compared with pure PVDF. The introduction of bulky CTFE makes the structure looser, which results in an easier orientation of dipoles under an external electric field.

2.2.3. P(VDF-HFP)

The integration of hexafluoropropylene on the PVDF polymer leads to the copolymer poly(vinylidene fluoride-co-hexafluoropropene), (P(VDF-HFP) Figure 5)^[30].

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Figure 5. Chemical structure of P(VDF-HFP).

Within the PVDF and its copolymers, P(VDF-HFP) shows a lower degree of crystallinity and is chemically inert^[10]. The ferroelectric properties of this copolymer are intrinsically dependent on the processing conditions, with maximum remnant polarization, obtained after processing by solvent casting, reaching up to 80 mC/m² for low HFP contents around 5%, decreasing as the HFP content increases^[10]. P(VDF-HFP) shows a piezoelectric coefficient $d_{31} \approx -30$ pC/N (always presented in modulus), becoming also useful for piezo and ferroelectric device applications^[10].

2.3. P(VDF-TrFE-CTFE)

Terpolymers can significantly improve the dielectric constant as well the electromechanical properties of polymers, which are necessary requirements for a wide range of applications, including electronics and energy areas. The introduction of CTFE in P(VDF-TrFE) leads to poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)) (Figure 6), considered a very promising ferroelectric material due to its high polarization, larger dielectric constant than other forms of PVDF-based polymers and high electromechanical response and elastic energy density^[31]. The combination of those properties leads P(VDF-TrFE-CTFE) to be particularly promising for the development of devices based on highly efficient electromechanical performance as well as a lack of degradation arising from dielectric leakage^[31].

Figure 6. Schematic chain conformations of P(VDF-TrFE-CTFE).

The main electroactive properties of PVDF and copolymers are presented in Table 1.

Table 1. Electroactive properties of PVDF and its copolymers.

Properties	$ d_{31} $ (pC·N ⁻¹)	$ d_{33} $ (pC·N ⁻¹)	k_{33}	P_r (mC·m ⁻²)	ϵ'	Ref.
PVDF	8-12	-24, -34	0.2	77	6-12	[10, 32]
P(VDF-TrFE)	12	-38	0.37	110	18	[10]
PVDF-CTFE	–	140	0.39	60	13	[10, 33]
P(VDF-HFP)	30	-24	0.36	80	5.6	[10]
P(VDF-TrFE)-CTFE	–	–	0.28	25.2	80	[10, 34]

Thus, PVDF and its copolymers are the main semicrystalline electroactive polymers, leading to wide variety of applications^[20]. Further, strong efforts have been carried out to develop innovative organic polymers with interesting pyro-, piezo- and ferroelectric properties^[20]. Although none of these materials has yet achieved the piezoelectric properties available in PVDF based polymers, the new materials may offer other advantages, including much higher operating temperatures and potentially new film/device forming techniques. Those materials include cyanopolymers, polyureas and polythiureas, aromatic polyamides, odd-numbered nylons and biopolymers^[27].

2.4. Biopolymers

Biocompatible materials are interesting due to their increasing use in biomedical applications, including tissue engineering^[13] and biodevices^[35]. Biopolymers can be natural or synthetic materials. Natural biopolymers generally show poor mechanical, electrical and electro-mechanical properties, being difficult to process in different forms^[13]. Natural biopolymers include collagen, polypeptides such as poly(γ -methylglutamate) and poly(γ -benzyl-L-glutamate), oriented films of deoxyribonucleic acid (DNA), poly(α -hydroxy acid) family, and chitin^[36]. Among the most used synthetic biopolymers are polyglycolide (PGA), polylactide (PLA) and its copolymers, including poly(lactide-coglycolide) (PLGA) or poly-L-lactic acid (PLLA). There are biomaterials approved by the Food and Drug Administration (FDA) federal agency and have been extensively tested for scaffold materials as bioerodible materials due to good controllable biodegradability and relatively easy processability^[37]. The piezoelectric constant of PLLA is $d_{14} \approx -10$ pC/N, with a T_g at 64 °C, T_c at 107 °C, and T_m at 171 °C^[38].

2.5. Polyamides

Commercially known as nylons, polyamides are polymers with amide (-CO-NH-) linkage in the repeating hydrocarbon units of the polymer chain^[20]. There are several nylon conformations, typically

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named after the number of carbon atoms present in the repeating unit of the polymer backbone^[20]. Nylons are identified as even or odd nylons, depending on the number of carbon atoms in the repeating unit^[20].

The odd nylons present aligned dipoles in the same direction and the all-trans conformation give rise to a large dipole moment and spontaneous polarization in each unit cell of the crystalline phase, showing good piezo-, pyro-, and ferroelectric properties^[20]. The monomer unit of odd nylons (nylon-5, nylon-7 or nylon-11) consists of even numbers of methylene groups and one amide group with a dipole moment^[30].

The dipolar moment magnitude is 4.9 and 3.4 D (debyes) for urea and amide bond, respectively^[30]. The piezoelectric strain constant for nylon 11 increases from $d_{31}=2$ pC/N at 20 °C to 14 pC/N at 180 °C^[20, 38]. Its dielectric constant is near 3 at 25 °C, and increases with increasing of temperature^[20].

The pyroelectric constant of nylon-11, -5 and -7 is around 100 pC/cm²·K^[20]. Nylon-11 is a biocompatible polymer and it the most used of the nylons in application devices. Odd nylons show problems due to moisture up taking^[39], and thus, dielectric response decrease over time due to the absorption of water.

2.6. Polyureas

Polyureas are a hard resin that exhibit excellent chemical, thermal and organic solvent resistance^[38]. They are formed by the rapid reaction of isocyanates and amines, showing microphase separation between hard and soft domains, with high and low T_g , respectively. The crystalline hard domains are dispersed in the continuous soft segment matrix, with elastomeric properties. The ferroelectric properties of polyureas are excellent when compared to other piezoelectric polymers, showing a large dipole moment for the urea bond (4.9 D), near twice than that of the P(VDF-TrFE)^[31]. Further, the remnant polarizations (P_r) of aliphatic polyureas is 440 mC/m²^[31]. Aromatic polyureas were the first polyurea structures identified as piezoelectric, showing pyro- and piezoelectric properties almost unvaried up to high temperatures, near 200 °C^[38]. The highest value of the piezoelectric constant is $d_{31}=10$ pC/N and the pyroelectric constant is $p_3=18$ μC/m²K^[38]. The overall properties of polyureas makes them a suitable candidate for many engineering applications. The aliphatic polyureas are synthesized at low temperatures. Their piezoelectric properties are smaller compared to aromatic polyureas^[38].

2.7. Amorphous polymers

Amorphous polymers are generally characterized by lower electroactive properties than semicrystalline polymers and are not good enough to attract commercial interest. Hereby, the literature is scarce in amorphous electroactive polymer.

The piezoelectric effect in amorphous polymers has a distinct physical principle than semicrystalline polymers, once the polarization phenomenon is rather a quasi-stable state due to the freezing-in of molecular dipoles and is not in a state of thermal equilibrium^[30].

Amorphous polymers must present several characteristics to show piezoelectric properties. The piezoelectricity in amorphous polymers is determined by the molecular dipoles orientation. The poling of these polymers is processed by an electric field, above their glass transition temperature due to the large increase of the mobility of the molecular chains that allows the dipole alignment with the applied electric field. The samples are then cooled below T_g at constant electric field and the remnant polarization is achieved, resulting in a piezoelectric-like effect proportional to the electric field of polarization^[31].

Literature reports several amorphous polymers with piezoelectric properties such as: polyamide and nitrile-substituted polymers, including polyacrylonitrile (PAN), poly(vinylidene cyanide-vinyl acetate) (PVDCN/VAc), poly(phenyl ether nitrile) (PPEN) and poly(1-biclobutanecarbonitrile). PVC and polyvinyl acetate (PVAc) show weak piezoelectric properties^[29]. Vinylidene cyanide and vinyl acetate copolymers show interesting properties, making these materials widely investigated due to their appropriate piezoelectric response and large dielectric relaxation strengths.

The effect of molecular orientation on piezoelectric properties in PAN is very large, as in PVDF. Although the stretching of PAN before poling leads to a large remnant polarization, the measured piezoelectric constant is low (only a few pC/N), 10 times smaller than that of PVDF^[15]. The dielectric constant can increase by using the copolymer with methylacrylate.

The dipole moment of PVDCN/VAc repeat unit is as large as 4.5 D in trans conformation^[15]. The copolymer shows piezoelectric activity quite similar to PVDF in the temperature range 20 – 100 °C^[15].

The piezoelectric properties of representative polymers, beyond PVDF and its copolymers, are summarized in Table 2.

Table 2. Ferroelectric properties of the polymers (beyond PVDF and its copolymers).

Properties	$ d_{31} $ (pC·N ⁻¹)	k_{31}	ϵ'	Ref.
Polyurea	<10	–	≈4	[40]
Nylon-7	17	0.054	–	[39]
Nylon-11	14	0.049	–	[40a]

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PAN	2	0.01	38	[39]
PVDCN/VAc	10	0.05	3	[39-40, 41]
PPEN	–	–	5	[42]
PVC	0.5 – 5	0.001	10	[39, 43]
PVAc	–	–	6.5	[39]
Polyimide	< 5	–	4	[23, 39, 44]

Advanced applications for materials require tailored properties that a single material often does not show, including mechanical, electrical or other properties^[45]. Thus, composite materials are excellent candidates to fabricate new materials with novel and unique properties for specific applications. These composites have been optimized in last decades and, it is recognized nowadays their relevance in devices.

The research for improved electroactive properties in composites mainly relies in the introduction of piezoelectric and high dielectric constant ceramic fillers such as barium titanate (BaTiO₃) or lead titanate zirconate (PZT)^[46]. Due to the its mechanical, thermal and chemical stability as well as due to its ferroelectric properties, PVDF polymer is often used as polymer matrix for those electroactive composites.

The mostly used composite connectivity is the 0-3 connectivity, where the fillers are randomly dispersed in a polymeric matrix. The goal of electroactive composite structures is to combine the best properties of the polymer matrices (mechanical, electrical or ferroelectric) with the exceptional ferroelectric properties of the ceramics or metallic materials. Nevertheless, there exist some disadvantages, such as the operation temperature of the devices, which is typically lower when compared to the ceramic or metallic materials, losses in particle-polymer interfaces and viable processing during the assembly of the device. Particle size, filler dispersion in the polymer, manufacturing using different types of solvents and homogenization of the general properties in the composites are the major obstacles to solve nowadays, to improve and tailoring the composites for applications^[47].

Ferroelectric composite materials increase the performance of energy harvester transducers particularly in applications as they combine the high ferroelectric coefficients (as pyro- and piezoelectric) of the ceramic filler with the excellent mechanical properties of the polymer as flexibility or stretchability^[46a]. The choice of the components (filler and polymer) and filler contents in composites allows the manufacturing of novel materials with tailored properties. Beyond the fillers, also the matrix is ferroelectric and the poling state of the matrix (or composite) provides an additional degree of freedom of materials. The ferroelectric properties of the most used ceramics and single

crystals for the fabrication of polymer composites are presented in Table 3.

Table 3. Electromechanical properties of typical piezoelectric ceramics (C) and single crystals (SC)^[46a].

Materials	T_C (°C)	ϵ'	d_{31} (pC·N ⁻¹)	d_{33} (pC·N ⁻¹)	k_{31}	k_{33}
PZT (C)	≈ 300	1000	-274	590	–	0.75
BaTiO ₃ (C)	≈ 280	3000	-115	483	0.4	–
PMN-PT (SC)	≈ 171	5000	-100	2000	0.7	0.9–0.94
PZN-PT (SC)	≈ 164	6800	-1400	1400	0.5	0.92–0.94
KNN (SC)	≈ 450	500	–	250	–	–

The dielectric properties of the polymer-based composites are lower than pure ceramics or crystals. The dielectric constant values range from near pure polymer (2 to 8, depending on the polymer) constant to some hundreds in composites with 50 wt.% of particles^[33b].

2.8 Ferroelectrets

The ferroelectrets, also known as piezoelectrets or cellular polymers, commonly consisting on voided charged polymer matrix structures with gas filling the voids. Polypropylene (PP), polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE) are the most used polymers in these structures. Ferroelectrets present large piezoelectric coefficients, higher than that observed for PVDF or its copolymers by a factor of 20 or even more^[21], being used for applications in electromechanical transduction. The polymers with the gas-filled voids are charged on the surface so that they develop internal dipolar structures, which change with the applied stress on the polymer film. In order to generate the dipolar structures, large electric fields are applied on the voided films, the gas molecules getting ionized and opposite charges being accelerated to each side of the voids. However, the piezoelectric response of these materials present limitations in terms of lifetime of the trapped charges and thermal stability^[21]. The study of these materials began in 1989 with PP foams showing d_{33} values around 600 pC·N⁻¹ but just for a temperature range up to 60 °C^[48]. Further improvements were achieved on polyethylene-naphthalate (PEN) foams with stable piezoelectricity up to temperatures of 100 °C^[49] and fluorinated ethylene-propylene (FEP) electret films fabricated by template patterning with d_{33} in the range of 1-3 nC·N⁻¹ and stable up to 120 °C after an annealing treatment^[50].

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3. Representative energy harvesting applications

In the following, some representative applications related to polymer-based energy harvesting systems will be presented. The next chapters do not intend to show a comprehensive state of the art in the area, but to show some of the most representative materials and applications, guiding the way to further developments.

3.1. Piezoelectric polymer-based energy harvesters

Used primarily to harvest energy from mechanical sources, piezoelectric polymer generators show increasing implementation in the area of small electronics. They are flexible, robust and of easy fabrication when compared to traditional ceramic or single crystal-based generators.

In the scope of harvesting energy from wind, a cantilever solution supported at one end was presented. This system was composed by two types of cantilever: a piezoelectric cantilever of flat PVDF film and a pre-rolled one. The systems were placed in a testing rig with an air blower and for wind speeds of 45 m.s^{-1} , a peak voltage of 45 and 50 V was obtained for the flat and pre-rolled cantilevers, respectively^[46a]. In the scope of biomedical devices, piezoelectric nanogenerator implants based on mesoporous PVDF were attached to the muscle of a mouse. The nanogenerator was composed by a PVDF film with dimensions of $1 \times 2 \text{ cm}$ and with interdigitated gold surface electrodes, sandwiched by two PDMS (polydimethylsiloxane) films. Before placing the device in the mouse, it was tested in a cantilever system deflecting the nanogenerator periodically with a force of 6 N, leading to an open-circuit voltage of 3.8 V and a short-circuit current of $3.5 \mu\text{A}$. The device was then placed between the epithelial and muscle layer in the thigh of the mouse. It was observed an open-circuit voltage of 0.26 V and a short circuit current of $0.17 \mu\text{A}$ when the rat moved. After 5 days with the device within the mouse, the voltage was stable around the 0.20 to 0.26 V, with no signs of toxicity or biocompatibility problems^[51]. A system capable of harvesting energy from the arterial pulse on the human wrist was also reported. This device was composed by a sensitive P(VDF-TrFE) piezoelectric layer with a PI (polyimide) support layer attached to the human skin with an area of 3.71 cm^2 , capable of harvesting energy in the range of 0.2 to $1.0 \mu\text{W}$. In addition, this device could also be used to monitor the vital signals of the host^[52]. A hybrid solution based on ZnO (zinc oxide) nanowires and PVDF film in a conductive fibre embedded in PS

(polystyrene) and PDMS was presented for harvesting energy from a human elbow (Figure 7). This single fibre device with dimensions of 2 cm of length was able to generate a voltage of 0.1 V, a current density of 10 nA/cm^2 and a power density of $16 \mu\text{W/cm}^3$ when a 90° elbow bending movement occurred^[53].

Figure 7. a) Hybrid-fibre generator attached to a human arm; b) Open-circuit voltage dependence with the bending of the elbow; c) Open-circuit voltage results after multiple bending movements; d) Current density results after multiple bends. Reprinted from^[53].

A human touch wireless sensor and energy harvester was fabricated based on a P(VDF-HFP) self-poled flexible sponge-like nanogenerator with ZnO nanoparticles, demonstrating ability to power 20 LEDs by finger tapping, also detecting pressure and movements from human activity. This material was capable to achieve a maximum power density of 1.21 mW/cm^2 with an impedance of $1 \text{ k}\Omega$ ^[54]. Harvesting energy from human walking was also investigated by a piezoelectric module underneath a parquet floor and harvesting the energy produced by the footsteps. Two PVDF films with $55 \mu\text{m}$ of thickness stacked alternately with two $5 \mu\text{m}$ of thickness aluminium foils were pressed together to a final dimension of $165 \times 95 \times 1.5 \text{ mm}$ and connected by copper foil stripes. The device was tested by loading with human footstep (70 kg) in the module, underneath a parquet floor of 10 mm of thickness. It is observed that some energy is lost by the damping effect of the parquet floor, but can spread out the mechanical load, not requiring the foot to be above the harvester. This system was used for storing energy in a capacitor using 14 harvesters with two stacked modules for each harvester. When the parquet floor was pressed by a load of 70 kg at a pace of 2 steps per second, a constant voltage of 2 V was harvested used to power up a device with an energy consumption of $210 \mu\text{W}$ ^[55]. Harvesting environmental vibrations has also been explored, such as ocean waves using sway movement by introducing dampeners in off-shore wind farms platforms fabricated with piezoelectric PVDF with silicone rubber composites. The efficiency of these materials was demonstrated in sandwiched and coiled sheet geometries. For testing both geometries, the materials were cut to have the same quantity of material and closely the same area, coiled type

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with a single layer of PVDF 4.5 cm wide and sandwiched with three layers of PVDF 1.5 cm wide (Figure 8). The system was cycled with a mechanical compressive load at a frequency of 2 Hz and a displacement of 3 mm and it was observed that the coiled type has a power generation capability of $982 \mu\text{W}/\text{cm}^2$ while the sandwiched type could just harvest $223 \mu\text{W}/\text{cm}^2$ ^[56].

Figure 8. Illustration of PVDF silicone composites: **a)** Coiled geometry; **b)** sandwiched geometry^[56].

An energy harvesting device to collect the wind-induced mechanical vibration energy was reported, based on flexible piezoelectric PVDF in a leaf configuration. This system oscillates like a leaf, flapping in the wind direction, producing a maximum power output of $600 \mu\text{W}$ and a maximum power density of $2 \text{ mW}/\text{cm}^3$ per leaf. Comparing this system to commercial wind farms, it can produce higher power densities being also characterized by a more compact and simple construction^[57]. An interesting approach for harvesting energy with a cantilever was implemented using a quarter-wave length straight tube acoustic resonator with PVDF cantilever beams placed inside. This system was designed to harvest energy from noise in airports, construction sites and factories. Through the excitation of the beams inside the resonator a maximum power of 313.3 nW at 100 dB was achieved^[58]. Cantilevers are very flexible, allowing a variety of designs. In this sense, a piezoelectric vibration energy harvester with three points of mass and an asymmetric M-shaped cantilever was proposed. This device, with a PVDF film bonded to the roots of the cantilever with a dimension of $40 \times 110 \text{ mm}$ was tested with a shaker at a frequency ranging between 10 and 30 Hz with an amplitude variation of 2.5 to 0.28 mm . The device achieved a short-circuit current value larger than $2.5 \mu\text{A}$ and an open-circuit voltage of 3 V ^[59]. Another cantilever approach for energy harvesting used for low frequency vibrations from the environment used a spiral-shaped PVDF cantilever. The device constructed by micromachining technology can harvest energy effectively in the range of 15 to 50 Hz with a maximum power output of 8.1 nW at the impedance of $100 \text{ M}\Omega$. The maximum output power density obtained was $0.81 \mu\text{W}/\text{cm}^3$ ^[60].

Environmentally friendly fabrication processes and materials also offer great potential for future applications on self-powered devices. In this field, it was reported a piezoelectric nanocomposite thin film of lead free BaTiO_3 nanoparticles embedded into P(VDF-TrFE) . This device was tested under mechanical stress in a bending system, with a bending radius of 10 mm , generating an open-circuit voltage of 9.8 V and short-circuit current of $0.69 \mu\text{A}$. The study demonstrated that the power output increased with higher concentration of BaTiO_3 nanoparticles, the device achieving an output power density of $13.5 \mu\text{W}/\text{cm}^2$ with a filler concentration of $40 \text{ wt}\%$ ^[61]. Vertically aligned piezoelectric nylon-11 nanowires were used for energy harvesting. A scalable capillary wetting technique was implemented in order to prevent fast drying of the nylon-11 solution and keep its reproducibility. The nanogenerator based on nylon-11 nanowires embedded in an anodized aluminium oxide template was able to reach an open-circuit voltage of 1 V and a short-circuit current of 100 nA at small amplitudes and low frequency physical signals, leading to a peak power of $\sim 0.027 \mu\text{W}/\text{cm}^2$ (Figure 9)^[62].

Figure 9. Power of a device measured across different load resistances^[62].

Some experiments based on PVC composites for polymer-based energy harvesting through fabrics were developed. A fabric based on a flexible piezoelectric fibre comprised by aligned BaTiO_3 nanowires and PVC polymer was produced. The PVC polymer was able to a flexible enough fibre in order to perform the woven process, as represented in Figure 10e. The aligned BaTiO_3 nanowires were used to enhance the piezoelectric properties as the active material in the composite. An output instantaneous power around 10.02 nW was achieved, provided by the bending of an elbow with the fabric around it (Figure 10).

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Figure 10. **a)** Fabric was attached to an elbow pad; **b)** Few segments of a height digit display were turned on from the converted biomechanical energy; **c)** Fabric voltage output; **d)** Fabric current output; **e)** Schematic representation of the flexible fabric nanogenerator structure^[45].

The electrical system harvesting peaked at 1.9 V and 24 nA with an external load of 80 MΩ. Thus, it is shown how to integrate an energy harvesting system into clothing solutions in order to make use of the mechanical energy of the natural human motion^[63]. Following the PVC approach, the energy harvesting of a microfiber composite (MFC) piezoelectric energy harvester in the water vortex-shedding field was developed, in order to obtain energy from the vibrations traveling through a liquid. This PEH is composed by an MFC (M8514-P2) beam and a PVC layer. The PEH system uses the acting force from the vortices shedding from the cylinder with the differential pressure between two sides of the PEH (Figure 11). With this methodology, the system was able to reach a peak power of 1.32 μW and a power density of 1.1 mW/m², with a water speed of 0.5 m/s and a cylinder diameter of 30 mm. It was verified, theoretically and experimentally, that the power output increased with the flow speed^[64].

Figure 11. Schematic representation of the PEH system^[64].

A nanofiber generator using P(VDF-TrFE) produced by electrospinning of nanofibers on interdigitated electrode plates, the system being evaluated by periodic bending with a maximum

displacement of 7 mm and generating a maximum power of 0.011 μW^[65]. Further, spin coated 12 μm thin films based on BaTiO₃/P(VDF-TrFE) composites provided a maximum output power of approximately 0.28 μW with a load of 1 MΩ when excited at 1 kHz^[66]. In the scope of sensor applications a touch sensor was reported by combining lead-free alkaline niobate microtubes K_{0.485}Na_{0.485}Li_{0.03}NbO₃ (KNLN) embedded in biocompatible PDMS. Films with 1.1 mm of thickness were used with an excitation force variation from 1, 3 and 10 N peak to peak. As an example, under a excitation of 5 N, the voltage remains steady at 16 V^[67]. The results demonstrate an open circuit voltage output larger than PVDF and ceramic PZT. A flexible electronic-skin sensor capable of detecting human physiological signals such as wrist pulse, muscle movements, speaking for voice recognition and disease diagnosis was presented. The device was fabricated by combining uniform micro-patterned PDMS into a silk mould with single-walled carbon nanotubes (SWCNT) films. The sensor presents a high response time (<10 ms), high repeatability and stability (>65000 cycles), with a detection limit of 0.6 Pa and a sensibility of 1.8 kPa⁻¹^[68].

A ferroelectric nanogenerator fabricated from platinum (Pt) nanoparticles/ P(VDF-HFP) nanocomposite films demonstrated an open-circuit output voltage of 18 V and 17.7 μA short-circuit current under a stress of 4 MPa. The application uses a bridge rectifier connected to the nanogenerator film capable of directly power 55 blue LEDs, 25 green LEDs and charge capacitors for energy storage^[69].

Error! Reference source not found. summarizes representative energy harvesters generators based on piezoelectric polymers, together with the output signals and main characteristics.

Table 4. Summary of representative polymer based piezoelectric energy harvesters.

Piezoelectric material	Excitation	Output	Characteristics	Ref.
ZnO/P(VDF-HFP)	0.36 MPa	1.21 mW/cm ²	Nanogenerator with ZnO	[54]
PVDF	Living rat muscle	0.26 V / 0.17 μA	Thin film	[51]
PVDF	Strain ~0.1%	16 μW/cm ³	Conductive fibre	[53]
PVDF	-	210 μW/transfer	Thin film for human walking	[55]
PVDF	δ=3mm f=2 Hz	982 μW/cm ²	Coiled PVDF silicone	[56]
PVDF	8 m/s wind	600 μW 2 mW/cm ³	Leaf for wind harvester	[57]
PVDF	100 dB/ f=146 Hz	313.3 nW	Cantilever	[58]

PVDF	Displacement (2.5 mm to 0.28 mm)	2.5 μA / 3 V	Cantilever	[59]
PVDF	Acceleration 0.2 g	0.81 $\mu\text{W}/\text{cm}^3$	Cantilever	[60]
PVDF	Wind speed 45 m/s	50 V	Cantilever	[46a]
P(VDF-TrFE)	-	13.5 $\mu\text{W}/\text{cm}^2$	Thin film	[61]
P(VDF-TrFE)	40 mmHg pulse waves	0.2 μW to 1 μW	Human skin attachment	[52]
P(VDF-TrFE)	-	0.011 μW	Spin coated film generator	[65]
BaTiO ₃ / P(VDF-TrFE)	-	0.28 μW	Spin coated film generator	[66]
Nylon-11	-	0.027 $\mu\text{W}/\text{cm}^2$	Nanogenerator	[62]
PVC	-	10.02 nW	Polymeric fabric	[63]
PVC	Water velocity: 0.5 m/s	1.1 mW/m ²	Microfiber composite	[64]
KNLN + PDMS	Force 5N	16 V	Thin film	[67]
PDMS + SWCN	0.8 Pa	1.8kPa ⁻¹	E-skin film	[68]
Pt-NPs + P(VDF-HFP)	4MPa	18V/17.7 μA	Nanogenerator	[70]
Fluoropolymer	a= 9.81 m/s ² m= 1 g	2000 μW	Nanogenerator	[71]

3.2. Pyroelectric polymer-based energy harvesters

Harvesting energy from thermal fluctuations in the environment is an important step for the development of low-power devices, reducing or even eliminating the need of batteries. Pyroelectricity is the ability of a material to generate electrical energy with time-dependent temperature changes. It is different from thermoelectricity, in which a temperature gradient is necessary. Pyroelectric energy harvesting can be up to ten times more efficient than the thermoelectric one^[72]. All ferroelectric materials are pyroelectric, and all pyroelectric materials are piezoelectric, but the converse is not true^[73]. Since the discovery of pyroelectricity in polymers in the early 1970s, effort has been focused mainly into engineering new materials. For polymer-based pyroelectric energy harvest applications, the available polymers are nearly restricted to PVDF and PVDF copolymers due to large pyroelectric constant^[17].

The second law of thermodynamics states that not all the thermal energy can produce work. Therefore, the Carnot efficiency specifies the maximum usable thermal energy, which is given by equation (1):

$$\eta_{\text{Carnot}} = 1 - \frac{T_H}{T_C} \quad (1)$$

where T_H and T_C are the temperatures in K of the hot and cold elements, respectively.

PVDF has a pyroelectric constant of about $\approx 30 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$, but some PVDF copolymers present higher pyroelectric constants, such as P(VDF-TrFE) and P(VDF-TrFE-CTFE) that are the most successful ferroelectric polymers known up to date for pyroelectric energy harvesting, with pyroelectric coefficients of $\approx 45 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ and $\approx 60 \mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$, respectively^[17, 47, 74]. The pyroelectric energy conversion is always rather inefficient due to large amounts of energy necessary to actually heat or cool the material, which typically results in a thermal-electrical conversion efficiency lower than 1% of Carnot's, and can be calculated by equation Error! Reference source not found.^[17]:

$$\eta = \frac{\pi}{4} k^2 \eta_{\text{Carnot}} \quad (2)$$

whereas k^2 is the electro-thermal coupling factor. Pyroelectric materials and their electro-thermal coupling factors are compared in^[75]. The low electrothermal coupling factors of the known pyroelectric materials always results in a low efficiency conversion, in particular for PVDF, $k^2 = 0.001194$. Stacking up several nonlinear pyroelectric elements might result in an increase of efficiency^[72]. Moreover, this efficiency can reach up to 70% of Carnot's for ferroelectric polymers when the Olsen cycle (aka Ericsson cycle) is used^[17, 74, 76]. It consists in a hysteresis loop of two isothermal and two isoelectric processes during which a high electric field is applied, and the polymer is heated above the T_C , with the external electric field preventing depolarization. It is a complex process which greatly limits the possible applications. The Olsen cycle has been reported to be successfully implemented in PVDF copolymers, namely P(VDF-TrFE) thin films, being obtained the following energy densities per temperature cycle: 130 J/L (69.3 - 87.6 °C)^[74b]; 521 J/L in commercial and 426 J/L in purified films (25 - 110 °C), and 188 J/L in porous films (25 - 100 °C)^[76]; 155 J/L (25 - 110 °C)^[74a]. The figures of merit of commercial materials, purified and porous films are reported as 7.93, 10.17 and 5.24 J m⁻³ K⁻², respectively^[76].

Pyroelectricity in PVDF films can be enhanced by inclusion of nanoparticles in small amount^[77]. For, example the, inclusion of Zinc Oxide (ZnO) nanoparticles in a proportion of 0.25 wt% can result in an increase of the pyroelectric coefficient in 25% as well as decreasing the necessary electric field to pole the PVDF film^[78]. Through the dispersion of the non-ferroelectric lanthanum oxide (La₂O₃) in a PVDF film in a ratio of 3 wt% it was possible to reach a pyroelectric coefficient of 42 $\mu\text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ ^[79]. The development of

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polymer-ceramic nanocomposites such as the inclusion of lithium niobate (LiNbO_3) in PVDF (LN/PVDF) leads to a pyroelectric coefficient of $127 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ for a 25 vol%^[46b], much higher than the registered values for P(VDF-TrFE). Recent innovations have led to the development of a P(VDF-TrFE) nanowire arrays synthesized by a template-wetting technique, a low-cost procedure, for the creation of NG for harvesting both thermal and mechanical energies^[80]. An illustration of the process is presented in Figure 12. The nanogenerator was supported in a Kapton film with a gold coating where P(VDF-TrFE) powder dissolved in DMF (N,N-dimethylformamide) was spin-coated, resulting in a layer of $45 \mu\text{m}$ of thickness. After the DMF solvent evaporation, an anodic aluminium oxide (AAO) nanoporous templates was slightly forced against it, and kept at 170°C for an hour, melting the P(VDF-TrFE) which fills into the cavities of the AAO template and forming nanowires. An annealing at 120°C followed to improve crystallinity. Then, the AAO was dissolved in a solution of 2 M sodium hydroxide (NaOH) in water, and a thin layer of PMMA was spin-coated on the nanowires to prevent short-circuiting. Finally, the conductive polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) was also spin-coated. The alignment of the dipoles is then achieved by a 50 MV/m electric field. The prototype had dimensions of $10 \times 10 \text{ mm}$ and could generate an output peak voltage of 3.9 V due to the pyroelectric effect when temperature changed from 21.85°C to 30.85°C , and a 2.0 V negative peak in the inverse change. The same device also presented an output voltage of 5.6 V from the piezoelectric effect under bending. This is reported as an average pyroelectric output voltage/current of $3.0 \text{ V}/50 \text{ nA}$, enough to supply a 7-segment LCD^[80a].

Figure 12. Representation of the fabrication process of a P(VDF-TrFE) nanogenerator with an array of nanowires^[80a].

Since PVDF presents both piezoelectricity and pyroelectricity, combining both effects for thermal energy harvesting should increase the harvested energy. SMAs (shape-memory alloys) have the ability to convert thermal energy into strain. Consequently, a composite material combining PVDF and SMA has been developed^[81]. When the composite increases temperature, the pyroelectric effect displaces electrical charge to the electrodes of the PVDF film, and the SMA deforms the PVDF which adds up to that through the piezoelectric effect. The flexible composite was developed based on $110 \mu\text{m}$ -thick PVDF film to which a layer of conductive epoxy glue was applied on both sides to create the electrodes and attach the SMA ribbons. Following, the $40 \mu\text{m}$ -thick SMA ribbons were placed. The SMA elements were composed by $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$. It is highly important that the piezo and pyroelectric effects are not counteracting each other, so the composite must be designed in a way that the polarity of both signals is the same, unlike some works^[81-82]. It is claimed an increase of 75% on the output pyroelectric voltage and 200% on the harvested pyroelectric energy. In the prepared sample ($25 \times 10 \text{ mm} \times 110 \mu\text{m}$ PVDF film with two SMA ribbons) this corresponds to an increase of 130 V output response comparatively to PVDF alone, and using an inefficient buck converter ($\approx 25\%$ efficiency) it was even possible to supply an LED per event (20°C variation)^[81]. As a result of the flexibility and

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thinness of the prepared composite allied to the relatively low-cost production, the use of PVDF with SMAs can be a good candidate for energy harvesting systems where thickness and flexibility are requirements. Pyroelectric materials are of high importance for applications when significant and fast temperature changes take place over time. One of such cases is during exothermic chemical reactions where waste energy is freed in the form of heat. Envisioning that, a pyroelectric device using PVDF polymer has been developed to be applied on the surface of a beaker^[83], as presented in Figure 13. It can both generate electrical energy and at the same time monitor the temperature of the reaction. The good chemical resistance and thermal stability of PVDF assures the well-functioning of the system^[73], further, other PVDF copolymers are also good candidates for this application^[10]. For the electrodes, multi-walled carbon nanotube (MWCNT) proved to be a stretchable and durable material, with high electrical conductivity and corrosion resistance. The often-used metals would also be at risk of corrosion when in contact with chemicals. The MWCNT layers were deposited in a 30 μm thick PVDF film by spin-coating method, with 10 to 20 μm each. The dimensions of the pyroelectric device were 8 $\times$ 3 cm. For the testing of the system, several chemical reactions were investigated, and sodium hydroxide with hydrochloric acid was the one providing the highest amount of pyroelectric energy conversion, reaching an open-circuit voltage of 9.1 V and a short-circuit current of 95 nA, enough to power up an LCD. As a temperature monitor, it was possible to detect temperature changes as low as 0.25 $^{\circ}\text{C}$ ^[83].

Figure 13. Schematic representation of the pyroelectric device for energy harvesting from chemical waste heat and images of the used materials. Reprinted from^[83].

Wearable electronics can also benefit from the use of pyroelectric devices^[84], since the temperature around the human body normally fluctuates during the day^[72]. Nevertheless, it is not an easy application, so thermoelectric-based NG alternatives have appeared^[85] such as the development of highly stretchable nanogenerators (HSNG) for pyro- and piezoelectric energy harvest, as developed in^[73], where it was developed a flexible and stretchable film based on P(VDF-TrFE) (Figure 14). The bottom electrode was fabricated from PDMS-CNT and the top electrode of graphene. The film was tested up to 30 % stretching and

presented a pyroelectric output voltage similar to the non-stretched one, which proved the pyroelectric output was not affected by the stretching of the material. In the developed prototype an output voltage of 1.4 V was obtained upon application of strain and heat simultaneously. The film was simulated to be heated up to 52.13 $^{\circ}\text{C}$ and then cooled off to 35.00 $^{\circ}\text{C}$ in 6.72 s^[73].

Figure 14. Highly stretchable pyroelectric and piezoelectric nanogenerator. Reprinted from^[73].

Searching for large thermal amplitude change around the human body, a pyroelectric NG has been developed for a respirator mask, based on PVDF films, to scavenge thermal energy from the human breathing^[86], as shown in Figure 15. The main focus is use it as a NG and as a self-powered sensor for monitoring human breathing in medical applications. It can produce an open-circuit output voltage of 42 V and a short-circuit current of 2.5 μA from the human breathing in a room at 5 $^{\circ}\text{C}$ ambient temperature. The piezoelectric effect could be neglected, since it was responsible for only 0.2 V/20 nA^[86].

Figure 15. Pyroelectric nanogenerator based on PVDF film for respirator mask. Reprinted from^[86].

NGs convert energy from our environment, and among the most abundant are thermal, mechanical and solar energies. Using multiple source types might help to harvest higher amounts of energy and more continuously. A hybrid cell for simultaneously harvesting of pyroelectric, piezoelectric and solar energies has been developed in a form of a flexible composite film^[87]. It is based on a PVDF film to scavenge pyro and piezoelectric energy, and on a layer of aligned ZnO nanowire arrays and ITO (indium tin oxide) for the solar cell. The solar cell was supported in a P3HT (poly(3-hexylthiophene)) layer, and all the electrodes of the film were fabricated from silver (Ag), except the top electrode that was ITO. The prototype of the hybrid cell for energy harvesting was

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about 600 mm², and it was able to generate 2.5 V/24 nA (open-circuit voltage/short-circuit current) through the pyroelectric effect when the film was heated from 21.85 to 40.85 °C, and an inverse pulse of 3.2 V/31 nA when the temperature returned to the initial value. The piezoelectric effect was responsible of generating 0.5 V/20 nA when compressive strain was applied on the film. The solar energy harvesting layer was able to produce 0.41 V, with a short-circuit current density of 31 µA/cm²[87]. There exist other hybrid cells for energy harvesting combining multiple effects, such as the pyroelectric and piezoelectric effects as complement of the triboelectric effect (displacement of electrical charge under frictional contact)[88]. Non-pyro- and thermoelectric polymers have also been used to improve thermal to electrical efficiency in pyroelectric or thermoelectric materials[89]. Thus, a nanocomposite of carbon black or graphene particles can be used as coating for a LiNbO₃ crystals pyroelectric layer, which greatly increases solar radiation absorption[89a]. **Error! Reference source not found.** shows a comparison of the discussed pyroelectric materials.

Table 5. Summary of representative polymer-based pyroelectric energy harvesting systems.

Pyroelectric material	Excitation Temperature	Output	Characteristics	Ref.
P(VDF-TrFE) (70/30)	21.85 - 30.85 °C 30.85 - 21.85 °C	3.9 V -2.0 V	Nanowire array, thin film	[80]
P(VDF-TrFE) (70/30)	52.13 - 35.00 °C	1.4 V	Stretchable thin film	[73]
PVDF	human breathing in a 5 °C room	42 V / 2.5 µA	Thin film	[86]
PVDF	-	9.1 V / 95 nA	Thin film	[83]
PVDF	21.85 - 40.85 °C	2.5 V / 24 nA	Flexible hybrid nanocomposite	[87]
ZnO/PVDF	-	25 % pyroelectric coefficient increase relatively to PVDF	Thin film	[78]
La ₂ O ₃ /PVDF	-	42 µC·m ⁻² ·K ⁻¹	Thin film	[79]
SMA ribbons/PVDF	-	75 % voltage increase, 200 % energy increase relatively to PVDF	Thin film	[81-82]
LN/PVDF	-	127 µC·m ⁻² ·K ⁻¹	Polymer-ceramic nanocomposite film	[46b]
P(VDF-TrFE) (60/40)	69.3 - 87.6 °C	130 J/L	Olsen cycle, thin film	[74b]
P(VDF-TrFE) (60/40)	25 - 110 °C	155 J/L	Olsen cycle, thin film	[74a]

P(VDF-TrFE) (60/40) (commercial)	25 - 110 °C	521 J/L (7.93 J m ⁻³ K ²)	Olsen cycle, thin film	[76]
P(VDF-TrFE) (60/40) (purified)	25 - 110 °C	426 J/L (10.17 J m ⁻³ K ²)	Olsen cycle, thin film	[76]
P(VDF-TrFE) (60/40) (porous)	25 - 100 °C	188 J/L (5.24 J m ⁻³ K ²)	Olsen cycle, thin film	[76]

3.3. Magnetoelectric polymer-based energy harvesting and respective circuits

During the last decade, magnetoelectric (ME) composites were subject of increasing study[90]. The ME effect consists in the transduction of magnetic energy into electric one and vice-versa. The ME transducer reacts with an electric polarization variation to an applied magnetic field (direct ME effect) or with a magnetization variation as a response to an applied electric field (converse ME effect) [91]. The bidirectional behaviour of these composites makes them suitable to work as both sensors and actuators. These transducers are typically composed by one or more magnetostrictive and piezoelectric layers. Each construction has its features, allowing it to operate as a sensor, actuator or energy harvester. By converting AC (alternating current) magnetic field into vibration and electric charge simultaneously, they can be employed as harvesters of magnetic field energy provided by mobile base stations, Wi-Fi routers, satellite communications, radio and TV transmitters and power distribution lines, among others[92]. As the ME coefficients obtained on polymer-based ME materials have reached the same order of magnitude as their best inorganic counterparts their use as energy harvesters is increasing[93]. Further, this technology may be an interesting approach due to high flexibility, lightweight and biocompatibility [93-94]. The common employed harvesting circuits reported are composed by a rectifier and a DC/DC converter with matched impedance in order to achieve maximum energy transfer [95]. For energy harvesting it is important to know how much average power can be drained from the source(s), thus the total output power must be transformed accordingly to the load's voltage range requirements. As this section is discussing energy harvesting, probably the worst-case scenario will always be low electrical amplitudes with no risk of over-voltages or over-currents. Depending on the load type, the requirement can be voltage, current or a minimum operating power. In case of batteries, a higher voltage level from the source is required in order to charge the battery, being important to sacrifice current and work with a slower charge. However, in order to light up an LED a minimum

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power is required. In order to acquire the wasted energy from environmental forces and common human processes in our daily lives, load customized circuits must be employed. The devices that can be powered from energy harvesting are all powered through DC (direct current) current, though the energy available in our environment that is captured by electroactive materials such as piezoelectric ones is AC current, creating the need for the circuits to guide the current to flow in one direction. Thereby, in order to keep the voltage level stable, the energy must be stored in a potential state among one or more levels of energy transformation modules along the circuit until it reaches the load. With the purpose of achieving the required energy transformation, some methods may be employed for piezoelectric sources, such as full-wave bridge voltage rectifier, Cockcroft-Walton and Dickson voltage multipliers among other possibilities [96]. These methods provide simple mechanisms in order to rectify the electrical output and handle the voltage-current ratio with few dissipating components. Some literature can be found uncovering experiments executed with polymer-based composites with the purpose of harvesting energy from magnetic sources. A ME composite sample with 30 μm -thick Metglas 2826 MB and 52 μm -thick PVDF bilayer composite with epoxy bonding, resulting in a total size of $40 \times 12.3 \text{ mm}$. Both DC and AC magnetic fields were generated through a pair of Helmholtz coils, varying both fields from 0 to 3 kA/m ($\approx 37.7 \text{ Oe}$) and varying the AC frequency from 0 to 200 Hz, controlling the magnetic field level with the aid of a Hall sensor [97]. Figure 16 displays a comparable system with the one used in [97].

Figure 16. Experimental setup used to measure ME signal voltage and frequency spectrum acquired from the ME sample response to Hac and Hdc through after a pre-amplification [98].

Applying AC magnetic field at the material's resonant frequency and a DC magnetic field simultaneously, the conditions to extract maximum voltage from the ME composite are suited [97]. In a bilayer sandwich ($\text{Fe}_{64}\text{Co}_{17}\text{Si}_7\text{B}_{12}$)/PVDF ME composite the power output was measured using a metallic glass as a magnetostrictive layer and PVDF. In this research, sample with sizes from 0.5 to 3 cm long were tested in order to verify the maximum power that

could be harvested at different operating frequencies from electromagnetic waves (Figure 17) [96b].

Figure 17. Schematic representation of electromagnetic signal harvesting with ME materials [96b].

Three different frequencies from 46.8 to 337 kHz were used in order to reach radio wave frequency range, being able to reach a maximum of 6.4 μW of power output by subjecting the ME composite to an alternated magnetic field (HAC) of 0.45 Oe @ 46.8 Hz and a continuous magnetic field (HDC) of 4.7 Oe. The power harvested at the highest frequencies (above 100 kHz) fell down to tenths/hundreds of nW order. In order to harvest the energy, it was implemented a two stages multiplier circuit based on the Cockcroft-Walton voltage multiplier topology (Figure 18) [96b].

Figure 18. Cockcroft-Walton half wave rectifier AC/DC converter with n multiplying stages.

More recently, an approach with a trilayer ME composite with a Metglas/PVDF/Metglas was presented. The sample was developed with two layers of Devcon 5 min epoxy and a size of $30 \times 5 \text{ mm}$ (Figure 19b, c), and both AC and DC magnetic fields were generated within two pairs of Helmholtz coils (Figure 19a). In this specific case, the approach aimed to measure the real practical power output, using common circuit components to rectify the electrical charge generated by the piezoelectric central layer and get a DC power source [99].

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Figure 19. a) AC and DC magnetic field double pair of Helmholtz coils set-up; b) Custom-made sample holder; c) Assembling method of the trilayer ME composite^[99].

It was possible to harvest up to $12.31 \mu\text{W}$ by applying an H_{DC} of 7 Oe and an H_{AC} of 0.4 Oe @ 54.5 kHz^[99]. Apart from the very simple circuit in Figure 19, the most interesting circuits employed (Figure 18 and Figure 201) were simple structures that can be escalated by selectable multiplication levels in order to acquire the most possible available power from the source.

Figure 20. Common topology of a full wave rectifier AC/DC converter.

Taking an overlook at the circuits being implemented for magnetoelectric and piezoelectric energy harvesting, the full-wave bridge voltage rectifier, is widely used for common electronic devices from the AC power outlets, as well as for energy harvesting applications (Figure 20)^[96a, 100]. This circuit has a simple structure operating with four diodes and one capacitor just before the load. The negative and positive components of the AC harvested power are conducted into the same direction (rectification) and in order to keep the output voltage stabilized an output capacitor holds the voltage level, being its size directly proportional to the output current. The voltage multipliers like Cockcroft-Walton (Figure 18) and Dickson (Figure 21) are used to multiply the input voltage levels by exchanging current for a higher voltage level. The available output power remains with few conversion losses due to voltage drops, which makes the output voltage level, sag after some multiplication levels.

Figure 21. Modified Dickson's half wave rectifier DC/DC converter with n multiplying stages.

The Cockcroft-Walton circuit is a half-wave rectifier with a voltage doubler circuit as a starting base, and then it keeps increasing the number of multiplications by n stages. Each stage is constituted by two diodes and two capacitors and so is the peak value of the power source multiplied by 2 at each stage. The capacitors of even and odd order have different roles: the even ones are the smoothing capacitors and the odd ones are transferring capacitors, which shift the negative peak to zero^[101]. A DC voltage is assigned with approximately twice the input of the peak voltage of the input wave at each stage. The Dickson charge pump is another variation of a voltage multiplier. However, the original Dickson's charge pump is a DC-DC converter with logic control. This method works by shunting the original DC input to ground and the AC input signal to be harvested replaces the logic control^[102]. Working with smaller current and within an adequate range of voltage/power source limits it is possible to obtain much higher voltages from a much lower voltage power source, in order to power up batteries, capacitors and other energy storing devices. The component values must be selected according to wave frequency, current amplitude and desired output voltage value. In energy harvesting applications low voltage drop diodes should be used, such as Schottky diodes, in order to minimize losses by heat and harvest the most energy possible in each generated wave cycle. Many other approaches and energy transformation may be used, but in order to keep the extraction circuit as simple as possible these ones were selected. Highly controllable pumps can be built for several voltage levels of power extraction^[103], though the problem can be addressed with simple structures like the ones aforementioned if the load can handle voltage variations. Despite polymer-based energy harvesters provide less energy than their ceramic counterparts, the production cost, flexibility, weight, multi-stack possibility for higher energy conversion and higher applicability, will bring opportunities for these polymer-

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based solutions in the printed electronics field. Their main disadvantage lies in the need of two simultaneous magnetic fields, alternated and continuous fields, though, for energy harvesting purposes, only the AC magnetic fields will be able to be harvested, while the DC magnetic field can be produced through a pair of permanent magnets in order enhance the harvester response, consuming no energy and validating applicability. At the present moment, publications on magnetoelectric polymeric films as energy harvesters are scarce, but they show suitable power output density, being reported up to 1.5 mW.cm^{-3} , their thickness and size can be tailored to work at several AC magnetic field frequencies, although using thin films, lower frequencies result in small voltage output and weaker transduction. Electronic solutions already provide microcontrollers, which can work below 2 V and 1 μA at lower processing frequency. However, these polymer-based material composites, as energy harvesters, still need research in specific real-life applications such as remote self-powered devices. Table 6 presents the summary of the main ME polymer-based energy harvesters systems reported, according to the magnetic fields provided using Helmholtz coils.

Table 6. Summary of representative polymer based ME energy harvesting systems.

Material	Output performance	Characteristics	Ref.
Metglas/PVDF	–	H_{AC} and H_{DC} : 0 - 37.7 Oe @ 0 - 200Hz	[97]
($\text{Fe}_{64}\text{Co}_{17}\text{Si}_{17}\text{B}_{12}$)/PVDF	6.4 μW @ 1.5 mW.cm^{-3}	H_{AC} : 0.45 Oe @ 46.8 kHz, H_{DC} : 4.7 Oe	[96b]
Metglas/PVDF/Metglas	12.31 μW @ 0.9 mW.cm^{-3}	H_{AC} : 0.4 Oe @ 54.5 kHz, H_{DC} : 7 Oe	[99]

4. Conclusions and Outlook

This manuscript summarizes the main recent advances in the topic of energy harvesting from polymer-based materials and systems. Following to a brief introduction of the phenomenon of ferroelectricity, and related effects such as piezoelectricity and pyroelectricity, the most frequently used ferroelectric polymers are presented as well as their main properties, limitations and advantages in view of developing energy harvesting device applications. Particular emphasis is devoted to the PVDF family, which due to its remarkable properties continues to be the most promising material for those applications. Finally, the main energy harvesting results were presented and discussed divided according to the polymer characteristics/effects which are at the basis of the application: piezoelectricity, pyroelectricity and magnetoelectricity. It is concluded that the available materials allow already collect wasted energy and transform it in useful

power for micro devices, allowing the development of autonomous sensor systems and sensors applications for remote of difficult to access places or environments. Thus, it is expected that the number of applications steadily increases in the near future. In any case, continuous efforts in have to be devoted in polymer processing and composite development to further improve their response, performance and integration, broadening their application areas in the field of low power portable electronics, self-powered and wearable sensors and remote locations sensors or devices.

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